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I hereby recommend that the thesis prepared under my supervision by Joseph F. Irew

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Approved by:

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Wayland M. Burgess, Chairman

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THE ACTION OF AQUEOUS SODIUM HYDROXIDE UPON ALIPHATIC NITRO COMPOUNDS

A dissertation submitted to the

Graduate School
of the University of Cincinnati

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by

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I

INTRODUCTION

The research discussed in this thesis is a continuation of the work started in this laboratory in 1931 on (1) the methods of preparation, and (2) a study of the action of aqueous sodium hydroxide solution upon nitromethane[1]. The first work, designed to ascertain the best laboratory method for the preparation of nitromethane and to investigate the possibility of its reduction to an aliphatic azoxy compound by sodium methylate in a methyl alcohol solution, gave unexpected results, which in turn led to an investigation of the action of aqueous sodium hydroxide upon nitromethane.

It was found that in the standard laboratory method of F. C. and M. G. Whitmore[2] which called for equimolar quantities of the reacting reagents, i.e., chloracetic acid and sodium nitrite, that the quantity of sodium nitrite used could be reduced to two-thirds the quantity called for without reducing the yields of nitromethane to any appreciable extent. Secondly, sodium methylate in methyl alcohol was found to convert to an undetermined extent nitromethane to ammonia and sodium formate. During an alkaline steam distillation in the

second stage of this previous investigation the ammonia did not distill in a brief interval of time, but continued to come over for several hours. This fact suggested that the aqueous sodium hydroxide formed from the hydrolysis of sodium methylate was reacting with the nitromethane causing the slow continuous formation of ammonia. Upon investigation of the action of concentrated aqueous sodium hydroxide upon nitromethane, it was found that not only ammonia but also sodium carbonate were the products of the reaction. They were also found to be present in a one to one molar ratio according to the requirements of an equation derived for the reaction, namely:

$$CH_3NO_2 + 2NaOH \longrightarrow Na_2CO_3 + NH_3 + H_2O$$

This reaction was explained in terms of a previously postulated reaction mechanism which arose from the quantitative study of the action of fused anhydrous caustic alkalies upon a variety of carbon compounds[3]. Two general type reactions for the abundant liberation of hydrogen or methane, and in some cases both hydrogen and methane, were found to conform to the following equations in which M = Na or K, and $R(OM)_n$ was an alkali carbonate:

$$R(H)_n + nMOH \longrightarrow R(OM)_n + nH_2$$

$$R(CH_3)_2 + nMOH \longrightarrow R(OM)_n + nCH_4$$

In proposing an explanation for the mechanism of these reactions, it was assumed that the alkali hydroxides apparently underwent an acidic dissociation, $MOH \rightarrow H + OM$.

The reactions of twenty-two carbon compounds, investigated from this point of view, were shown to conform to the following generalization or rule[4]. "Each hydrogen atom or each methyl radical, which in the carbon compound is united to a carbon atom, which carbon atom is in turn united to an oxygen atom, is liberated as a molecule of hydrogen or as a molecule of methane, respectively, through its combination with an atom of hydrogen the anhydrous caustic alkali, MOH". Furthermore, each compound to which the rule was not directly applicable was shown to react as if it suffered an oxidation-reduction reaction, yielding its equivalents of products to each of which the rule is applicable.

Now if the general type reaction $R(H)_n + nNaOH \longrightarrow R(ONa)_n + nH_2$ is applied to the hydrogen atoms of the methyl radical of nitromethane, a reaction represented by the following equation may be assumed to occur:

$$CH_3NO_2 + 3NaOH \longrightarrow C(ONa)_3NO_2 + 3H_2 \qquad (a)$$

The hydrogen thus available is not liberated but may reduce the intermediately formed compound $C(ONa)_3NO_2$, thus:

$$C(ONa)_3NO_2 + 3H_2 \longrightarrow C(ONa)_3NH_2 + 2H_2O \qquad (b)$$

The saponification of the latter intermediate compound $C(ONa)_3NH_2$, would yield sodium ortho carbonate and liberate ammonia:

$$C(ONa)_3NH_2 + NaOH \longrightarrow C(ONa)_4 + NH_3 \qquad (c)$$

The hydrolysis of sodium ortho carbonate then follows:

$$C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2NaOH \qquad (d)$$

The summation of equations (a), (b), (c), and (d) of the above reaction mechanism scheme gives the following simplified equation, (e), for the oxidation-reduction of nitromethane by concentrated aqueous sodium hydroxide[5]:

$$CH_3NO_2 + 2NaOH \longrightarrow Na_2CO_3 + NH_3 + H_2O \qquad (e)$$

The experimental data, based upon the reaction of 0.25 mole of nitromethane according to the equation, $CH_3NO_2 + 2NaOH \longrightarrow Na_2CO_3 + NH_3 + H_2O$, were as follows:

Run	Normality of NaOH	Yields of CO_2 (Moles)	Yields of NH_3 (Moles)	Molar Yield Ratio CO_2 : NH_3
Ia	5	0.1163	0.1115	1 : 0.958
		0.1167	0.1112	1 : 0.955
Ib	5	0.1140	0.1175	1 : 1.031
		0.1139	0.1173	1 : 1.029
IIa	10	0.1239	0.1295	1 : 1.045
		0.1240	0.1292	1 : 1.042
IIb	10	0.1236	0.1233	1 : 0.998
		0.1238	0.1235	1 : 0.997
IIIa	15	0.1206	0.1240	1 : 1.029
		0.1205	0.1240	1 : 1.021
IIIb	15	0.1187	0.1139	1 : 0.959
		0.1186	0.1141	1 : 0.962
Average		0.1196	0.1199	1 : 1.002

Since the use of 5N, 10N, and 15N sodium hydroxide gave about the same yields, i.e., about 50% of the theory, of ammonia and sodium carbonate, it was one purpose of the present investigation (A) to determine the extent of the occurrence of the postulated reaction, when aqueous sodium hydroxide solutions of lower concentrations were reacted with nitromethane.

The other objectives of this research were to investigate the nature and the extent of the action of aqueous sodium hydroxide upon other aliphatic nitro compounds, namely, (B) nitrourea, (C) nitroguanidine, (D) nitrobarbituric acid, and (E) chlorpicrin.

II

HISTORICAL

The historical part of this thesis resolved itself into two parts for each of the five nitro compounds studied; namely, nitromethane, nitrourea, nitroguanidine, nitrobarbituric acid and chlorpicrin. With the exception of nitromethane which was reported in a previous thesis [1], the literature was searched for the reduction of these nitro compounds by various reagents and the extent of these reductions. Secondly, the literature was reviewed for the action of alkalies upon all five of these aliphatic nitro compounds.

A. The Action of Alkalies upon Nitromethane

P. Friese[6] was apparently the first to investigate any reaction between an alkali and nitromethane. In 1876 he obtained a white crystalline powder, the sodium salt of nitromethane, by the action of alcoholic sodium hydroxide upon nitromethane.

By the use of sodium ethylate upon nitro methane and evaporating from ether, V. Meyer[7] in 1894 obtained the free sodium salt of nitromethane and not the double salt of sodium nitromethane with water or alcohol as is obtained with alcoholic sodium hydroxide.

Likewise in 1894 Nef[8] obtained the sodium salt of nitromethane by adding sodium to an ethereal solution of nitromethane and evaporating to dryness.

Furthermore Nef showed that the sodium salt of isonitromethane and not the sodium salt of nitromethane was the correct one formed. That is, the formula was found to be $H-\underset{H}{C}=N=O\overset{O}{}Na$ and not $H-\underset{Na}{\overset{H}{C}}-N\overset{O}{\underset{O}{}}$. Nef proved this to be true from the following facts:

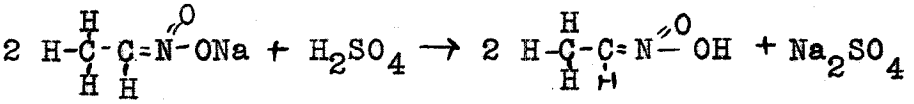
1. When a cold aqueous solution of a salt of a nitroparaffine was decomposed by cold dilute acids, the nitroparaffine was regenerated to a very small extent, the larger part was decomposed into nitrous oxide and aldehyde (from primary nitro compounds) or ketones (from secondary nitro compounds) according to the following equations:

$$2R\underset{H}{C}=N-O\overset{O}{}Na + 2HCl \rightarrow 2R\underset{H}{C}=O + N_2O + H_2O + 2NaCl$$

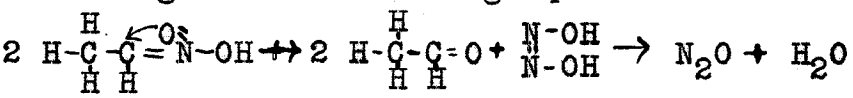
$$2\ \begin{matrix}R\\ R'\end{matrix}\!\!>C=N-O\overset{O}{}Na + 2HCl \rightarrow 2\ R\underset{R}{C}=O + N_2O + H_2O + 2NaCl$$

This indicated that the salts did not have the same constitution as the original compounds, for if this had been the case the sodium salts would have been completely reverted to the original nitro compound upon the addition of the acid.

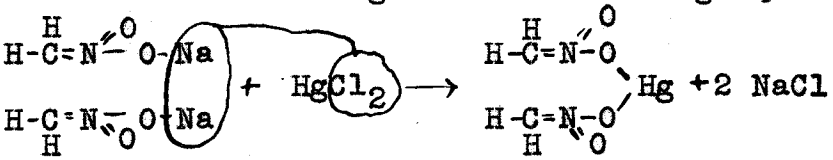
With sodium isonitroethane and dilute sulfuric acid the following reaction was almost quantitative:



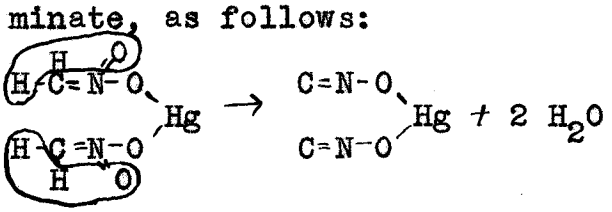
Intramolecular oxidation-reduction then occurred forming acetaldehyde and an intermediate compound which decomposed into nitrous oxide and water, according to the following equation:



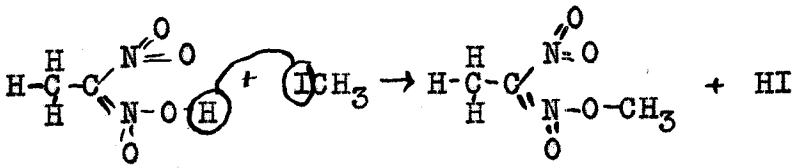
2. When aqueous mercuric chloride was added to aqueous sodium isonitromethane, mercuric fulminate was formed according to the following equations:



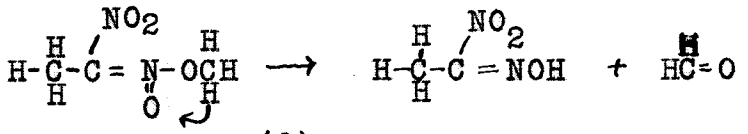
This compound lost water forming mercuric fulminate, as follows:



3. The action of methyl iodide upon the silver salt of dinitromethane to give ethyl nitrolic acid and formaldehyde was readily explained by the application of this formula, as follows:



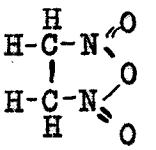
This intermediate compound underwent intramolecular oxidation-reduction, giving ethyl nitrolic acid and formaldehyde, as follows:



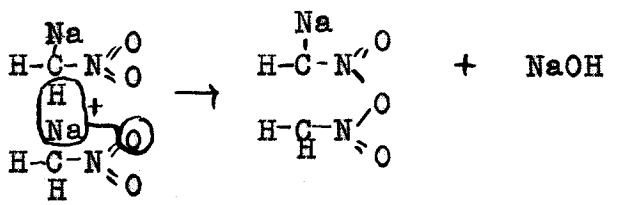
In 1876 Lecco[9] discovered a light brown powder, the sodium salt of methazonic acid, by heating nitromethane with sodium ethylate. Lecco proposed the following correct empirical equation for the formation of methazonic acid:

$$2\ CH_3NO_2 \longrightarrow H_2O + C_2H_4N_2O_3$$

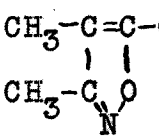
However he erroneously supposed methazonic acid to have the following structural formula:



This erroneous supposition was based upon the false formula for sodium nitromethane, which lead to the following equation for the formation of the sodium salt of methazonic acid:

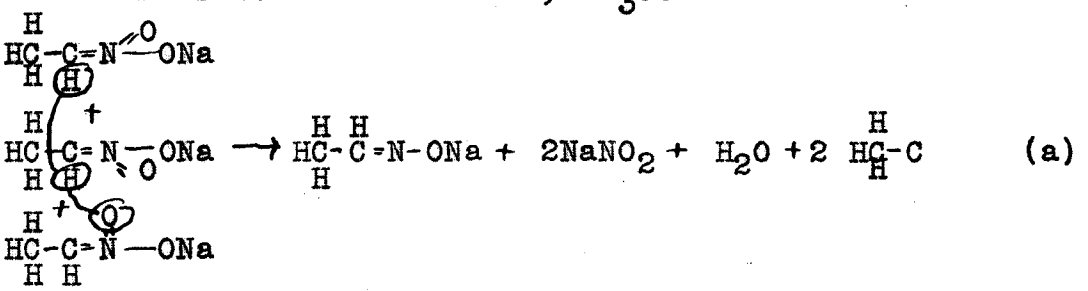


Dunstan and Dymand[10] found there was no reaction between dry sodium or potassium carbonate and nitroethane.

