A STUDY OF GUANYL-NITROUREA.

A Thesis

Submitted to the Faculty of Graduate Studies and Research of McGill University in Partial Fulfillment of the Requirements for the Degree of Master of Science.

by

Kenneth Savard.

Montreal, Canada

September, 1942

The author gratefully acknowledges the assistance and direction of Dr. J.H. Ross and Dr. Raymond Boyer, under whom the greater part of this research was completed, and the encouragement shown him by Dr. W. H. Hatcher.

For the chemical analysis made for this work, the author thanks Dr. A. S. Cook, of Ayerst, McKenna and Harrison Co. Ltd.

TABLE OF CONTENTS

INTRODUCTION

The importance and tremendous advantages of a truly flashless propellent for combat use by army, naval and anti-craft units, particularly at night, are self-evident. Just after the last Great War, nitroguanidine, a previously known compound of only academic interest, was found to be an explosive equal in force to T.N.T., and possessing the exceptional property of exploding with a cool flame and hardly any visible flash (1). When this compound was incorporated with nitrocellulose and nitroglycerine, the resulting cordite was found to possess both the cool explosion temperature of nitroguanidine and the same propellant power of ordinary cordite.

Picrite, as nitroguanidine is more commonly known, and flashless cordite containing Picrite, have several disadvantages, which if overcome would render more easy the preparation, and greatly improve the properties of this new type of propellent. It was during the course of a study, bent on improving Picrite or finding a substitute for it, that N-guanyl-N'-nitrourea was investigated. This compound, previously reported in the literature (2) has been thoroughly studied both from the technical and ballistic points of view by the Department of Munitions and Supply, and has been found to fulfill all the specifications required of the flashless component in flashless cordite. Furthermore, it is prepared from the same primary product as that used for Picrite, by a much simplified process, and possesses many of the desired properties of bulk and crystal structure which are lacking in the latter.

Guanyl-nitrourea has been given the name of Rossite, after Dr. J. H. Ross who was director of research at the time that the investigation was made.

From the theoretical point of view, guanyl-nitrourea presents a certain interest, because it may be considered a member of the "Urea Series". The chemistry of this series of compounds has been explained by a simple process called "Urea De-arrangement". This theory, proposed by T.L. Davis (3) has been applied to the decomposition and reaction of guanyl-nitrourea and has resulted in a study which has added to the knowledge of the chemistry of guanyl-nitrourea itself and to that of the "Urea Series".

HISTORICAL AND THEORETICAL PART.

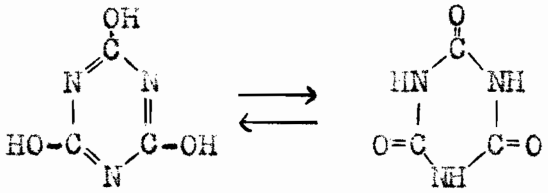
Chemistry of Cyanic Acid and Cyanamide.

Before undertaking the discussion of the reactions of the urea series, it would be quite relevant to review briefly the chemistry of cyanic acid and cyanamide, first because of their importance in the preparations of the members of this series, secondly because both may be found in varied forms, individually or together, as products resulting from the breakdown of urea derivatives, and thirdly because the chemistry of the urea series is essentially that of the unsaturated isocyanate and cyanamide linkages.

Cyanic acid has long been known to react according to two tautomeric forms, giving rise to cyanate derivatives which correspond to the enol or normal form $H-O-C\equiv N$, and to isocyanates which correspond to the keto or iso form $H-N=C=O$. Emil Werner's theory that in urea rearrangement reactions, cyanic acid reacts solely in its unsaturated state, that is, as isocyanic acid (4) has been confirmed by recent Raman spectrum studies which show that free cyanic acid, many inorganic salts and all alkyl and aryl derivatives exist as, and react according to the isocyanate structure (5)(6).

Only potassium, lead and tetramethylammonium salts have the cyanate structure. Fulminic acid, H-O-N≡C, might be considered a tautomeric form of cyanic acid, but is in no way similar to it.

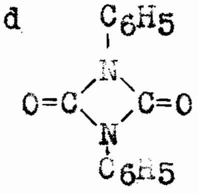
In view of its unsaturated character, isocyanic acid is exceedingly reactive. It reacts with ammonia to form urea, (Wöhler's famous reaction (7)),with amines it forms substituted ureas, and with alcohols forms esters of carbamic acid, or urethanes. Its readiness to trimerize to the cyclic cyanuric acid is explained by Werner (8) as due to the "unstable group of four atoms, which, in virtue of the closely related electrochemical nature of three (C,N, and O) is not capable of assuming a simple molecular configuration which can give rise to a condition of electrostatic equilibrium. This end is attained by polymerization to a six membered ring, the most stable of cyclic molecules". Cyanuric acid, like cyanic acid exists in two tautomeric forms.



The dimer of isocyanic acid, dicyanic acid, was discovered by Davis (9) who proposed as its structure the formula $NH_2 \cdot CONCO$*. Dicyanic acid is unstable and does not exist in the free state, but it reacts in a manner analogous to that of isocyanic acid with ammonia and amines to form biuret and substituted biuret, and with alcohols to form allophanic esters.

Cyanamide differs from isocyanic acid in that the oxygen atom is replaced by an imido group. Like isocyanic acid it exists and reacts according to two tautomeric forms, the acidic or imide form $NH=C=NH$, and the basic or nitrile form $NH_2 \cdot C \equiv N$. Raman-spectrum studies have shown the free compound and various derivatives to have the nitrile form. Instances of the imide structure are also evident (10). Cyanamide reacts, (in a manner analogous to that of cyanic acid), with ammonia and amines to form guanidine and substituted guanidines. When heated in the dry state it polymerizes to the well-known dimer dicyandiamide, and to the trimer melamine. Cyanamide in aqueous solution also dimerizes to dicyandiamide, but there is a simultaneous hydrolysis of cyanamide to urea. This for a long while was thought to

*Hofmann has reported a substance (11) which he, and later authors (12) considered to be a dimer of phenylisocyanate, and to which has been ascribed this structure:



be a competitive reaction, but it has been found that polymerization occurs in solutions whose pH is less than 6.0, whereas in solutions of pH greater than 12, polymerization is inhibited and hydrolysis is complete (13)(14).

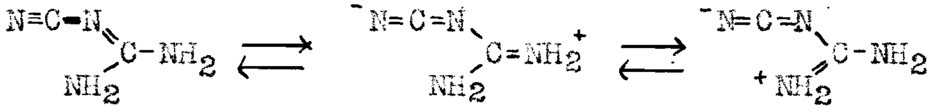
Despite the numerous studies on the subject, the structural composition of dicyandiamide is, according to Chastellain (15) still debatable. Of the five proposed structures, discussed by this author, the α-cyanoguanidine form (I) suggested by Bamberger (16) is now generally accepted. Strecker's (17)(18) cyclic form (II) presents

$NH_2\cdot C(NH)NH\cdot CN$

I

II

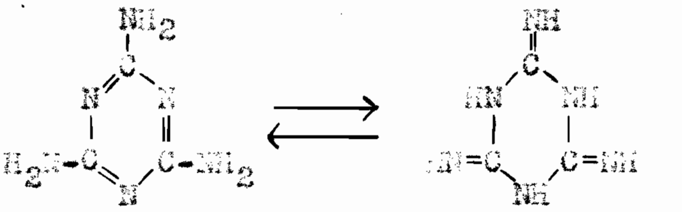
a certain interest which will be discussed later. Recent studies (19), based on bond-distance measurements, have



Ia

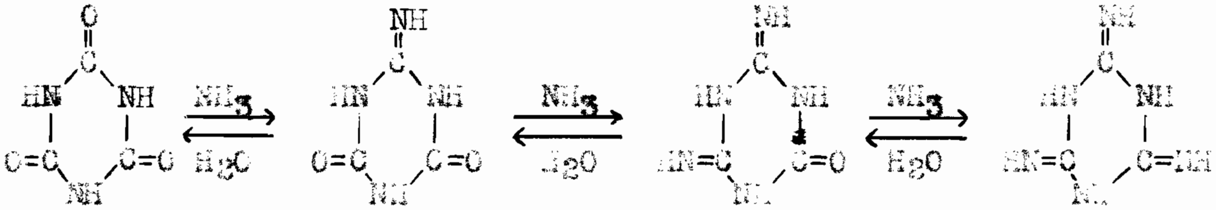
shown dicyandiamide to exist as a resonance hybrid, and have brought into consideration the structure (Ia) previously proposed by Pohl (20).

Cyanamide polymerizes to melamine with equal readiness as it does to dicyandiamide, but as a rule, only at higher temperatures (21)(22)(23). Melamine may also be formed in aqueous solutions from dicyandiamide, in the presence of ammonia (14). The industrial preparation of melamine, which to-day is used to form melamine-formaldehyde plastics (25) consists in heating a mixture of dicyandiamide and guanidine carbonate (26). Melamine, like cyanuric acid, is extremely stable; it may be sublimed without decomposition (27) and also exists in two tautomeric forms:



(normal form) (imide form)