They found however that if they let nitroethane stand with a strong aqueous solution of potassium carbonate that the mixture became yellow and crystals of potassium acid carbonate separated. Upon warming the mixture, it darkened and separated into two layers. The top oily layer contained methyl cyanide, while the lower aqueous layer contained nitrite, ammonia, and a new compound which was proven to be trimethyl-isoxazole,  .

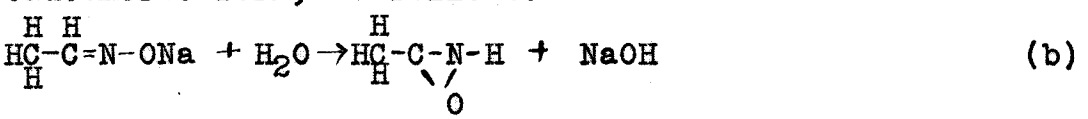
Dunstan and Goulding[11] offered the following mechanism for the reaction of alkalies on nitroethane:

> Representing the sodium salt of nitroethane as sodium isonitroethane, based upon Nef's formula for the isonitroparaffines, the sodium derivative of acetaldoxime was formed together with sodium nitrite and a residue, CH_3C:



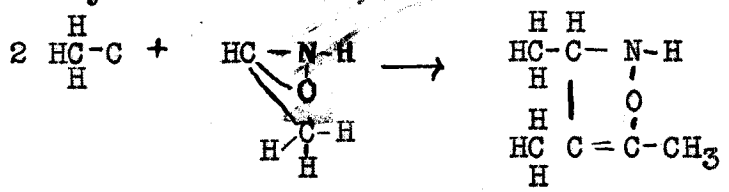
(a)

The sodium derivative of acetaldoxime dissociated in the presence of water and the oxime seemed to change into its tautomeric form, as follows:



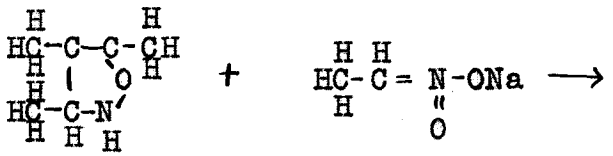
(b)

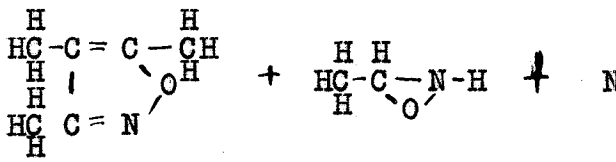
This then combined with the CH_3 C residue forming trimethyl isoxazoline, thus:



(c)

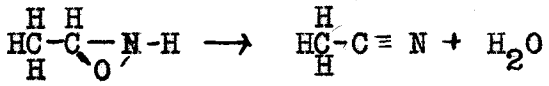
which in the presence of unaltered sodium nitroethane was immediately oxidized, yielding trimethyl isoxazole and acetaldoxime, according to the following equation:





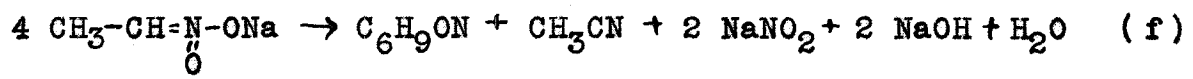
(d)

The acetaldoxime was dehydrated forming the acetonitrile:



(e)

The summation of equations (a - e) gave the following completed equation:

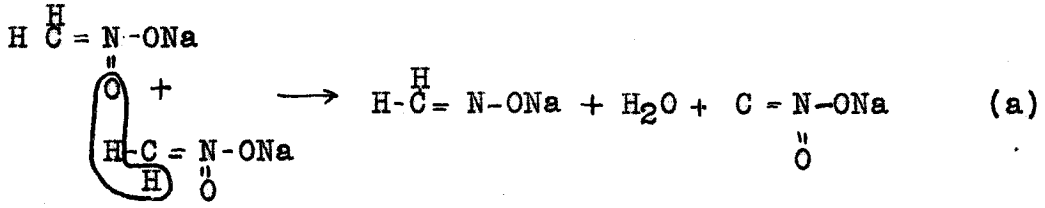


(f)

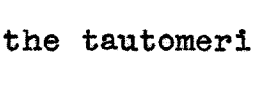
Although Dunstan[10] claimed the reaction was in stoicimetric relation, I was unable to find in his work the extent of yields of more than one of his products. Furthermore, his mechanism of reaction does not seem to be very sound since he has postulated univalent carbon.

Dunstan[10] likewise determined qualitatively the action of several other alkalies upon nitroethane. He found that warm aqueous sodium hydroxide or potassium hydroxide acted upon nitroethane to give a nitrite, trimethyl isoxazole, ammonia, acetate, and an undetermined brown resin. The ammonia and acetic acid resulting from the hydrolysis of acetonitrile which was first formed. Alcoholic soda or potash with nitroethane gave trimethyl isoxazole, an aldehyde, nitrite and the brown resin. Calcium hydroxide gave no reaction with nitroethane. Dry ammonia at 0° C. readily united with nitroethane to give a snow white mass of tabular crystals of the following composition, $C_2H_5NO_2 \cdot NH_3$. Aqueous ammonia and aqueous ethylamine acted much less energetically upon nitroethane. Concentrated aqueous ammonia heated with nitroethane in a sealed tube at 110° - 120° C. gave ammonium nitrite, acetonitrile, and trimethyl isoxazole. Alcoholic ammonia with nitroethane produced aldehyde, ammonium nitrite, acetonitrile and trimethyl isoxazole.

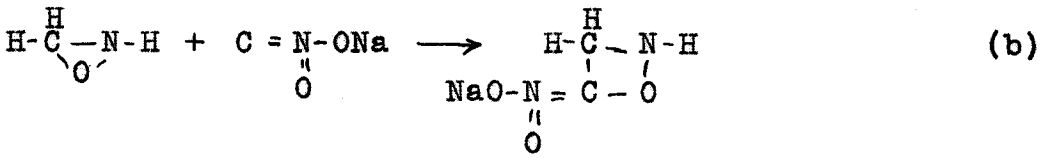
When Dunstan[10] mixed aqueous ammonia or potassium carbonate with nitroethane he obtained an immediate reaction and darkening in color to almost black. The products consisted of nitrite, hydrogen cyanide and methazonic acid. Dunstan[11] postulated the following mechanism of reaction, based upon Nef's formula for sodium isonitromethane:



(a)

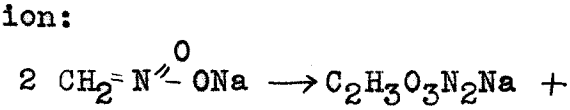
The sodium salt of formaldoxime thus generated then dissociated into the tautomeric form of oxime, 

which condensed with the nitromethane residue yielding the sodium salt of methazonic acid, as follows:

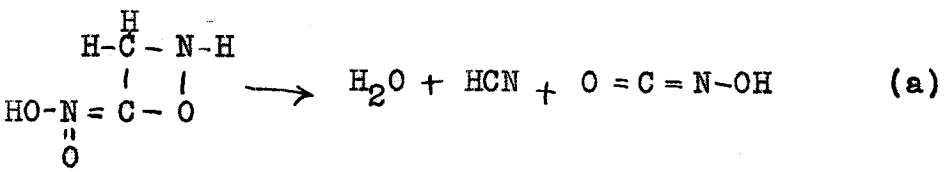


(b)

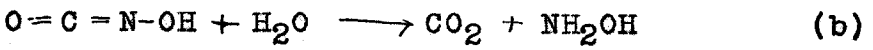
The summation of these equations gave the following equation:



Dunstan based this formula of the sodium salt of methazonic acid upon the products of hydrolysis of sodium methazonate, i.e., carbon dioxide, hydrogen cyanide, and hydroxyl amine. The equations were represented as follows:



(a)



(b)

The summation of (a) and (b) gave the following equation. The yields were about 96% of the theory in conformity with this equation:

$$C_2H_4N_2O_3 \longrightarrow CO_2 + NH_2OH + HCN$$

Upon continued heating of methazonic acid with aqueous alkalies, the hydroxylamine formed decomposed into nitrate and ammonia according to the following equation:

$$4\ NH_2OH \longrightarrow HNO_3 + 3\ NH_3 + H_2O$$

Although Dunstan showed the percentage yield of the decomposition products of methazonic acid, he did not show the percentage yield of methazonic acid from the original nitromethane. Furthermore his structural formula for methazonic acid is in disagreement with Hantzsch's formula for methazonic acid based upon absorption curves and with Meister's chemical reactions of methazonic acid.

Dunstan[11] obtained the ammonium salt of methazonic acid by passing ammonia into a solution of aqueous ammonia and nitromethane below 10°C. until the solution was saturated with ammonia.

Dunstan[10] found that alkalies acted upon primary nitropropane at 100°C. to give triethyl isoxazole, ethyl cyanide and nitrous acid according to the following equation:

$$4\ C_3H_7NO_2 \longrightarrow C_9H_{15}NO + C_2H_5CN + 2\ HNO_2 + 3\ H_2O$$

However like the rest of his work Dunstan did not quantitatively prove this reaction.

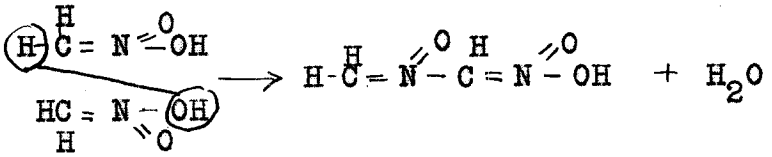
Secondary nitropropane with aqueous sodium hydroxide in a sealed tube at 115° C. gave acetone, nitrous acid, hydroxylamine and cyanide.

Meister[12] obtained good yields of free methazonic acid by neutralizing the sodium salt with sulfuric acid. Steinkopf and Bohman[13] obtained 90% free methazonic acid by just neutralizing the sodium methazonate with sulfuric acid and then evaporating the crystals from ether in a vacuum desiccator containing sulfuric acid.

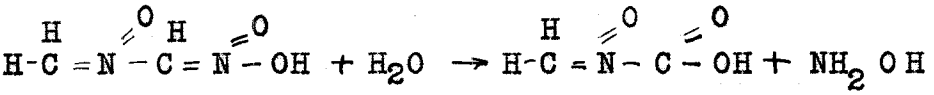
Steinkopf[14] obtained free methazonic acid from nitromethane by heating it with sodium hydroxide below 55° C. The solution was neutralized directly with hydrochloric acid, separated, strongly acidified and dried upon a porous plate in a desiccator. It was purified by crystallization from ether and dried over calcium chloride.

Scholl[15] attacked Dunstan's formula for methazonic acid from the standpoint that Dunstan's theory for the production of methazonic acid was too involved and furthermore that the formula did not best explain the products of hydrolysis. Scholl believed under these conditions of hydrolysis that there would not be a carbon-carbon rupture but some other type of rupture. Scholl believed the formation should show a nitrogen analogue to acetic acid and be monobasic, since Schultze[16] showed methazonic acid to be monobasic in character.

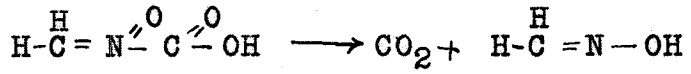
Scholl represented the formation of methazonic acid in the following simple manner:



He also explained the hydrolysis to hydroxylamine, carbon dioxide, and hydrogen cyanide according to the following equations. The methazonic acid first hydrolyzed to the nitrogen analogue pyruvic acid and hydroxylamine as follows:

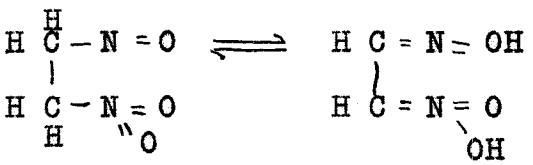


This nitrogen analogue of pyruvic acid then decomposed into formaldoxime and carbon dioxide:

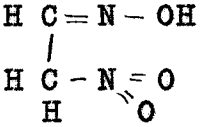


The formaldoxime then decomposed into hydrogen cyanide, and water:

Meister[17] thought it existed as tautomers of the following forms:



However, from his data, the formula

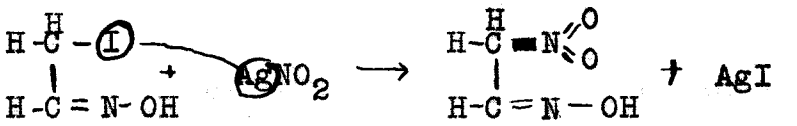


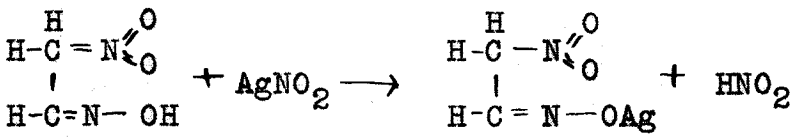
seems to be the tautomer in preponderance.

Meister showed the radical N OH to be present from the reaction of methazonic acid with aniline, chloraniline, and phenylhydrazine. A nitro group ($N\begin{matrix}O\\O\end{matrix}$) was indicated by the fact that these derivatives reacted with nitrous acid to give a nitrolic acid test. A carbon-carbon linkage was shown by the fact that hydrolysis of the derivatives yielded acetaldehyde.