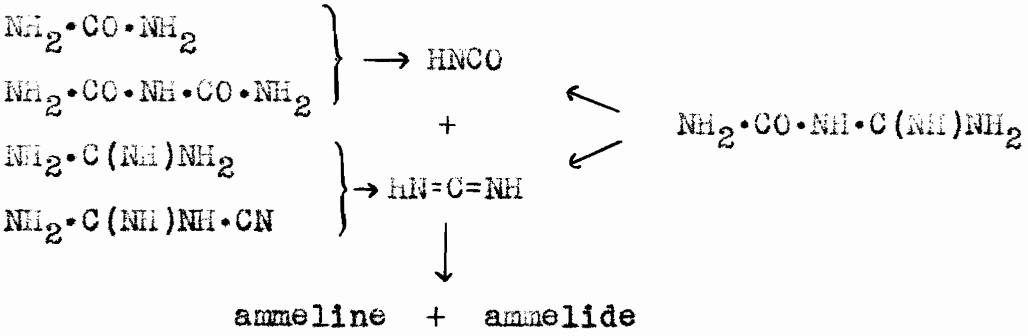
Melamine, besides being considered the trimer of cyanamide, may also be considered the triamide of cyanuric acid. These two compounds are interconvertible by a stepwise hydrolysis of melamine (28) or a stepwise ammonolysis of cyanuric acid (29), the two intermediate compounds being ammelide (III) the monoamide, and ammeline (IV) the diamide of cyanuric acid. These progressive reactions may be illustrated as follows, using only the keto or imide formulae for simplicity.



III IV

Like both cyanuric acid and melamine, these compounds exist in tautomeric forms.

It is evident that these compounds may also be considered mixed trimers of isocyanic acid and cyanamide. This mixed polymerization occurs when urea, biuret or dicyandiamidine (guanylurea) are heated together in the presence of either guanidine or dicyandiamide, since both ammeline and ammelide are found in the products (30).



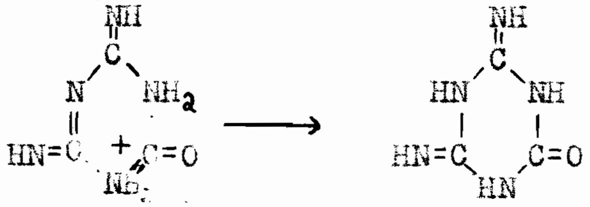
Urea and biuret evidently decompose to form isocyanic acid; guanidine and dicyandiamide form cyanamide, and guanylurea may form both, and then the isocyanic acid and cyanamide co-polymerize to form ammeline and ammelide.

Very little speculation has been made as to the mechanism involved in these co-polymerizations. Only two authors have attempted to interpret the formation of these cyclic trimers. In the case of the formation of ammelide and cyanuric acid from biuret, Das Gupta (31) has proposed that the hypothetical compound triuret is first formed as an intermediate, which, forms ammelide by loss of water, and cyanuric acid by loss of ammonia.

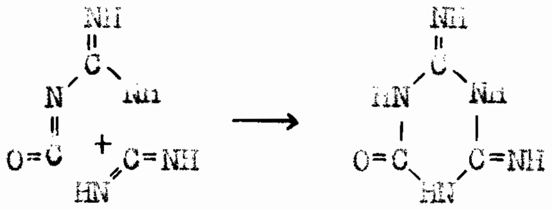
$$\text{Ammelide} + H_2O \longleftrightarrow NH_2\cdot CO\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH_2 \longrightarrow \text{Cyanuric Acid} + NH_3$$

However, Das Gupta based the formation of triuret on a reaction between dicyanic acid and urea (both products of the decomposition of biuret), which has been found not to take place (32).

The other theory, advanced by Davis (18), suggests that cyclization occurs through a reaction between a monomer (cyanamide or isocyanic acid) and a dimerized form of these two (dicyandiamide or dicyanic acid). In the particular case studied by Davis, cyanamide reacts with dicyandiamide to form melamine, and isocyanic acid reacts with dicyandiamide to form ammeline. This reaction is of interest and is illustrated below



This mechanism is applicable to the various formations of all four cyclic trimers, and is of particular interest in the study of guanyl-nitrourea. Evidence has been found by the author which indicates that a similar reaction takes place between the compound guanylisocyanate and cyanamide itself, with formation of ammeline.



The guanylisocyanate, mentioned above, has been called a mixed dimer of cyanamide and isocyanic acid, a point which is a subject for much speculation. The existence of such a dimer has not been mentioned in the literature, but is highly probable in view of the fact that cyanamide and isocyanic acid both form stable dimers, and that together they form stable mixed trimers. If the structure of this mixed dimer is similar to that of dicyandiamide (I), then it may be considered as having the cyanourea form indicated in (V); if it is similar to dicyanic acid (VI), then it has the guanylisocyanate structure (VII).