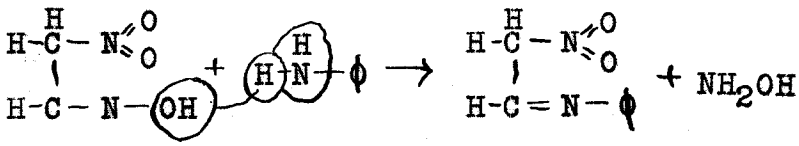
Meister found that iodoacetaldoxime reacted with silver nitrite to give a silver salt of aldoxime, this indicated that the nitrogens were attached to two different carbon atoms, furthermore it conformed with the above stated formula, $H\text{-}C(=N\text{-}OH)\text{-}C(H)\text{-}N\rightarrow O$, of methazonic acid.

The reaction may be indicated as follows:

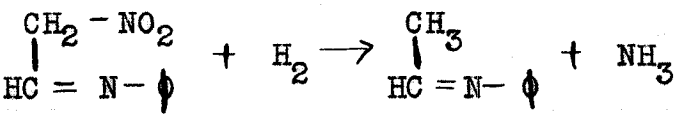




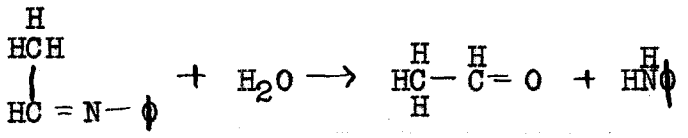
The reaction of aniline with methazonic acid yielding nitro ethylidineanil and hydroxylamine was indicated as follows:



This compound then reacted with nitrous acid indicating a primary nitro group. Furthermore upon reduction ammonia was split off leaving the anil according to the following equation:

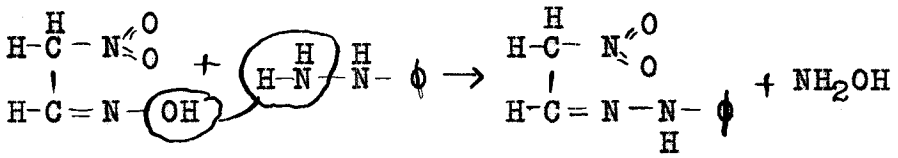


This anil in neutral solution then hydrolyzed to acetaldehyde and aniline, indicating a carbon-carbon linkage of two carbon atoms in methazonic acid. The hydrolysis may be represented thus:



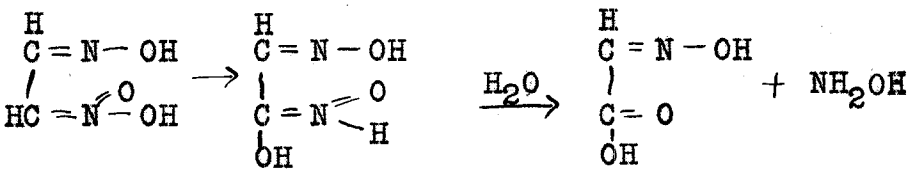
p-chloraniline and p-nitroaniline gave similar results.

Meister furthermore showed that methazonic acid reacted with phenyl hydrazine yielding nitroacetaldehyde phenylhydrazone, according to the following equation;

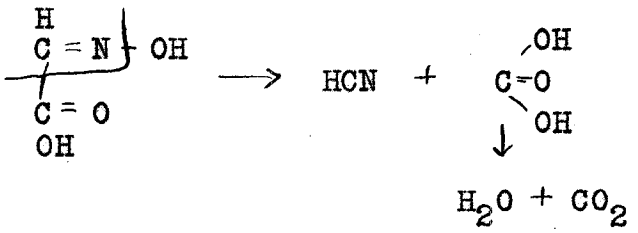


This derivative also gave a nitrolic acid test indicating a primary nitro group.

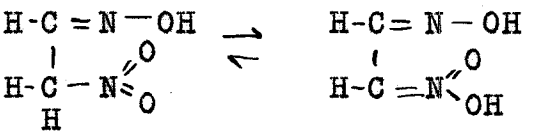
Meister showed the following set of equations to explain the hydrolysis of methazonic acid to hydroxylamine, carbon dioxide and hydrogen cyanide:



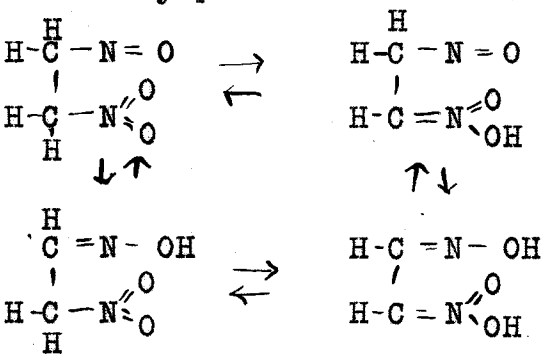
The oxamido acetic acid then decomposed into hydrogen cyanide, carbon dioxide and water:



Hantzsch[18] by spectral analysis showed methazonic acid to be present in the following two forms:



It seems very plausible to me that the following four tautomers might be present at various times depending upon the prevailing conditions. The fourth tautomer has not been postulated any place in the literature.

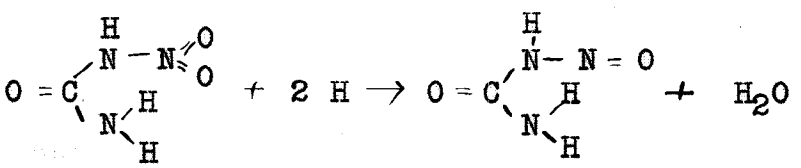


Pritzl[19] determined that the loss of formation of nitromethane from chloracetic acid and sodium nitrite due presumably to the formation of methazonic acid was 23 - 24 %.

Franklin and Krause[26] found at -33°C. and 105 millimeters that liquid ammonia formed a crystalline addition compound with nitromethane of the formula $CH_3NO_2 \cdot 2NH_3$. Furthermore he found at a pressure of a few millimeters and -33°C. the compound was $CH_3NO_2 \cdot NH_3$.

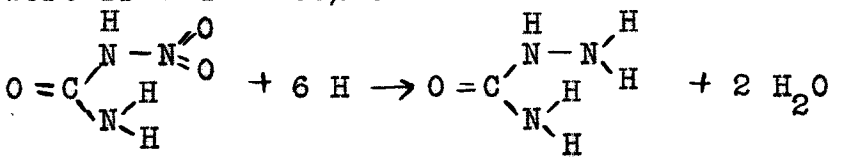
B. Nitrourea

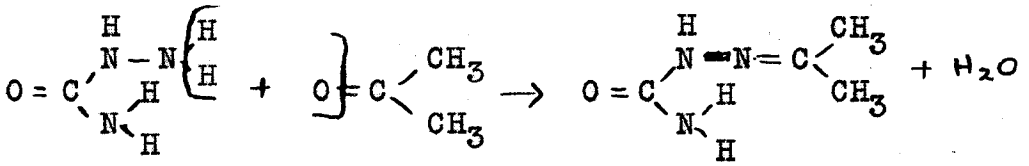
Thiele and Lachman[21] thought that they obtained nitroso-urea by the action of 20% NaOH and zinc or aluminum in the cold upon nitrourea. Although they could not isolate the compound nor any nickel or copper derivatives nor any benzoyl derivative, they obtained a purple red coloration upon the addition of ferrous sulfate and upon acidifying the solution supposed to contain nitrosourea noted a yellow coloration similar to nitrosoguanidine and nitrous acid. These latter facts indicated qualitatively the following reaction in which nitrourea was reduced to nitrosourea:

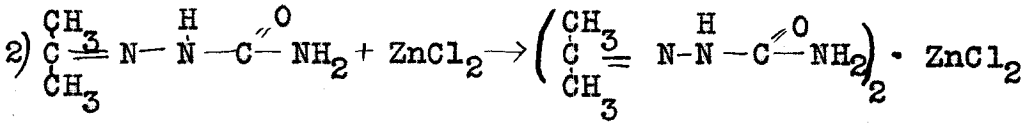


Nitrourea has been reduced to semicarbizide by Thiele and Lachman[22] and extracted as the benzaldehyde compound, i.e., benzylidine semicarbizide. Thiele and Heuser[23] added ice cold nitrourea and concentrated hydrochloric acid to a paste of zinc dust and ice.

After standing, filtering, addition of sodium chloride and sodium acetate and the addition of acetone they obtained acetone semicarbizide. The theoretical yields as the double salt with zinc chloride, according to the following equations, were from 40 - 55% :







Holyrod[24] electrolytically reduced nitrourea in an aqueous solution of NH_4Cl to semicarbizide. He obtained 66% yields of benzylidine semicarbizide when recrystallized from commercial alcohol. From the solution of unpurified benzylidine semicarbizide with concentrated hydrochloric acid he obtained 89% semicarbizide hydrochloride according to the method of Thiele and Stange[25].

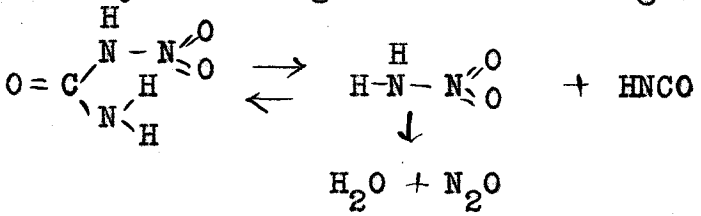
Cardier[26] decomposed nitrourea with sodium hypobromite obtaining nitrogen.

Thiele and Lachman[22] obtained some nitroamide (NH_2NO_2) by the action of hypochlorous acid on nitrourea.

Thiele and Lachman[27] observed that nitrourea, a strong acid easily expelling carbonic acid, formed neutral alkali salts and decomposed in the presence of warm alkalies with the formation of a gas. They[22] also observed that nitrourea decomposed upon melting or evaporation and that a concentrated aqueous solution decomposed above 60 C. Thiele and Lachman[22] also found that the potassium salt of nitrourea separated if alcoholic potash were added to a solution of nitrourea.

Willstätter and Pfannensteil[28] observed only qualitatively that aqueous sodium hydroxide with nitrourea evolved nitrous oxide in the cold, and ammonia upon warming.

Davis and Blanchard[29] heated aqueous nitrourea in a sealed tube and obtained nitroamide and cyanic acid quantitatively according to the following equation:

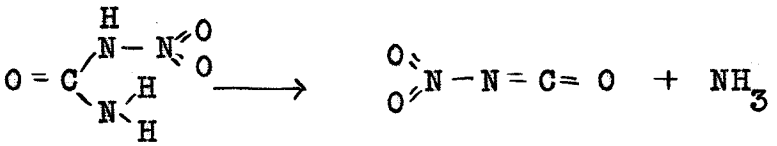


They found that bases promoted the previous reaction while acids hindered it. The above reaction is irreversible in so far as nitrourea is produced from silver cyanate, nitroamide and hydrochloric acid.

Davis and Blanchard found that nitrourea heated to 170 C. in vacuum decomposed giving a sublimate and a residue.

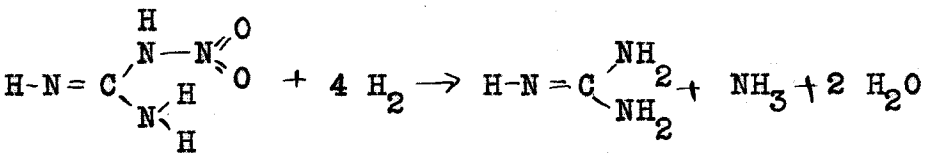
The gases consisted of water, nitrous oxide, cyanic acid, carbon dioxide and ammonia, while the solids found were urea ($O=C(NH_2)_2$), biuret ($H_2N-C(=O)-NH-C(=O)-NH_2$), ammonium cyanurate ($NH_4-O-C_3N_3(OH)_2$), and ammelide ($C_3N_3(NH_2)(OH)_2$).

From the above products they believed only from qualitative data that nitrourea also decomposed according to the following equation yielding ammonia and nitrocyanic acid:



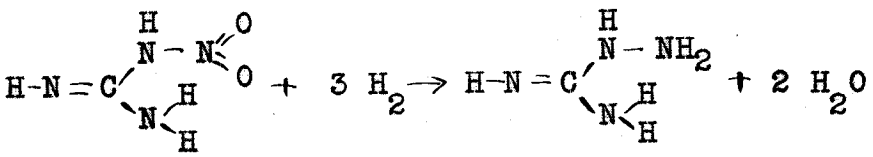
C. Nitroguanidine

Pellizzari[30] warmed nitroguanidine with a dilute solution of stannous chloride in an attempt to obtain aminoguanidine. However instead he found guanidine and ammonia which was represented by the following assumed equation:

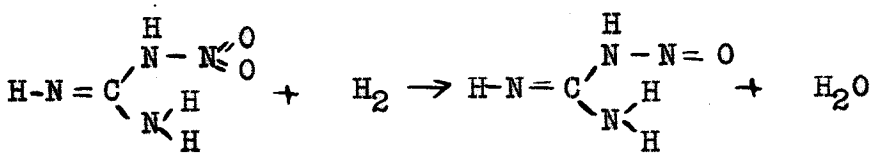


Thiele[31] succeeded in reducing nitroguanidine to aminoguanidine by adding nitroguanidine to a paste of zinc dust ice and glacial acetic acid. Although nitroguanidine was first reduced to nitrosoguanidine he was

unable to isolate it. The equation for the formation of aminoguanidine was proposed as:



However the following year Thiele[32] isolated nitrosoguanidine by reducing nitroguanidine with zinc dust and sulfuric acid. The equation was represented thus:



Friedlander[33] reported that Boehringer electrolytically reduced nitroguanidine to aminoguanidine to an extent of 81.3% by using a zinc cathode in a sulfuric acid bath.