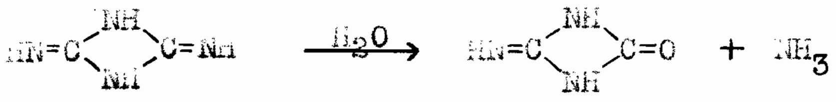
$NH_2\cdot C(NH)NH\cdot CN$ I

$NH_2\cdot CO\cdot N{=}C{=}O$ VI

$NH_2\cdot CO\cdot NH\cdot CN$ V

$NH_2\cdot C(NH)N{=}C{=}O$ VII

A compound obtained from dicyandiamide by hydrolysis in baryta, was reported in 1870 by Hallwacks (33) who named it amido-dicyanic acid (VIII). At that time, the accepted structure of dicyandiamide was the cyclic form (II), and accordingly, this product was given a similar structure, indicated in (VIII). However, when structure (II) was



II VIII

discarded in favor of the cyanoguanidine form (I), amidodicyanic acid was given the name and structure of cyanourea (V). This compound is also formed by the co-polymerization of cyanamide and isocyanic acid (33) thereby identifying it as the true mixed dimer of these two compounds.

The guanylisocyanate structure (VII) was proposed by Blair (34) as a tautomeric form of cyanourea. In the opinion of the author, this is highly improbable and is discussed later. However, it presents a certain amount of interest since it is similar in some respects to dicyanic acid (VI). There is indication of its formation in a reaction reported by Blair (35) in which guanylurea reacts with ethanol to form the ethyl ester of guanidine carboxylic acid, and ammonia. In this reaction guanylurea probably undergoes a decomposition to form in part ammonia and guanylisocyanate (i), which, acting in its unsaturated character adds ethanol to

$$NH_2 \cdot C(NH) \cdot NH \cdot CO \cdot NH_2 \rightleftarrows NH_2 \cdot C(NH) \cdot N{=}C{=}O + NH_3 \qquad (i)$$

$$NH_2 \cdot C(NH) \cdot N{=}C{=}O + HO \cdot C_2H_5 \longrightarrow NH_2 \cdot C(NH)NH \cdot CO \cdot OC_2H_5 \qquad (ii)$$

form the ester (ii). In the decomposition of guanyl-nitrourea there is evidence of its formation, for when this is carried out in presence of ammonia, guanylurea may be detected, indicating the reaction (iii). In this way

$$NH_2 \cdot C(NH)N{=}C{=}O \quad + \quad NH_3 \longrightarrow NH_2 \cdot C(NH)NH \cdot CO \cdot NH_2 \qquad \text{(iii)}$$

guanylisocyanate (VII) closely resembles dicyanic acid (VI) in structure, mode of formation and mode of reaction, since the latter is formed from biuret (31) and nitrobiuret (36), and reacts with ammonia and alcohols to form biuret and allophanic esters, respectively (9).

It is the opinion of the author that cyanourea and guanylisocyanate are not tautomeric forms of the same compound, because the former (V) can be hydrolyzed to biuret (37), a reaction which cannot be accounted for by (VII) and because (V) cannot react with ethanol to form guanidine carboxylic ester. It follows then that cyanourea only, is the result of co-polymerization of cyanamide and isocyanic acid, and that guanylisocyanate can only be formed from compounds having the guanylurea structure, even though it may decompose into the two monomers.

The Urea Dearrangement:

The conversion of the cyanates of ammonia and primary amines to urea and substituted ureas, by the evaporation of their aqueous solutions, has long been known as examples of "urea rearrangement". This type of reaction is best illustrated in Wöhler's preparation of urea (7)

$$NH_4OCN \longrightarrow NH_2{\cdot}CO{\cdot}NH_2$$

In this reaction both ammonia and cyanic acid react as though they had two-fold chemical characters. If the cyanic acid functions as an acid, and the ammonia functions in its basic character, there is the simple acid-base reaction, and ammonium cyanate is formed (i). If the cyanic acid reacts in its unsaturated character (that is, as isocyanic acid), there is the reaction of addition of an amine-type compound to the unsaturated isocyanate linkage, with formation of urea (ii).

$$NH_3 + HOCN \longrightarrow NH_4OCN \qquad (i)$$

$$H\text{-}NH_2 + HN{=}C{=}O \longrightarrow NH_2{\cdot}CO{\cdot}NH_2 \qquad (ii)$$

Werner has postulated the latter mechanism (8) stating that urea is formed as the addition compound of ammonia and isocyanic acid which changes from the enol (or normal) form to the keto (or iso) form as the former is liberated by the dissociation of ammonium cyanate.

This has been confirmed by recent Raman-spectrum studies in which it was found that cyanic acid exists and reacts solely in its unsaturated character, that is as isocyanic acid (5)(6).