Smith and Sabetta[34] reduced nitroguanidine to nitrosoguanidine in a solution of ammonium chloride and zinc. Then they determined the oxidation-reduction potential of nitro $\rightleftharpoons$ nitrosoguanidine.

Cardier[26] split off two atoms of nitrogen from nitroguanidine with sodium hypobromite.

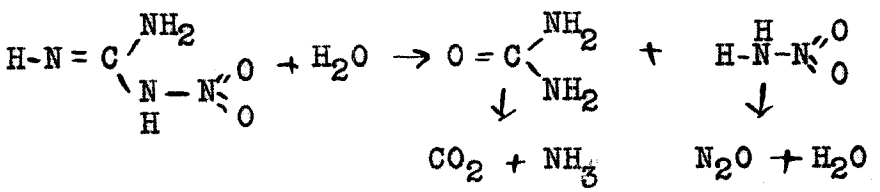
The following investigators reported that nitroguanidine melted with decomposition, giving off ammonia:

Jousselein[35] at 220°; Pellizzari[30] at 225°;
Franchimont[36] at 222°; and Thiele[34] at 230°.

Jousselein[38] noticed that a concentrated solution of potassium hydroxide, sodium hydroxide or barium hydroxide with nitroguanidine, (he erringly thought it was nitrosoguanidine), immediately evolved ammonia.

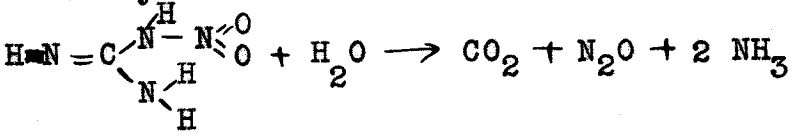
Pellizzari[30] found in an alkaline solution that nitroguanidine decomposed to nitrous oxide, ammonia and carbon dioxide. However he reported that he could not get any constant quantitative results.

Franchimont[36] found that nitroguanidine dissolved readily in aqueous ammonia and that this solution evolved nitrous oxide at ordinary temperatures. Furthermore he reported that nitroguanidine dissolved in an aqueous solution of potash or baryta also evolved nitrous oxide, that in the latter case there was a precipitate of barium carbonate and that the liquid smelled strongly of ammonia. He proposed the following equation which was not quantitatively verified:



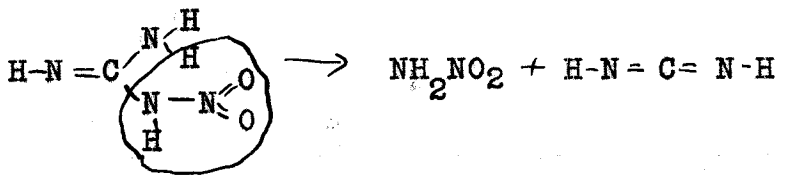
Thiele[37] discovered that upon warming an alkaline solution of nitroguanidine there was a lively evolution of nitrous oxide and ammonia and that the liquid residue contained carbonate. He offered the following

equation, but did not perform and quantitative experiments to verify the stoichimetric relation:

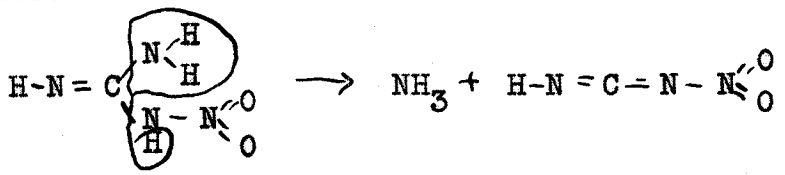


T. L. Davis[39] found that nitroguanidine when heated decomposed, yielded cyanamide, cyanic acid, carbon dioxide, prussic acid, cyanuric acid, melamine, melam, melem, ammeline, ammelide, mellon, cyanogen, paracyanogen and nitroguanidine.

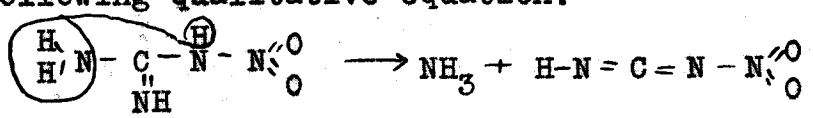
Davis[39] expected nitroguanidine to decompose in two different ways. The first was to yield nitramide and cyanamide according to the following equation:

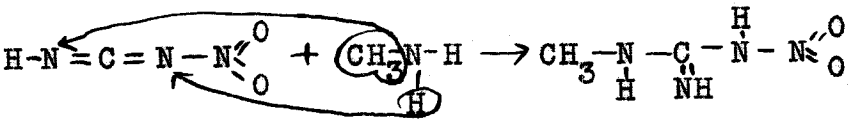


In the second, it decomposed to yield ammonia and nitrocyanamide:

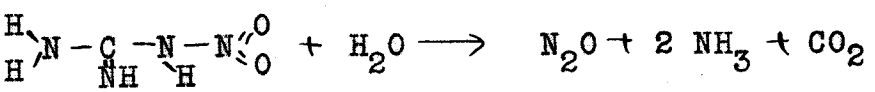


He believed that the second reaction occurred from the fact that methylamine with aqueous nitroguanidine produced ammonia and methyl nitroguanidine, according to the following qualitative equation:





Davis offered the decomposition of nitroguanidine in concentrated sulfuric acid in support of his first reaction. He noticed that if nitroguanidine were heated with concentrated sulfuric acid for a long time at an elevated temperature, that nitrous oxide, ammonia, and carbon dioxide were formed. He claimed that the ammonia and carbon dioxide were produced quantitatively in accordance with the following equation:



Since his reaction was in an acid medium this ammonia would have been retained in the reaction mixture and would have necessitated a Kjeldahl determination to estimate the ammonia. He did not describe or mention this or any other method for the determination of ammonia, i.e., he did not determine the ammonia at all.

He claimed that from 380 milligrams of nitroguanidine, using oxygen to sweep out the system, he obtained the following results:

79.0 c.c. of CO_2; 44.5 c.c. of O_2;

77.0 c.c. of N_2O; 31.0 c.c. of N_2.

Davis does not describe how he analytically determined the amounts of these various gases. He contended

that the yield of nitrous oxide was not quantitative since there was elementary nitrogen present. For 380 milligrams of nitroguanidine there should have been 81.8 c.c. of N_2O present (104.06/ 0.380 = 22,412/x, x = 81.8 c.c.; $NH_2NO_2 \rightarrow N_2O + H_2O$). He found 77 c.c. N_2O, therefore there was a shortage of 4.8 c.c. This would correspond to 5.6 c.c. of nitrogen according to the following equations which were previously described by Davis[40]:

$$6\ NH_2NO_2 + 6\ H_2O \rightarrow 6\ NH_3 + 6\ HNO_3$$

$$6\ HNO_3 \rightarrow 3\ H_2O + 6\ NO_2 + 1\tfrac{1}{2}\ O_2$$

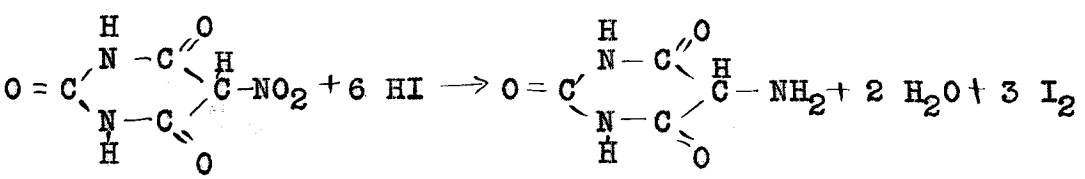
$$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$$

Therefore $6\ NO_2 \rightleftharpoons 6\ NH_2NO_2 \rightleftharpoons 7\ N_2$, so 4.8 c.c. NO_2 would be equivalent to 7/6 x 4.8 c.c. = 5.6 c.c. N_2. Davis found 31.0 c.c. of nitrogen.

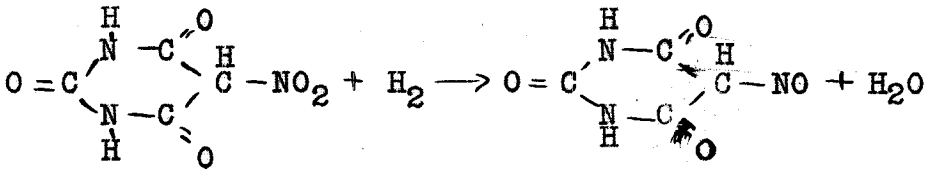
It thus appears that the occurrence of this reaction was not quantitatively verified.

D. Nitrobarbituric Acid

Bayer[41] found that nitrobarbituric acid was reduced to aminobarbituric acid by hydroiodic acid, presumably according to the following equation:



Bayer found that nitrobarbituric acid was reduced to nitrosobarbituric acid by glycerine or that the iron salt of barbituric acid was reduced by potassium cyanide to nitrosobarbituric acid, thus:



Bayer[42] obtained the mono- and di-alkaline salts of barbituric acid. Blitz[43] claimed that nitrobarbituric acid acted as a mono-, di-, or tribasic acid. Blitz and Sedlatscheck[44] stated that nitrobarbituric acid was quite stable to caustic alkalies, which is contradicted by the data secured in the present study.

E. Chlorpicrin

Stenhouse[45] found that chlorpicrin decomposed if warmed gently with potassium. If it were not heated, then in the course of a couple of days he found potassium chloride and potassium nitrate. Although he does not mention it, evidently the nitrate came from previously formed nitrite oxidized by the air. He claimed that chlorpicrin was stable towards cold aqueous sodium or potassium hydroxide, but decomposed yielding potassium chloride and nitrate when warmed. Stenhouse claimed that chlorpicrin boiled at 120 but could be heated to 150 without suffering decomposition. If the vapor of chlorpicrin was

passed through a heated glass tube below red heat chlorine, nitric oxide and perchlorethane (C_4Cl_6) were formed.

Cassa[46] reported that chlorpicrin exploded when rapidly heated or when the vapor was led into a red hot tube.

Geisse[47] used iron and acetic acid to reduce chlorpicrin to methylamine. He claimed the product was free from ammonia. Methylamine was also obtained by reduction of chlorpicrin with ferrous sulfate and potassium hydroxide. Geisse offered the following qualitative equation:

$$CCl_3NO_2 + 12\ H \longrightarrow CH_3NH_2 + 3\ HCl + 2\ H_2O$$

Wallach[48] also obtained methylamine from chlorpicrin by reduction with tin and hydrochloric acid.

Frankland, Challenger and Nicholls[49] used iron filings and hydrochloric acid to obtain methylamine. They also obtained some ammonia. The yields and purity depended upon conditions and concentrations.

Hoffman[50] heated chlorpicrin with a strong alcoholic ammonia solution and obtained guanidine and hydrochloric acid.

Raschig[51] by the action of stannous chloride and hydrochloric acid upon chlorpicrin obtained trichloraminomethane which decomposed into cyanogen chloride and hydrochloric acid. He gave no quantitative data but offered the following equations:

$$CCl_3NO_2 + 3\ SnCl_2 + 6\ HCl \rightarrow 3\ SnCl_4 + CCl_3NH_2 + 2\ H_2O$$

$$CCl_3NH_2 \rightarrow NCCl + 2\ HCl$$

There were also traces of ammonia and hydroxylamine present.

Bassett[52] mixed 40 grams of chlorpicrin with 10 oz. of anhydrous ethyl alcohol in a flask with a vertical condensor. To this he added 24 grams of sodium in 0.5 gram pieces, little by little. The flask was refluxed upon a water bath, the alcohol distilled off and the residue dissolved in water, whence an oily layer of ortho ethyl carbonate separated above. The action followed according to the equation:

$$CCl_3NO_2 + 4\ C_2H_5ONa \rightarrow 3\ NaCl \rightarrow NaNO_2 + C(OC_2H_5)_4$$

Besides the sodium chloride and sodium nitrite the water also contained some sodium carbonate. Bassett claimed that its formation undoubtedly depended upon a secondary decomposition of a part of the oily product according to the following equation:

$$C(OC_2H_5)_4 + 2\ NaOC_2H_5 \rightarrow Na_2CO_3 + 3\ (C_2H_5)_2O$$

He claimed that the odor of ether was distinctly noticeable in the first portion of the alcoholic distillation. There was also some ammonia evolved along with the hydrogen gas. He presented no quantitative data to verify either of the above reactions.

Bewad[53] let zinc methyl stand with chlorpicrin for 2 - 5 months. He found that it formed tertiary nitrobutane according to the following equation:

$$CCl_3NO_2 + 3\ ZnCH_3 \rightarrow (CH_3)_3CNO_2 + 3\ ZnCH_3Cl$$

Also some nitromethane, nitroethane, and secondary nitropropane were formed.

With zinc ethyl Bewad[54] obtained tertiary nitroheptane, secondary nitropentane and primary nitropropane.

Gardner and Fox[55] slowly decomposed chlorpicrin into phosgene and nitrosyl chloride by merely boiling it. They absorbed the nitrosyl chloride in concentrated sulfuric acid which formed nitrosyl sulfuric acid and hydrochloric acid. They separated the sulfuric from the nitrosylsulfuric by distillation. Then after hydrolysis of the nitrosylsulfuric acid the amount of sulfuric found was a measure of the amount of nitrosyl chloride. The carbonyl chloride was absorbed in benzene and reacted with potassium hydroxide to form potassium carbonate and chloride which could be quantitatively determined. The following equation represents the chemical reaction which occurred:

$$CCl_3NO_2 \rightarrow COCl_2 + NOCl$$

Piutti[56] found that freshly distilled chlorpicrin became yellow in diffused light and assumed the color of nitrous vapors. Solutions of chlorpicrin in ethyl alcohol, methyl alcohol, benzene, turpentine, etc., remained unchanged in the dark, but they all became colored in the light except the alcohols. The solutions in alcohol contained ammonia.