Other examples of urea rearrangements are Wurtz's preparations of methylurea (38)(39) from methylamine and isocyanic acid (i) and from ammonia and methylisocyanate (ii)

$$CH_3\cdot NH_2 + HNCO \longrightarrow CH_3\cdot NH\cdot CO\cdot NH_2 \qquad (i)$$

$$NH_3 + CH_3\cdot NCO \longrightarrow CH_3\cdot NH\cdot CO\cdot NH_2 \qquad (ii)$$

The formations of guanidine and thiourea follow the same pattern of urea rearrangement, by the action of ammonia with cyanamide (40) and isothiocyanic acid (41) respectively; and the general preparation of their substituted derivatives consists in heating the corresponding amine with cyanamide and thiocyanic acid. In general it may be said that the urea rearrangement consists of two types of reactions,

a) the reaction between a substituted amine and isocyanic acid,

$$R\cdot NH_2 + HNCO \longrightarrow R\cdot NH\cdot CO\cdot NH_2$$

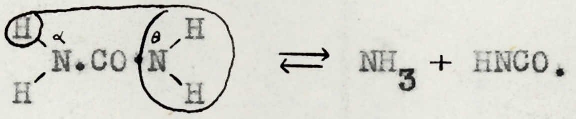
and b) the reaction between a substituted isocyanate and ammonia.

$$R\cdot NCO + NH_3 \longrightarrow R\cdot NH\cdot CO\cdot NH_2$$

The reverse reaction of urea rearrangement has long been known. As early as 1838 it was found that a boiling aqueous solution of urea gave a precipitate of silver cyanate when silver nitrate was added (42)(43); and the treatment of a cold aqueous solution of urea with nitrous acid yielded ammonium nitrate and "cyanic acid" (44): and also, that when urea was heated above its melting point, certain compounds were formed in addition to biuret, which would result from the dry heating of ammonium cyanate (45)(46). The implications of these findings were not fully interpreted until Emil Werner suggested that the "urea rearrangement" was really a reversible system (8). This author, in his numerous publications on "the constitution of carbamides" (8)(47), has added much to the study of the reactions of this series and much may be said in favor of his proposed structure of urea and its derivatives. However, what Werner failed to do was to give a simple picture of the mechanism of reaction in the urea series, one which would explain the many apparently complex reactions which occur.

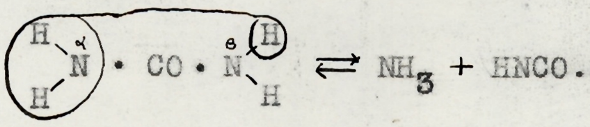
The first and only widely applicable theory that has been advanced was published in 1923 by Tenney L. Davis (3). This theory has been found to apply to the reactions of urea, thiourea, guanidine, in fact to all the members of this series and their substituted derivatives. Davis named the reverse reaction of urea rearrangement, "urea dearrangement" (46). Davis states that since the breakdown of a urea derivative is an orderly and well-defined pattern, the term dearrangement was chosen in preference to dissociation or disassociation, which apply to polarized atoms or molecules, and in preference to decomposition or disarrangement, which imply a disorderly breakdown.

In Davis' words, the urea dearrangement "consists of the breaking apart of the urea derivative, (usually on heating) in such a way that the hydrogen, previously attached to one of the nitrogen atoms goes off in combination with the other nitrogen atom and the atoms or groups previously attached to it, deserting the rest of the molecule."



$$H_2\overset{\alpha}{N}\cdot CO\cdot \overset{\beta}{N}H_2 \rightleftarrows NH_3 + HNCO.$$

Thus in the case of urea, a hydrogen attached to theαnitrogen goes off with the β-nitrogen and the hydrogen attached to it, forming ammonia, and leaving isocyanic acid. In the same way, a hydrogen attached to the β-nitrogen goes

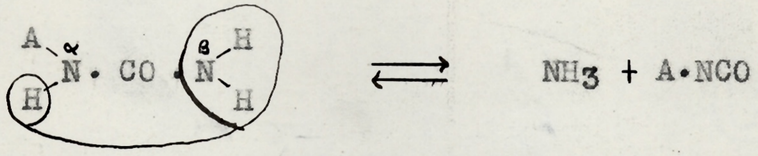


$$H_2\overset{\alpha}{N}\cdot CO\cdot \overset{\beta}{N}H_2 \rightleftarrows NH_3 + HNCO.$$

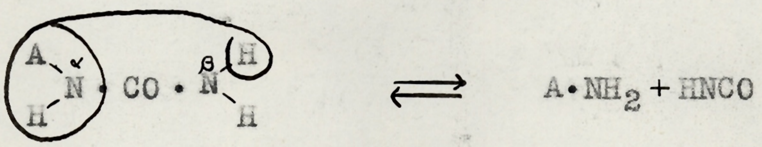
off with the α-nitrogen and its hydrogens to form ammonia and leave isocyanic acid; thus the unsubtituted urea, thiourea and guanidine molecules may dearrange in only one manner.

It may be noted that the urea dearrangement is illustrated as a reversible process; this has been found to be always true, the urea, thiourea and guanidine derivatives dearranging (often in more than one manner) to yield those smaller molecules by the direct combination of which the compounds may be synthesized (48).