Henderson and Macbeth[57] found that hydrazine slowly removed the chlorine atoms. Titanium chloride reduced the nitrogroup but had no effect upon the chlorine atoms. Potassium ferrocyanide had no effect.

Petrov and Savel'ev[58] found little decomposition at 100 , but at the boiling point 112.7 there was a ten fold decomposition. Metals had little catalytic action upon the rate of decomposition.

Chmutov and Zhukor[59] stated that above 500 in a heated tube chlorpicrin colored starch iodide paper because of the formation of ozone. (This is doubtful).

Kretov and Melnikov[60] found that alcoholic chlorpicrin refluxed with sodium hydrogen sulfide gave carbon dioxide, carbon monoxide, oxygen, nitric oxide, nitrogen, sulfur, sodium chloride, sodium nitrite, ammonia and hydroxylamine.

Alekseevski[61] found that the acceleration of decomposition of chlorpicrin in water on exposure to actinic rays increased in the following order of source of illumination: Rontogen, voltaic arc, mercury quartz lamp. Analogous action was effected with activated charcoal. The reactions formulated were as follows:

$$CCl_3NO_2 \longrightarrow COCl_2 + NOCl$$

$$COCl_2 + 2\ H_2O \longrightarrow H_2CO_3 + 2\ HCl$$

$$NOCl + H_2O \longrightarrow HCl + HNO_3$$

III

EXPERIMENTAL

A. Nitromethane

The nitromethane used in this part of the work was prepared from chloracetic acid and sodium nitrite according to directions given by the author in a previous thesis (1). The chloracetic acid (300 grams), was dissolved in 500 c.c. of water in a 2-litre long neck round bottom flask. This was neutralized to methyl orange by the slow addition, with stirring of 26.7 grams of anhydrous sodium bicarbonate. There was considerable evolution of carbon dioxide and the temperature of the solution dropped to 12 C. where it was maintained throughout neutralization. The sodium nitrite (140 grams), was dissolved in 200 c.c. of water in a 2-litre short neck round bottom flask.

The reaction was run in a 2-litre short neck flask which was fitted with a two-hole rubber stopper equipped with a constant level dropping funnel, and an exit tube connected to a long Liebig condenser. To the end of the condenser was attached an adapter which led into a vertical separatory funnel. This funnel had a two-hole rubber stopper at the top, one of which held the end of the

adapter and the other a piece of glass tubing that led to a suction flask which was stoppered at the top by a one-hole rubber stopper. The bottom of the suction flask which caught the overflowing distilled water was covered with solid sodium chloride to decrease the solubility of the remaining nitromethane. The lower end of the separatory funnel led to an Erlenmeyer flask which received the nitromethane over calcium chloride.

After the chloracetic acid was neutralized it was permitted to rise to room temperature and placed in the dropping funnel from time to time until it had all run into the sodium nitrite which was in the two-litre short neck flask. The nitrite was kept at room temperature for an hour while the acetate was slowly added. There was little effervescence but no nitromethane appeared on the surface. The distillation temperature was then raised to 80° C. and permitted to go to 100° C., where it was maintained for two and one-half hours by the heat of the reaction. The solution deepened in color and the nitromethane along with steam distilled over. The nitromethane was separated as it came over and the water collected in the suction flask. The aqueous salt solution was then redistilled through the same condenser, receiving a few more c.c. of nitromethane. The nitromethane was dried over a second portion of dry calcium chloride, redistilled, redried over a third portion

of calcium chloride and redistilled. This gave a yield of about 67 grams of nitromethane boiling at 102 C.

The formation of nitromethane is represented by the following equations:

$$ClCH_2CO_2H + NaHCO_3 \rightarrow ClCH_2CO_2Na + H_2O + CO_2$$

$$ClCH_2CO_2Na + NaNO_2 \rightarrow NO_2CH_2CO_2Na + NaCl$$

$$NO_2CH_2CO_2Na + H_2O \rightarrow NO_2CH_3 + NaHCO_3$$

Since a previous investigation[1] of tha action of three different concentrations of aqueous sodium hydroxide i.e., 15 N, 10 N and 5 N, upon nitromethane gave the same yields of ammonia and sodium carbonate it was the purpose of this present work to determine the reaction and yields of more dilute solutions of aqueous sodium hydroxide, i.e., 3 N, 1 N, and 0.5 N, upon nitromethane. Each concentration was run in simultaneous duplicates in the same oil bath.

For the first run 250 c.c. of approximately 3 N sodium hydroxide, 13.34 c.c. of nitromethane ($\frac{1}{4}$ mole) and 1.0014 grams of copper turnings were placed in a 500 c.c. copper flask. A vertical Liebig water concenser was connected to the copper flask through a tightly fitting one-hole rubber stopper. A piece of glass tubing led from the top of the condenser to a safety bottle, which in turn led to a Mulligan gas washing bottle containing a known amount of standard sulfuric acid. Previous runs had formed ammonia so rapidly that a vacuum was formed

which sucked the acid from the Mulligan bottle back into the copper flask. This was overcome by making an open system and drawing air through the complete apparatus while the flask was being heated in an oil bath. Thus a drying tube filled with calcium chloride as attached to the open end of the Mulligan washing bottle, while the other end of the drying tube was attached to a safety bottle which in turn was connected to an aspirator. A long piece of glass tubing was inserted through the inside of the inner tube of the condenser, almost to the liquid. The upper end of the glass tubing was connected to a drying tube filled with ascarite so that the air sucked through the system would be free from carbon dioxide. Thus when the aspirator was turned on a stream of air was continuously passing through the system preventing the acid from being sucked back and aiding in the sweeping out of the ammonia as it was formed.

Two copper flasks were simultaneously charged with nitromethane, sodium hydroxide and copper turnings, and placed in an oil bath which was maintained between 130° - 140°C. during the course of the reaction. The first Mulligan bottle contained 200.60 c.c. of 2.028 N sulfuric acid while the second one contained 200.00 c.c. of 2.028 N sulfuric acid. The aspirator was in operation during the period of reaction which lasted 10 hours. Air was also

drawn through the systen for about 1.5 hours afterwards until the flasks had cooled to room temperature. After cooling both the acid solution and alkaline solution respectively for each run were made up to one litre in volumetric flasks.

The acid solution was titrated with sodium hydroxide of known strength (1 c.c. base $\simeq$ 5/46.57 c.c. of 2.028 N sulfuric acid) using methyl red as an indicator.

Since 200.60 c.c. of 2.028 N sulfuric acid were placed in the first Mulligan bottle and 20 c.c. aliquot portions(1/50) were withdrawn from the litre flask and titrated with the above mentioned sodium hydroxide using methyl red as an indicator the following amount of ammonia resulted from the reaction:

Run	NaOH x 5/46.57 x 50 = c.c.	c.c. 2.028 N H_2SO_4 left	less 200.60 =
I_A	29.18	156.69	
	29.19	156.64	

c.c. acid used by NH_3	x .002028 =	Eq. or Moles of NH_3
43.91		0.08905
43.96		0.08915

The determination of the ammonia in the second run was identical in manner except 200.00 c.c. of 2.028 N sulfuric acid was used.

The results were as follows:

Run	c.c. NaOH	x 5/46.57 x 50 =	c.c. 2.028 N H_2SO_4 left	less 200.00 =
I_B	28.60		153.53	
	28.58		153.42	

c.c. acid used by NH_3	x .002028 =	Eq. or Moles of NH_3
46.47		0.09424
46.58		0.09447

The analyses for the yields of sodium carbonate which were expected to be equavalent to the yields of ammonia in conformity with a previously proposed equation for the reaction:

$$CH_3NO_2 + 2\ NaOH \longrightarrow NH_3 + Na_2CO_3 + H_2O$$

were made with satisfactory results according to the directions given by Foles[62]. The sodium hydroxide was analyzed for any carbonate present in it before the run. A 50 c.c. aliquot of the 3 N sodium hydroxide was used. It gave the following results:

	1.	2.
Weight of carbon dioxide	0.0225 g.	0.0226 g.
Weight of carbon dioxide in 250 c.c. of 3 N NaOH	0.1125 g.	0.1150 g.
Average weight of carbon dioxide	0.11275 g.	

For the carbonate analyses on the alkaline solution 50 c.c. (1/20 aliquot) portions were withdrawn from the litre flask and determined by the above stated method of adsorbtion in ascarite with the following results for I_A:

	1.	2.
Weight of carbon dioxide	0.2046 g.	0.2022 g.
Total carbon dioxide	4.0920 g.	4.0440 g.
Carbon dioxide from reaction	3.9792 g.	3.9312 g.
Moles of carbon dioxide	0.09043	0.08979
Average Moles of carbon dioxide	0.09011	

The results for the carbonate analysis on run I_B were as follows:

Weight of carbon dioxide	0.2161 g.	0.2170 g.
Total carbon dioxide	4.3220 g.	4.3400 g.
Carbon dioxide from reaction	4.2092 g.	4.2212 g.
Moles of carbon dioxide	0.09566	0.09593
Average Moles of carbon dioxide	0.095795	

For the second run 250 c.c. of approximately 1 N sodium hydroxide, 13.34 c.c. of nitromethane ($\frac{1}{4}$ mole), and 1.0014 grams of copper turnings were placed in a 500 c.c. copper flask. The Mulligan bottles contained 200.00 c.c. of 2.028 N sulfuric acid. The apparatus was set up and run identical with the preceeding run. The flasks were both heated as before in the same oil bath which was maintained between 130° - 140°C. during the course of the reaction which lasted through ten hours. The acid solutions in the

Mulligan bottles were both made up to one litre in volumetric flasks. The alkaline residues were also made up to one litre in one-litre volumetric flasks.

20 c.c. aliquot portions (1/50) of the acid solution were titrated with sodium hydroxide of known strength (a fresh solution of sodium hydroxide was made; 1 c.c. base $\rightleftharpoons$ 5/46.34 c.c. of 2.028 N sulfuric acid) using methyl red as an indicator.

The following results were obtained:

Run	c.c. NaOH	x 5/46.34 x 50 =	c.c. 2.028 N H_2SO_4 left	less 200.00 =
II_A	34.30		185.04	
	34.30		185.04	

c.c. acid used by NH_3	x .002028 =	Eq. or Moles of NH_3
14.96		0.03034
14.96		0.03034

Run	c.c. NaOH	x 5/46.34 x 50 =	c.c. 2.028 N H_2SO_4 left	less 200.00 =
II_B	34.04		183.65	
	34.04		183.65	

c.c. acid used by NH_3	x .002028 =	Eq. or Moles of NH_3
16.35		0.03316
16.35		0.13316

However unexpected difficulties were encountered when the carbonate was analyzed. The silver in the silver sulfate-sulfuric acid U-tube precipitated, the ascarite in the ascarite tower turned yellow and ascarite tower had gained considerable more in weight than that corresponding to the ammonia formed. When the silver sulfate solution and precipitate from this U-tube were acidified the odor of hydrogen cyanide was quite noticeable. It was then suspected that some methazonic acid was present from a second reaction of the nitromethane since the residual alkaline solution was not homogeneous and clear as in previous runs, but contained a brown flocculent precipitate.

If this were methazonic acid then it could have broken down into hydroxylamine, carbon dioxide, and hydrogen cyanide according to Dunstan and Goulding[63]. The equations for the formation of methazonic acid from nitromethane and the subsequent decomposition of this product into hydroxylamine, carbon dioxide and hydrogen are as follows:

$$2\ CH_3NO_2 \longrightarrow C_2H_4N_2O_3 + H_2O$$

$$C_2H_4N_2O_3 \longrightarrow NH_2OH + CO_2 + HCN$$

The silver sulfate precipitate was examined for hydrogen cyanide by two methods described in Prescott and Johnson's Qualitative Analysis revised by McAlpin and Soule[64].

A small amount of the sample is treated with ferrous sulfate and a few drops of alkali added. After shaking, a drop or two of ferric chloride is added and the whole acidified with sulfuric acid. If cyanide is present a blue precipitate of Prussian Blue (ferric ferrocyanide) separates.

Or secondly, to a sample in an evaporating dish is added 1 - 2 drops of ammonium polysulfide. This is digested on a water bath until the mixture is colorless and free from sulfide. It is slightly acidified with hydrochloric acid and a drop of ferric chloride added. The blood red color of ferric thiocyanate will appear if cyanide was present. This color remains upon heating but is discharged upon addition of mercurous chloride due to the reduction of the ferric iron to the ferrous iron.

However the Prussian Blue test was almost negative. In spite of this test cyanide was believed to be present because of its pronounced odor. The fact that silver cyanide is so slightly ionized might explain the fact that no more than a green color is obtained at first when testing for cyanide. A blank test for cyanide from known silver cyanide gave identical results with those of the unknown. The presence of ammonia also hinders the formation of Prussian Blue. Weith[65] recommends a solution of silver nitrate in ammonia for the decomposition of

many cyanogen compounds such as potassium ferrocyanide, Prussian Blue, and potassium cobalticyanide.

The fact that the ammonia and the carbonate do not check does not invalidate the following equation,

$$CH_3NO_2 + 2\ NaOH \rightarrow Na_2CO_3 + NH_3 + 2\ H_2O\ ,$$

because the excess carbonate may be due to that formed from the decomposition of the methazonic acid.

However there must also have been another reaction occurring simultaneously to form methazonic acid. Tests on the alkaline residue for methazonic acid showed that the solution contained a compound in accordance with those properties attributed to methazonic acid by Dunstan and Goulding[63]. The neutral solution gave a yellow precipitate with silver nitrate. This was soluble in dilute nitric acid or ammonia. It also gave a brownish yellow precipitate with mercuric chloride, which was soluble in hydrochloric acid. The neutral solution gave a grayish yellow precipitate with lead acetate, which compound upon heating exploded.

Upon testing the residue from the carbonate determination the presence of the strong odor of hydroxylamine was confirmed by the fact that the solution reduced an ammoniacal solution of silver nitrate yielding a heavy black precipitate.

Thus it has been shown that methazonic acid was formed during the run and that part of it decomposed into carbonate, cyanide and hydroxylamine during the analytical determination for carbonate.

If the amount of hydroxylamine left in the flask after carbonate determination corresponded with the excess carbonate then a measure of the extent of decomposition of methazonic acid according to the following equation could be determined:

$$C_2H_4N_2O_3 \longrightarrow NH_2OH + CO_2 + HCN$$

The residue from a carbonate determination was filtered twice and the solution evaporated to but 5 c.c. of brown liqiud in the presence of sulfuric acid. This was done on a glycerine bath so that it would be above the boiling point of nitromethane (101.5°C.) and below the melting point of hydroxylamine sulfate (140°C.). The hydroxylamine sulfate was digested with copper sulfate and potassium sulfate. By a Kjeldahl analysis more base was found than corresponded to the excess carbonate.

This means that either all the nitromethane or methazonic acid had not been removed before the hydroxylamine determination. Certainly all of both of these products did not decompose during the run or the carbonate determination.

Or it is possible that part of the hydroxylamine decomposed during the carbonate determination to give ammonia and nitrate as Dunstan and Goulding[63] obtained, according to the following equation:

$$2\ NH_2OH + O_2 \rightarrow NH_3 + HNO_3 + H_2O$$

Mellor[66] gave the following equations for the decomposition of hydroxylamine at 150° C.:

$$3\ NH_2OH \rightarrow N_2 + NH_3 + 3\ H_2O$$

$$4\ NH_2OH \rightarrow N_2O + 2\ NH_3 + 3\ H_2O$$

Addition of base suppresses the second reaction in favor of the first, while addition of acid suppresses the first in favor of the second.

For the third run 250 c.c. of 0.5 N sodium hydroxide, 13.34 c.c. of nitromethane ($\frac{1}{4}$ mole) and 1.0006 grams of copper turnings were placed in a 500 c.c. copper flask. The Mulligan bottles contained 100 c.c. of 2.028 N sulfuric acid. The apparatus was set up and run identical as in the previous runs. The flasks were heated as before in an oil bath which was maintained between 130° - 140° C. for a period of ten hours. The solutions were all made up as before in one-litre volumetric flasks.

The amount of ammonia found was as follows:

Run	c.c. NaOH	x 5/46.34 x 50 =	c.c. 2.028 N H_2SO_4 left	less 100.00 =
III_A	16.35		88.28	
	16.35		88.28	

c.c. acid used by NH_3	x .002028 =	Eq. or Moles of NH_3
11.72		0.02377
11.72		0.02377

Run	c.c. NaOH	x 5/46.34 x 50 =	c.c. 2.028 N H_2SO_4 left	less 100.00 =
III_B	16.45		88.53	
	16.45		88.53	

c.c. acid used by NH_3	x .002028 =	Eq. or Moles of NH_3
11.47		0.02326
11.47		0.02326

The results obtained for the action of 3 N, 1 N, and 0.5 N solution of sodium hydroxide upon nitromethane in terms of the postulated reaction,

$$CH_3NO_2 + 2\ NaOH \longrightarrow Na_2CO_3 + NH_3 + H_2O$$

are as follows:

Run		Concentration of NaOH	Moles of CO_2	Moles of NH_3	Molar Yield Ratio CO_2 : NH_3
I_A	1	3 N	0.09043	0.08905	1 : 0.985
	2		0.08979	0.08915	1 : 0.993
I_B	1		0.09566	0.09424	1 : 0.985
	2		0.09593	0.09447	1 : 0.988
II_A	1	1 N	0.05698	0.03034	1 : 0.532
	2		0.05748	0.03034	1 : 0.528
II_B	1		0.06289	0.03316	1 : 0.521
	2		0.06021	0.03316	1 : 0.551
III_A	1	0.5 N		0.02377	
	2			0.02377	
III_B	1			0.02326	
	2			0.02326	

The results obtained from the action of 3 N sodium hydroxide solution in this present work like those obtained with 15 N, 10 N and 5 N solutions in a previous investigation upon nitromethane were in accordance with the above equation. However with 3 N sodium hydroxide the extent of the reaction was only 36% of the theoretical yield in the one run and 38% in the other, as compared with about 48% theoretical yields in the former runs of 15 N, 10 N and 5 N solutions.

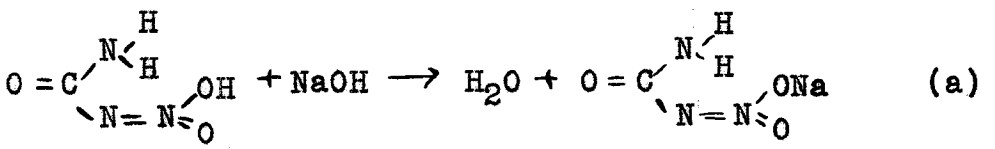
With the 1N sodium hydroxide solution it was believed that the postulated reaction occurred to an extent of 12 - 13% of the theoretical even though the carbonate was in excess of the amount of the ammonia required by it. This excess carbonate was believed to be due partially

to the decomposition of methazonic acid which had been formed in an undetermined extent in a side reaction from the condensation of two moles of nitromethane. This methazonic acid was then decomposed to an undetermined extent into carbondioxide, hydrogen cyanide, and hydroxylamine.

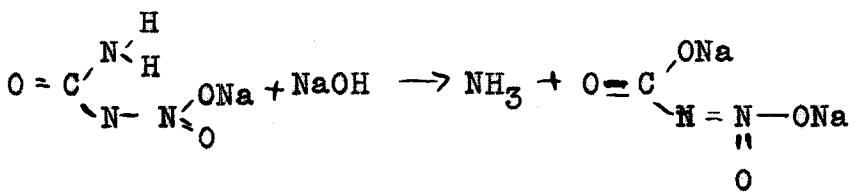
The postulated reaction evidently occurred to at least an extent of 9% theory with 0.5 N sodium hydroxide while the side reaction forming methazonic acid also occurred.

B. Nitrourea

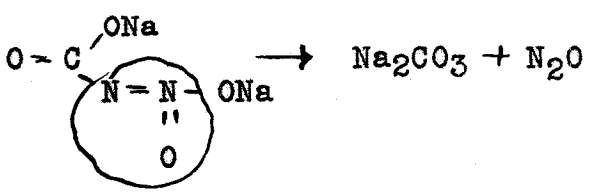
The following reaction-mechanism is proposed to explain the reaction between sodium hydroxide and nitrourea:



(a)



(b)



(c)

A summary of equations (a), (b) and (c) gives the following completed equation:

$$CH_3N_3O_3 + 2\ NaOH \longrightarrow N_2O + H_2O + NH_3 + Na_2CO_3$$

The formation of nitrous oxide in this reaction seems to indicate that it has the following structural formula; $N \equiv N = O$. The ease with which nitrous oxide loses its oxygen would also seem to support this formula. However if the structural formula for hyponitrous acid is HO-N = N-OH the structure of its anhydride would be $N=N$ (O bridging). Mellor[67] states that H. Henstock, K. A. Hoffman, L. Paulding and S. B. Hendricks favor the formula $N \equiv N = O$ over $N=N$ (O bridging). It may be possible that nitrous oxide exists in two tautomeric forms, thus:

$$N \equiv N = O \rightleftarrows N=N \text{ (O bridging)}$$

The experimental evidence confirming the occurrence of the reaction in conformity with the derived equation noted above is as follows:

The set up for the run of nitrourea and sodium hydroxide was the same as that in the run with nitromethane and sodium hydroxide except that a glass pyrex flask was substituted for the copper flask. Moreover there was a constant level dropping funnel connected to this glass flask for the introductiom of the sodium hydroxide solution.

In the first run 200 c.c. of approximately 5 N sodium hydroxide were added to the constant level dropping funnel. Approximately 1/10 mole, 10.2663 grams of Eastman's nitrourea (10.2663 ÷ 105 = 0.0977 mole) in the first run, were placed in a 500 c.c. glass pyrex wide mouth flask. In the second run 10.5896 grams of nitrourea (0.10094 mole) was used, while 11.9622 grams of nitrourea (0.11307 mole) was used in the third run. The Mulligan gas washing bottles each contained 200.00 c.c. of 1.8499 N sulfuric acid.

The sodium hydroxide was slowly run into the flask containing the nitrourea. The flask was heated upon an oil bath which rose from room temperature to 130° C. within an hour and maintained between 130° - 140° C. for a period 6 hours.

The gas evolved ignited a glowing splint and supported combustion. It was quite soluble in alcohol and did not give red fumes with nitric oxide, which showed it to be nitrous oxide. The formation of nitrous oxide was so great in the first part of the run that suction was not necessary, however in the later stages the aspirator was turned on as in the previous runs. The nitrous oxide was permitted to escape. The acid solution in the Mulligan bottle was made up to one litre in a volumetric flask as was also the alkaline residue. These were analyzed for ammonia and carbon dioxide respectively.

The sodium hydroxide was analyzed for the carbonate present before the run according to the directions given by Fales[62]. A 50 c.c. aliquot of 5 N sodium hydroxide gave the following results:

	1.	2.
Weight of CO_2 in 50 c.c.	0.0432 g.	0.0428 g.
Weight of CO_2 in 200 c.c. of 5 N NaOH	0.1728 g.	0.01712 g.
Average weight of CO_2 for the analyses	0.1720 g.	

For the carbonate analyses of the alkaline solution 50 c.c. (1/20 aliquot) portions were withdrawn from the litre flask and determined as before with the following results for I :

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.2189 g.	0.2195 g.
Total carbon dioxide	4.3780 g.	4.3900 g.
CO_2 from reaction	4.2060 g.	4.2180 g.
Moles of CO_2	0.09559	0.09586
Average Moles of CO_2	0.09573	

The carbonate results obtained for II were as follows:

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.2272 g.	0.2270 g.
Total carbon dioxide	4.5440 g.	4.5400 g.
CO_2 from reaction	4.3720 g.	4.3680 g.
Moles of CO_2	0.09936	0.09929

Average Moles of CO_2 0.09933

The carbonates found in III were as follows:

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.2544 g.	0.2541 g.
Total carbon dioxide	5.0880 g.	5.0820 g.
CO_2 from reaction	4.9160 g.	4.9100 g.
Moles of CO_2	0.1117	0.1116

Average Moles of CO_2 0.1117

The ammonia was determined by titration of 20.00 c.c. portions (1/50 aliquot) of the acid solution with standard sodium hydroxide (1 c.c. base $\simeq$ 5/40.65 c.c. of 1.8449 N sulfuric acid) using methyl red as an indicator. The results obtained are listed below:

Run	c.c. NaOH	c.c. H_2SO_4 left	c.c. acid used by NH_3	Eq. or Moles of NH_3
I	23.60	145.14	54.86	0.1012
	23.60	145.14	54.86	0.1012
II	23.04	141.69	58.31	0.1076
	23.04	141.69	58.31	0.1076
III	21.73	133.64	66.36	0.1224
	21.73	133.64	66.36	0.1224

A summary of the results obtained with nitrourea and 5 N sodium hydroxide is as follows:

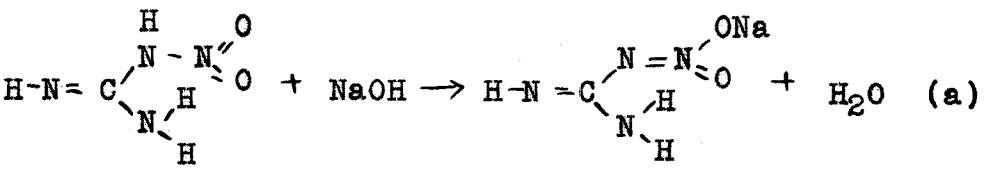
Run	Moles Nitro-urea	Moles CO_2	Moles NH_3	% CO_2	% NH_3	Molar Ratio CO_2 : NH_3 Theory 1 : 1
I	0.0977	0.0977	0.10121	97.97	103.49	1 : 1.055
II	0.10094	0.1044	0.10758	99.38	106.57	1 : 1.083
III	0.11307	0.11307	0.12243	98.76	108.27	1 : 1.096

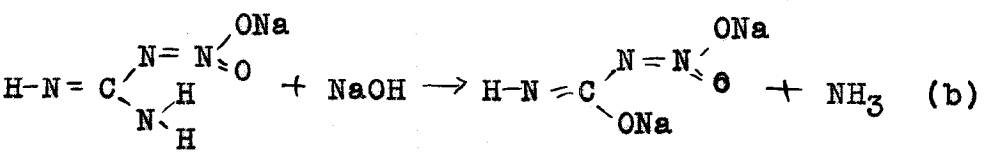
It has thus been shown that the following reaction occurs to an extent of almost 100% in conformity with the proposed equation:

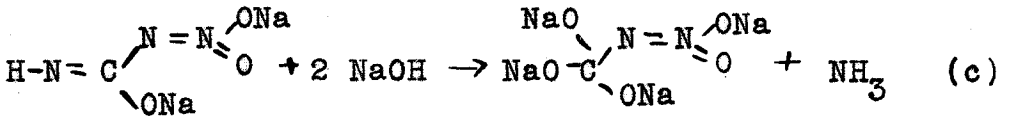
$$CH_3N_3O_3 + 2\ NaOH \rightarrow N_2O + H_2O + NH_3 + Na_2CO_3$$

C. Nitroguanidine

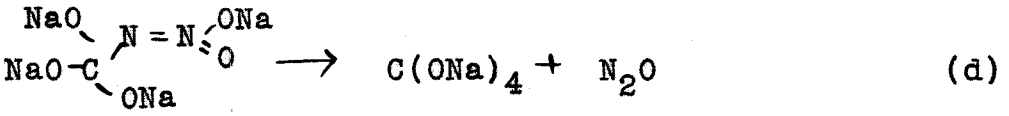
The following reaction mechanism is postulated to explain the reaction between sodium hydroxide and nitroguanidine:



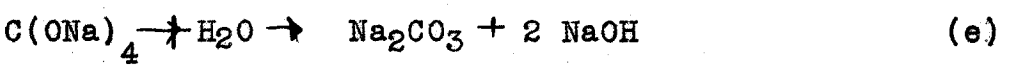




(c)

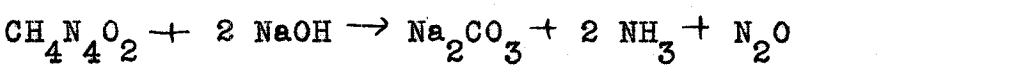


(d)



(e)

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



The formation of nitrous oxide here again supports the possibility of the structure $N \equiv N \rightarrow O$.