In the case of a mono-substituted urea (thiourea or guanidine) one of the nitrogen atoms has a substituent group, and accordingly, the dearrangement takes place in two manners.



The hydrogen attached to the α-nitrogen goes off in combination with the β-nitrogen and its hydrogens to form ammonia leaving a substituted isocyanate.



On the other hand, a hydrogen attached to the β-nitrogen goes off with the α-nitrogen and its hydrogen and substituent group forming an amine and leaving isocyanic acid.

Phenylurea as an example, dearranges in two modes (46); forming on the one hand phenylisocyanate and ammonia, from which it may be prepared (49), and forming on the other hand aniline and isocyanic acid, from which phenylurea may also be prepared (50). Mono-substituted guanidines and thioureas behave in an analogous manner, dearranging in two modes, corresponding to two ways in which they may be prepared (46)(51)(52).

Attention may here be called to the dearrangement of cyanourea (V). Blair and Smith (12) were unable to account for the formation of guanidine and urea during the acid hydrolysis of this compound to biuret, and were obliged to propose a tautomerism between (V) and guanyliso-cyanate (VII).

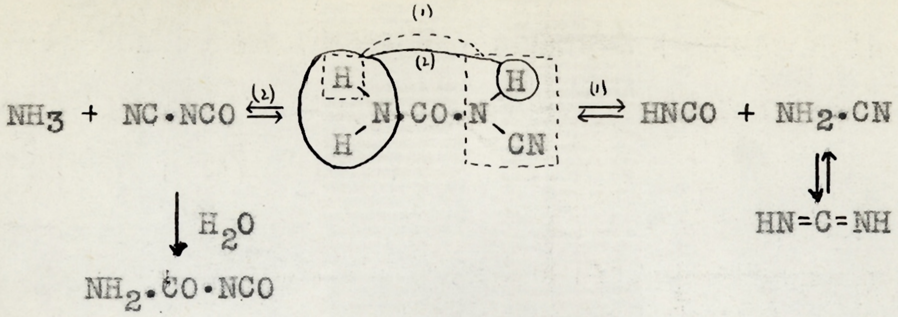
$NH_2 \cdot CO \cdot NH \cdot CN$ $NH_2 \cdot C(NH)NCO$

V   VII

Structure (V) they claimed could account for the formation of biuret and urea, but not guanidine, and hence the necessity of structure (VII) which could hydrolyze to give, in part, guanidine.

If however, this reaction is studied as a "urea dearrangement" the formation of these compounds is easily explained by the interaction of the dearrangement products, and the proposed tautomerism is unnecessary.

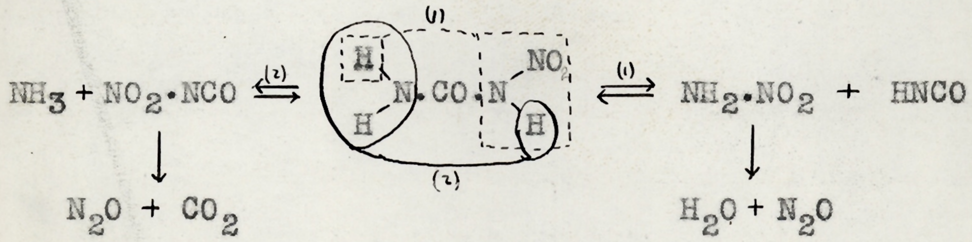
During the course of normal hydrolysis of cyanourea to biuret, a certain portion of the former undergoes dearrangement in the following manner:



The isocyanic acid and cyanamide then react with ammonia to form urea and guanidine respectively, and "cyano-isocyanic acid" may hydrolyze to dicyanic acid, which with ammonia forms biuret.

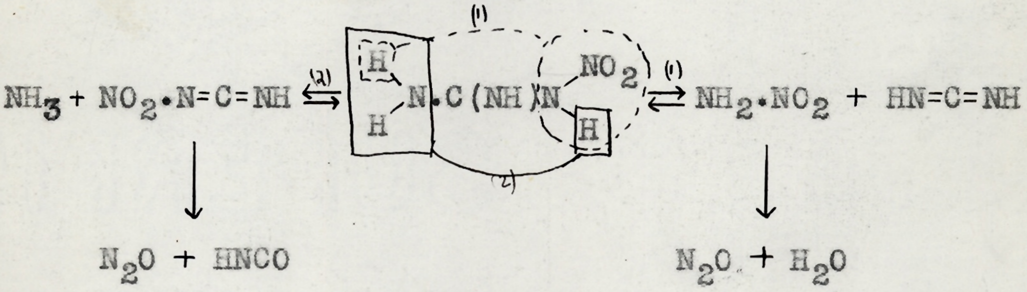
The two compounds of the mono-substituted urea class which are of special interest are nitrourea and nitroguanidine. Davis has made a detailed study of the dearrangement of these compounds and has found that the introduction of a nitro grouping into a molecule of the urea series, greatly increases its tendency to dearrange (48)(53).

Nitrourea in boiling water dearranges in two modes (53) forming mainly isocyanic acid and nitramide on the one



hand, and small amounts of ammonia and nitroisocyanic acid on the other. Both nitramide and nitroisocyanic acid breakdown instantaneously on formation into nitrous oxide and water, and nitrous oxide and carbon dioxide respectively; nitramide however, may be isolated from the solution, but not without difficulty. The ease with which nitrourea dearranges has caused Davis to suggest it as a ready source of isocyanic acid for synthesis; this method has the unique advantage that all other compounds formed decompose into gases.

Nitroguanidine, on heating, dry or in aqueous solution, dearranges along the same pattern (48) forming

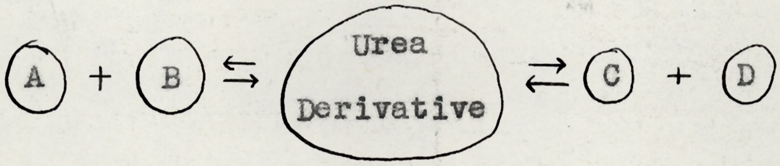


$$\begin{array}{ccccc} NH_3 + NO_2{\cdot}N{=}C{=}NH & \overset{(2)}{\leftrightarrows} & \boxed{\begin{matrix}H\\H\end{matrix}}N{\cdot}C(NH)N\begin{matrix}NO_2\\ \boxed{H}\end{matrix} & \overset{(1)}{\rightleftarrows} & NH_2{\cdot}NO_2 + HN{=}C{=}NH \\ \downarrow & & & & \downarrow \\ N_2O + HNCO & & & & N_2O + H_2O \end{array}$$

nitramide and cyanamide by one mode and ammonia and nitrocyanamide by the other. Nitrocyanamide, previous to Davis' work was not known; at temperatures close to 100°C. it decomposes to nitrous oxide and isocyanic acid, but at 60-70°C. it is capable of reacting with amines to form symmetrical-alkylnitroguanidines.

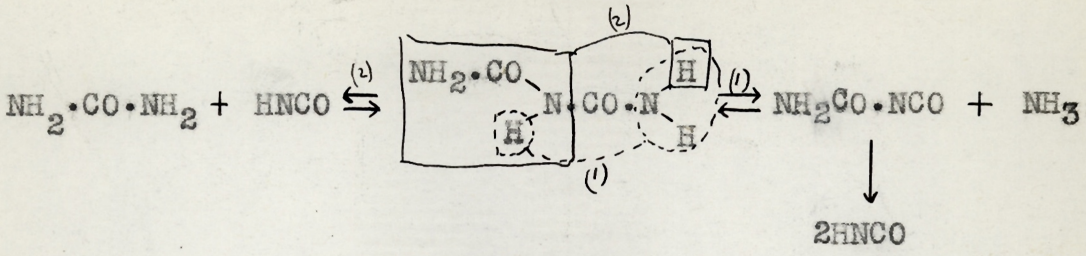
$$NO_2{\cdot}N{=}C{=}NH + R{\cdot}NH_2 \longrightarrow NO_2{\cdot}NH{\cdot}C(NH)NH{\cdot}R$$

Attention may be called here to a very interesting point in the dearrangement reaction. When a urea derivative undergoes dearrangement in two modes, both reactions occur simultaneously. Although the velocity of one may be greater than that of the other, there is however, an equilibrium system set up. Referring to the diagram below, it may happen that substances A and B are formed



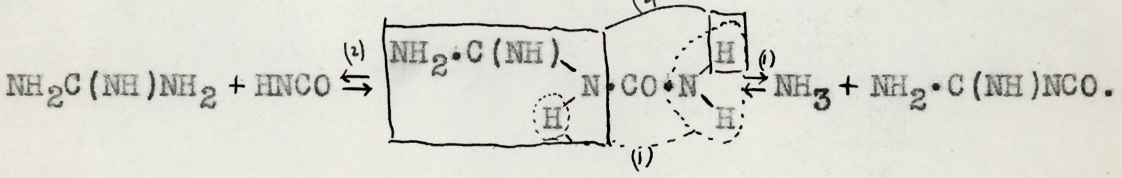
in greater quantities than substances C and D as the urea derivative dearranges. If there is present another substance with which, for example, C is capable of reacting, C is then removed from the equilibrium and A and B recombine to form the urea derivative, which produces more of C, and this may continue until no more of A and B are present in the dearrangement products. This may be used to advantage in synthesis when the compound C (or D) is not readily available, but when the urea derivative or even the substances A and B are. Davis has clearly illustrated the practicality of his urea dearrangement theory by using this point to prepare alkylnitroguanidines from nitroguanidine as mentioned above.