The experimental evidence to confirm the occurrence of the reaction according to the developed equation follows.

The set up for the run of nitroguanidine and 5 N sodium hydroxide was identical with that for nitrourea and 5 N sodium hydroxide. The charge in the first run consisted of 11.5606 grams of Eastman's nitroguanidine, (11.5606 ÷ 104 = .11115 mole) and the charge in the second run consisted of 11.8709 grams of nitroguanidine (11.8709 ÷ 104 = .11421 mole). The Mulligan bottles each contained 200.00 c.c. of 1.7195 N sulfuric acid. 200 c.c. of approximately 5 N sodium hydroxide were placed in the constant level dropping funnel and allowed to run into pyrex flasks containing the nitroguanidine. The oil bath was

heated from room temperature to 130° C. within 1.5 hours. The reaction was quite vigorous at 90° C. The temperature of the bath was then maintained between 130° - 140° C. for 8.5 hours while carbon dioxide free air was drawn through the system. Air was drawn through for one hour after the reaction while the solution cooled to room temperature. After the presence of nitrous oxide had been proven as before, it was permitted to escape. Each solution was made to one litre in a volumetric flask.

50 c.c. portions of the alkaline solutions (1/20 aliquot) were analyzed for carbonate as before with the following results on run I_A:

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.2508 g.	0.2509 g.
Total carbon dioxide	5.0160 g.	5.0180 g.
CO_2 from reaction	4.8440 g.	4.8460 g.
Moles of CO_2	0.11008	0.11013

Average Moles Of CO_2 0.110105

The results for the carbonate for I_B were as follows:

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.2579 g.	0.2569 g.
Total carbon dioxide	5.1580 g.	5.1580 g.
CO_2 from reaction	4.9860 g.	4.9860 g.
Moles of CO_2	0.113318	0.113318

Average Moles of CO_2 0.113318

The ammonia was determined by titrating the excess acid with standardized sodium hydroxide (1 c.c. base ≡ 5/41.24 c.c. of 1.7195 N sulfuric acid) using methyl red for an end point indicator. 20 c.c. aliquots gave the following results:

Run	c.c. NaOH	c.c. H_2SO_4 left	c.c. acid used by NH_3	Eq. or Moles of NH_3
I_A	12.16	73.71	126.29	0.217156
	12.16	73.71	126.29	0.217156
I_B	11.72	71.04	128.96	0.220747
	11.72	71.04	128.96	0.220747

A summary of the results obtained with nitroguanidine and 5 N sodium hydroxide is as follows:

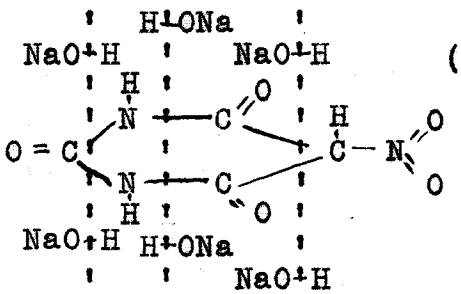
Run	Nitroguanidine Moles	Moles CO_2	Moles NH_3	% CO_2	% NH_3	Molar Ratio CO_2 : NH_3 Theory 1 : 2
I_A	0.11115	0.11008	0.217156	99.04	97.73	
		0.11013	0.217156	99.08	97.73	
	Average	0.110105	0.217156			1 : 1.972
I_B	0.11421	0.113318	0.220747	99.21	96.64	
		0.113318	0.220747	99.21	96.64	
	Average	0.113318	0.220747			1 : 1.948

Thus it has been shown that the reaction occurs to an extent of almost 100% theory in conformity with the equation:

$$CH_4N_4O_2 + 2\ NaOH \longrightarrow Na_2CO_3 + NH_3 + N_2O + H_2O$$

D. Nitrobarbituric Acid

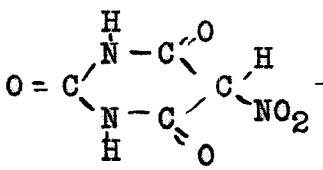
The following mechanism is postulated to explain the reaction between nitrobarbituric acid and sodium hydroxide:



(6 NaOH) $\longrightarrow$ $3\ Na_2CO_3 + 2\ NH_3 + CH_3NO_2$ (a)

$$CH_3NO_2 + 2\ NaOH \longrightarrow Na_2CO_3 + NH_3 + H_2O \qquad (b)$$

Summation of equations (a) and (b) gives the following completed equation:



$+ 8\ NaOH \longrightarrow 4\ Na_2CO_3 + 3\ NH_3 + H_2O$

The first run of nitrobarbituric acid with 5 N sodium hydroxide was identical with that used for nitrourea and nitroguanidine. The charge consisted of 11.4474 grams of Eastman's nitrobarbituric acid (0.05042 mole of the trihydrate). The Mulligan gas washing bottle contained 200.00 c.c. of 1.8475 N sulfuric aicd. Approximately 200 c.c. of 5 N sodium hydroxide were run from the constant level dropping funnel into the pyrex flask containing the nitrobarbituric acid. The flask was in an oil bath which was kept between

130° - 140° C. for 25 hours. Carbondioxide free air was drawn through the system during the run and while cooling to room temperature. Each solution was made to one litre in a volumetric flask.

The carbonate present in the sodium hydroxide before the run was as follows on a 50 c.c. aliquot:

	1.	2.
Weight of carbon dioxide	0.0420 g.	0.0420 g.
Weight of carbon dioxide in 250 c.c. 5 N NaOH	0.2100 g.	0.2100 g.

Average weight of carbon dioxide 0. 2100 g.

The carbonate analyses on run I from 50 c.c. gave the results listed below:

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.4216 g.	0.4211 g.
Total carbon dioxide	8.4320 g.	8.4220 g.
CO_2 from reaction	8.2200 g.	8.2120 g.
Moles of CO_2	0.1868	0.1866

Average Moles of CO_2 0.1867

20 c.c. aliquot portions of the litre acid solution were titrated with sodium hydroxide (1 c.c. NaOH $\rightleftharpoons$ 5/41.23 c.c. of 1.8475 N sulfuric acid) with the following results:

Run	c.c. NaOH	c.c. H_2SO_4 left	c.c. acid used by NH_3	Eq. or Moles of NH_3
I	20.31	123.09	76.91	0.14409
	20.31	123.15	76.85	0.14398

The second and third runs were made in 500 c.c. copper flasks similar to the earlier runs on nitromethane. The first flask contained 11.6730 grams of nitrobarbituric acid (0.05211 mole) while the second flask contained 10.3489 grams of nitrobarbituric acid (0.04620 mole). The Mulligan gas washing bottles contained 200.00 c.c. of standard hydrochloric acid (1 c.c. HCl $\simeq$ 2.010 c.c. of 0.48715 N sodium hydroxide). The flasks were heated for 25 hours in an oil bath which was maintained between 130 - 140 C. Air was drawn through the process. The solutions were each made up to one litre in volumetric flasks.

The carbonate present in the sodium hydroxide before the run determined from 50 c.c. aliquot portions was as follows:

	1.	2.
Weight of carbon dioxide	0.0254 g.	0.0261 g.
Weight of carbon dioxide in 250 c.c. 5 N NaOH	0.1270 g.	0.1305 g.

Average weight of carbon dioxide 0.12875 g.

For the carbonate analyses on the alkaline solution, 50 c.c. (1/20 aliquot) were withdrawn from the litre flask and determined with the following results for II:

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.2084 g.	0.2087 g.
Total carbon dioxide	4.1680 g.	4.1740 g.
CO_2 from reaction	4.03925 g.	4.04525 g.
Moles of CO_2	0.09180	0.09193
Average Moles of CO_2	0.09187	

The carbonate results for III are listed below:

	1.	2.
Weight of CO_2 (1/20 aliquot)	0.1960 g.	0.1962 g.
Total carbon dioxide	3.9200 g.	3.9240 g.
CO_2 from reaction	3.79125 g.	3.79525 g.
Moles of CO_2	0.08616	0.08625
Average Moles of CO_2	0.08621	

50 c.c. aliquot portions of the litre acid solution were titrated with 0.48715 N sodium hydroxide with the following results:

Run	c.c. NaOH 0.48715 N	c.c. NaOH formed	NH_3	Total NH_3	Eq. or Moles of NH_3
II	13.11	6.99		139.80	0.06810
	13.11	6.99		139.80	0.06810
III	13.34	6.76		135.20	0.06586
	13.32	6.78		135.60	0.06606

A summary of the results obtained with nitrobarbituric acid and 5 N sodium hydroxide is listed below:

Run	Moles Nitrobarbituric acid	Moles CO_2	Moles NH_3	% CO_2	% NH_3	Molar Ratio NH_3 : CO_2 Theory 1 : 1.333
I	0.05042	0.1868	0.14409	92.61	95.19	1 : 1.297
Pyrex		0.1866	0.14398	92.49	95.18	1 : 1.296
II	0.05211	0.09180	0.06810	44.04	43.56	1 : 1.348
Copper		0.09193	0.06810	44.05	43.56	1 : 1.349
III	0.04620	0.08616	0.06586	46.60	47.51	1 : 1.308
Copper		0.08625	0.06606	46.67	47.66	1 : 1.305

The results show that the reaction occurs to an extent of 93% of the theoretical yields in a glass flask and 45% of the theoretical yields in a copper flask in conformity with the proposed equation:

$$C_4H_3N_3O_5 + 8\ NaOH \longrightarrow 4\ Na_2CO_3 + 3\ NH_3 + H_2O$$

From the results on nitromethane and nitrobarbituric acid giving 45% - 48% yields in copper flasks and the results on nitrourea, nitroguanidine and nitrobarbituric acid in glass pyrex flasks giving yields of 95% - 100%, it appears as though the copper acts as an inhibitor of the reaction or that the glass may promote the reaction due to surface reactions.

E. The Interaction of Chlorpicrin and Sodium Methylate

In studying the action of sodium methylate upon chlorpicrin the several reaction naturally expected to occur would be as follows:

First, the chlorine and nitro radicals would be replaced by the oxymethyl radical, thus,

$$CCl_3NO_2 + 4\ NaOH \longrightarrow 3\ NaCl + NaNO_2 + C(OCH_3)_4 \quad (a)$$

The methyl orthocarbonate formed would presumably decompose to give dimethyl ether and methyl carbonate:

$$C(OCH_3)_4 \longrightarrow (CH_3)_2O + (CH_3)_2CO_3$$

This assumption is warranted by the similar decomposition of ortho ethyl carbonate reported by Bassett[52].

On the other hand, if only the chlorine atoms of chlorpicrin are replaced by the oxymethyl radical, nitrotrimethyl ortho carbonate would be formed, thus,

$$CCl_3NO_2 + 3\ NaOCH_3 \longrightarrow 3\ NaCl + C(OCH_3)_3NO_2 \quad (b)$$

If this aliphatic nitro compound were formed, it may be reducible by sodium methylate as are its aromatic nitro compounds with oxidation of sodium methylate to sodium formate in conformity with the equation:

$$4\ C(OCH_3)_3NO_2 + 3\ NaOCH_3 \longrightarrow 2\ [C(OCH_3)_3N]_2O + 3\ HCOONa + 3\ H_2O \quad (c)$$

In order to have sufficient methylate in the reaction mixture to effect all of the above reactions, the quantity of sodium (36.8 grams) necessary was converted into sodium methylate and solution of the same in methyl reacted with 0.1006 mole of chlorpicrin.

Freshly prepared sodium methylate was reacted with chlorpicrin in order to determine what reactions occur and the extent to which they occur. 36.8 grams of sodium was cleaned and cut into small pieces under ligroin and then weighed under ligroin in a weighing bottle. To 250 c.c. of Merk's C. P. methyl alcohol, free from acetone, in a 500 c.c. Kjeldahl flask, the dried sodium was added through the top of an extra long vertical Liebig water condenser. After all the sodium had been added the condenser was washed down with 50 c.c. more of methyl alcohol. The solution was heated on a hot plate until all the sodium went into solution. This was done in duplicate simultaneously.

The flasks containing the sodium methylate were then immersed into the same water bath and 10 c.c. (0.1001 moles) of Eastman's chlorpicrin slowly added from a constant level dropping funnel through the inside of the condenser to each reaction flask. A crystalline white precipitate was immediately formed. Since 10 c.c. of

chlorpicrin weighed 16.5419 grams, 0.1006 moles (16.5419÷ 164.38) were used in each run. The water was maintained at boiling for 5 hours. Tests for the production of any dimethyl ether formed during the run were negative.

The contents of the reaction flask were transferred to a round bottom flask. The Kjeldahl flask was washed with methyl alcohol which was also transferred to the round bottom flask. The largest part of the excess methyl alcohol was driven off by distillation on a water bath and then an oil bath. Redistillation of the distillate using a Glinsky fractionating column gave the entire liquid boiling from 64.0° - 64.8° C., showing that it was entirely methyl alcohol.

The residue from which the largest quantity of methyl alcohol had been removed by distillation was dissolved in water and steam distilled until free from alcohol. This solution was then cooled and filtered in the presence of nitrogen to remove any silica which might have been present due to the strong alkali attacking the glass. The filtrate was then made up to 500 c.c. in a volumetric flask and analyzed for chloride, nitrite, and formate, which was known to be present.

The chloride was determined according to the method of Smith[68]. To a 10 c.c. portion (1/50 aliquot) of the solution in the 500 c.c. volumetric flask was added

150 c.c. of water and 70 c.c. of approximately 0.1 N silver nitrate. This was heated on a hot plate almost to boiling until the supernatant liquid was clear. The solution was tested with silver nitrate for complete precipitation. The solution was decanted and washed while hot with water containing nitric acid into a weighed Gooch crucible. It was washed free of silver and dried to constant weight at 120 C. The following results were obtained for the chlorides:

Run	AgCl Grams	Total AgCl Grams	Chloride Weight	Chloride Moles	% Cl
I	0.8531	42.6550	10.5516	0.2975	98.54
	0.8522	42.6100	10.5404	0.2973	98.50
II	0.8646	43.2300	10.6938	0.30159	99.89
	0.8609	43.0450	10.6481	0.30031	99.50
III	0.8619	43.0950	10.6604	0.30066	99.63
	0.8598	42.9900	10.6344	0.29992	99.37

This data shows that practically all of the chloride of chlorpicrin was recovered as sodium chloride.

The nitrite yield was determined by the Devarda Method as described by Scott[69]. 25 c.c. of the solution (1/20 aliquot) from the 500 c.c. flask were placed in a Kjeldahl flask with 25 c.c. of 20% NaOH, 100 c.c. of water, 3 grams of Devarda's Alloy and a piece of paraffin. The ammonia was collected in 75 c.c. of 0.1067 N sulfuric

acid. The excess acid was determined by titrating sodium hydroxide (1 c.c. NaOH $\rightleftharpoons$ 0.90909 c.c. of 0.1067 N sulfuric acid) using methyl red as an indicator. The following amount of nitrite resulted:

Run	NaOH c.c.	Acid c.c.	c.c. Acid used by NH_3	c.c. Acid Total NH_3	Total $HNO_2 \rightleftharpoons NH_3$	HNO_2 % Theory
I	35.80	32.545	42.455	849.10	0.090599	90.05
	35.70	32.455	42.545	850.90	0.090791	90.24
II	34.25	31.136	43.864	877.28	0.093606	93.04
	33.25	30.227	44.773	895.46	0.095566	94.99
III	34.50	31.364	43.636	872.72	0.093120	92.56
	34.44	31.309	43.691	873.82	0.093237	92.68

These results show that while practically all of the chlorine of the chlorpicrin was eliminated on interaction with sodium methylate, approximately only 90 - 95% of the nitro radical has been eliminated.

The formate was determined by the method described in "Methods of Analysis of the Association of the Official Agricultural Chemists"(70). A 50 c.c. portion (1/10 aliquot) was withdrawn from the 500 c.c., acidified with hydrochloric acid and any silica filtered off. To this was added 80 c.c. of water, 10 c.c. sodium acetate solution, 2 c.c. of 10% hydrochloric acid and 25 c.c. of mercuric chloride. It was allowed to stand on a hot water bath for 2 hours,

filtered hot into a Gooch crucible, washed with hot water and dried to constant weight. A blank run on sodium to nitrite gave no precipitate of mercuric chloride.

The following results were obtained:

Run	Grams HgCl	Total HgCl	Total Formate Grams	Moles Formate
II	0.1503	1.303	0.14654	0.003206
	0.1885	1.885	0.18379	0.003993
III	0.2606	2.606	0.25409	0.00552
	0.2611	2.611	0.25457	0.00553

To this point, it is evident that chlorpicrin reacts with sodium methylate to give practically 100% of the theoretical yield of sodium chloride based upon the equation;

$$CCl_3NO_2 + 4\ NaOCH_3 \longrightarrow C(OCH_3)_4 + 4\ NaCl + NaNO_2 \quad (a)$$

But as only 90 - 95% of sodium nitrite was found, the remaining 5 - 10% of the initial chlorpicrin which did not yield sodium nitrite must have effected oxidation of sodium methylate to sodium formate in as much as 6 - 7% sodium formate was found based upon the equation:

$$4\ C(OCH_3)_3NO_2 + 3\ NaOCH_3 \rightarrow 2\ [C(OCH_3)_3N]_2O + 3\ HCOONa + 3\ H_2O \quad (c)$$

For run II on the basis of equation (a) the average molar yield of sodium chloride was 0.30095 mole (theory 0.3018), and the average yield of sodium nitrite was 0.094586 mole (theory 0.1006).

If there were 0.30095 moles of chloride then there should have been 0.30095/3 = 0.10031 moles of nitrite; or if there were 0.094586 moles of nitrite then there should have been 0.094586 x 3= 0.28376 moles of chloride.

The excess chloride presumably came from the following side reaction:

$$CCl_3NO_2 + 3\ NaOCH_3 \longrightarrow 3\ NaCl + C(OCH_3)_3NO_2 \quad (b)$$

	Moles		Moles		Moles
(a)+(b)	0.10031	(a)+(b)	0.30095		0.005724
(a)	0.094586	(a)	0.28376		
(b)	0.005724	(b)	0.01719		

Or 0.005724 x 3= 0.01717 moles of chloride formed in equation (b), therefore 0.005724 moles of the compound $C(OCH_3)_3NO_2$ was formed in (b).

If this compound were then reduced to sodium formate by the sodium methylate the following secondary equation holds true:

$$4\ C(OCH_3)_3NO_2 + 3\ NaOCH_3 \longrightarrow 2\ [C(OCH_3)_3N]_2O + 3\ HCOONa + 3\ H_2O \quad (c)$$

Moles formed in (b) 0.005724 and used in (c)

Therefore 0.005724 x $\frac{3}{4}$ = 0.004290 moles of formate that should have been formed in (c).

If the small amount of chlorpicrin that did not decompose according to (a) and (b) decomposed according to the following equation,

$$4\ CCl_3NO_2 + 2\ NaOCH_3 \longrightarrow 2\ [CCl_3N]_2O + 3\ H_2O + 3\ HCOONa \quad (d)$$

then the amount of chlorpicrin reacting according to (d) was 0.00028 moles $\left[(0.3018 - 0.30095) \div 3\right]$. If 0.00028 moles of chlorpicrin reacted according to (d) then $\frac{3}{4}$ x 0.00028 = 0.00021 moles of formate should have been found. The total formate that should have been formed from (c) and (d) was then 0.00450 moles (0.004290 + 0.00021), while 0.003599 mole was found.

For run III on the basis of equation (a) the average molar yield of sodium chloride was 0.30029 mole (theory 0.3018) and the average yield of sodium nitrite was 0.093175 (theory 0.1006).

If there was 0.30029 mole of chloride then there should have been 0.30029/3 = 0.10009 mole of nitrite; or if there was 0.093175 mole of nitrite then there should have been 0.093175 x 3 = 0.279525 mole of chloride.

The excess chloride came from the following side reaction:

$$CCl_3NO_2 + 3\ NaOCH_3 \rightarrow 3\ NaCl + C(OCH_3)_3NO_2 \qquad (b)$$

	Moles		Moles	Moles
(a)+(b)	0.10009	(a)+(b)	0.30095	0.006915
(a)	0.093175	(a)	0.28376	
(b)	0.006915	(b)	0.020765	

Or 0.006915 x 3 = 0.020745 mole of chloride formed in equation (b), therefore 0.006915 mole of the compound $C(OCH_3)_3NO_2$ was formed in (b).

If this compound were then reduced to sodium formate by the sodium methylate the following secondary reaction holds true:

$$4\ C(OCH_3)_3NO_2 + 3\ NaOCH_3 \rightarrow 2\ [C(OCH_3)_3N]_2O + 3\ H_2O + 3\ HCOONa \qquad (c)$$

0.006915 formed in (b) and used in (c), therefore 0.006915 x $\frac{3}{4}$ = 0.005186 mole of formate that should have been formed in (c).

If the small amount of chlorpicrin that did not react according to (a) and (b) decomposed according to the following equation,

$$4\ CCl_3NO_2 + 2\ NaOCH_3 \rightarrow 2\ [CCl_3N]_2O + 3\ H_2O + 3\ HCOONa \qquad (d)$$

then the amount of chlorpicrin reacting according to (d) was 0.00050 mole [(0.3018 - 0.30029) ÷ 3]. If 0.00050 mole of chlorpicrin reacted according to (d) then $\frac{3}{4}$ x 0.00050 = 0.000375 mole of formate that should have been formed. The total formate that should have been formed from (c) and (d) was then 0.005561 mole (0.005186 + 0.000375), while 0.005525 mole was found.

IV

SUMMARY

This investigation involved five objects: (1), a continuation of a previous investigation of the reaction between nitromethane and 15 N, 10 N and 5 N solutions of sodium hydroxide, in order to determine the nature and extent of reaction between nitromethane and 3 N, 1 N and 0.5 N sodium hydroxide. Also the nature and extent of the reaction of 5 N sodium hydroxide solution with (2), nitrourea, (3), nitroguanidine, (4), nitrobarbituric acid and finally (5), the action of methyl alcohol solutions of sodium methylate upon chlorpicrin.

The results were respectively as follows:

1. (a) The action of 3 N sodium hydroxide solution in this present work like the action obtained with 15 N, 10 N and 5 N solutions in the previous investigation was in accordance with the following postulated equation:

$$CH_3NO_2 + 2\ NaOH \rightarrow NH_3 \uparrow + Na_2CO_3 + H_2O$$

(b) However with 3 N sodium hydroxide the theoretical yields of ammonia and sodium carbonate were only 36% of the theory in one run

and 38% in the other, as compared with about 48% of the theory in the former runs of 15 N, 10 N and 5 N solutions.

(c) With 1 N sodium hydroxide solution it was apparent that the postulated reaction occurred to an extent of 12% - 13% of theoretical. A concurrent reaction also occurred to an undetermined extent producing methazonic acid from the condensation of two moles of nitromethane. This methazonic acid was then decomposed to an undetermined extent into carbon dioxide, hydroxylamine and hydrogen cyanide.

(d) The postulated reaction occurred to an extent of 9% theory in conformity with the postulated equation with 0.5 N sodium hydroxide.

2. (a) It was shown that the following reaction between nitrourea and sodium hydroxide occurred to an extent of almost 100% theory based upon the postulated equation:

$$CO(NH_2)NHNO_2 + 2\ NaOH \rightarrow N_2O \uparrow + NH_3 \uparrow + Na_2CO_3 + H_2O$$

(b) From the point of view of the proposed reaction mechanism the structural formula

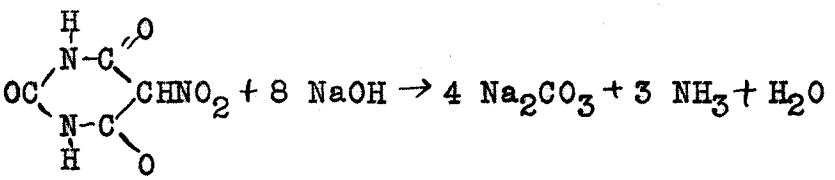
of nitrous oxide would be $N \equiv N = O$ rather than $N = N$ (O).

3. (a) It was shown that the following reaction between nitroguanidine and sodium hydroxide occurred to an extent of 100% based upon the postulated equation:

$$HNC(NH_2)NHNO_2 + 2\ NaOH \longrightarrow N_2O + 2\ NH_3 + Na_2CO_3$$

(b) Again from the point of view of the proposed reaction mechanism the structural formula of nitrous oxide would be $N \equiv N = O$ rather than $N = N$ (O).

4. (a) The following reaction between nitrobarbituric acid and sodium hydroxide was shown to occur to an extent of 95% of theory in glass pyrex flasks and 45% of theory in copper flasks based upon the postulated equation:



(b) From the results with nitromethane and nitrobarbituric acid giving 45% - 48 % yields in copper flasks and the results with nitrobarbituric acid, nitrourea and nitro-

guanidine giving 95% - 100% in pyrex glass flasks, it appears as though the copper acts as an inhibitor of the reactions or that the glass may promote the reaction due to surface catalysis.

(c) A complete reaction-mechanism scheme has been postulated to explain the reaction.

5. (a) Chlorpicrin reacts with sodium methylate eliminating practically all (98 - 100%) of its chlorine content as sodium chloride.

(b) About 90 - 95% of sodium nitrite was found in various runs.

(c) The formation of sodium formate shows presumably that the nitro radical of 6 - 7% of the initial chlorpicrin oxidized sodium methylate to sodium formate.

V

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VI

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