At first sight, the dearrangement of compounds like biuret would appear complex, but they are found to behave like mono-substituted urea derivatives. Biuret dearranges as follows:



forming urea, ammonia, isocyanic acid and dicyanic acid, the last two polymerizing to cyanuric acid (54)(55)(56)(57). Biguanide behaves like a monosubstituted guanidine and dearranges in the same way as biuret, yielding guanidine and cyanamide on the one hand, and ammonia and dicyandiamide on the other (58)(59).

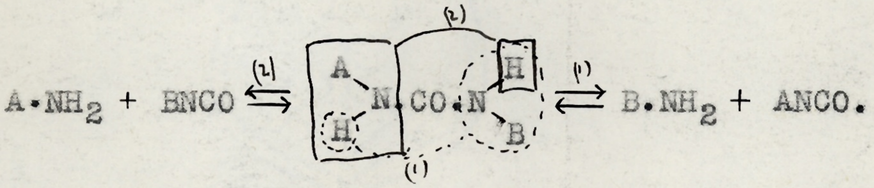
Guanylurea (dicyandiamidine) however, is slightly different, and would be expected to dearrange either as a substituted guanidine or a substituted urea. The literature cites evidence which would indicate that the urea portion of the molecule is the first to break down, because when a current of carbon dioxide is passed through a boiling aqueous solution of guanylurea, guanidine carbonate and ammonia are produced (60). This implies that dearrangement takes place in the following way:



The formation of guanylisocyanate by the first mode is indicated in the reaction of ethanol with guanylurea to form guanidine-carboxylic acid ethyl ester (35), the alcohol evidently adding to the isocyanate molecule:

$$NH_2 \cdot C(NH)N{=}C{=}O \; + \; HO \cdot C_2H_5 \longrightarrow NH_2 \cdot C(NH)NH \cdot CO \cdot OC_2H_5 \; .$$

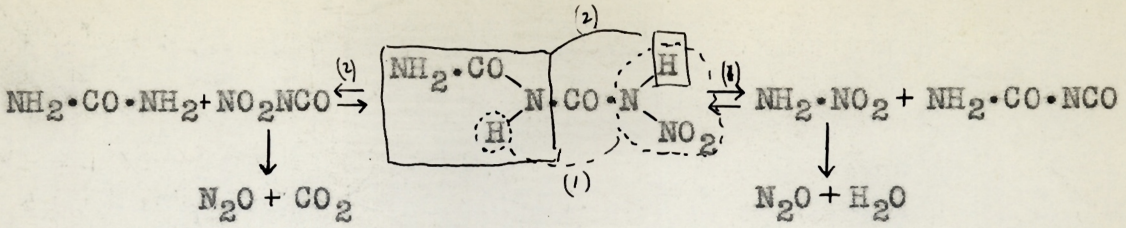
Another class of urea derivatives of special interest to this discussion, are the symmetrical disubstituted ureas. In these compounds, both nitrogens have a substituent group, and on dearranging follow the pattern described below:



$$A \cdot NH_2 + BNCO \overset{(2)}{\rightleftarrows} \begin{matrix} A & & & H \\ & N \cdot CO \cdot N & & \\ H & & & B \end{matrix} \overset{(1)}{\rightleftarrows} B \cdot NH_2 + ANCO.$$

There are formed two different amines and two different isocyanates. An example of this is sym-ethylphenylurea, which, by one mode of dearrangement, forms aniline and ethylisocyanate, and by the other, forms ethylamine and phenylisocyanate (61). It may be pointed out that if the groups A and B are identical, the products of dearrangement are the same by both modes; in this way symdiethylurea forms only ethylisocyanate and ethylamine (61).

Nitrobiuret has been found by Davis (36) to behave like a symmetrical disubstituted urea, and on dearranging forms nitrous oxide, carbon dioxide, urea, and dicyanic acid.



$$\begin{tikzcd} NH_2\cdot CO\cdot NH_2 + NO_2NCO \arrow[r, shift left, "(2)"] \arrow[d] & NH_2\cdot CO\cdot NH\cdot CO\cdot NH\cdot NO_2 \arrow[l, shift left] \arrow[r, shift left, "(1)"] & NH_2\cdot NO_2 + NH_2\cdot CO\cdot NCO \arrow[l, shift left] \arrow[d] \\ N_2O + CO_2 & & N_2O + H_2O \end{tikzcd}$$

This dearrangement permitted the same author to make a detailed study of the previously unknown dicyanic acid (9) which was found to react as a typical isocyanate derivative, forming substituted biurets and allophanic esters with amines and alcohols respectively.

Guanyl-nitrourea differs from nitrobiuret only in having the oxygen atom furthest removed from the nitro group replaced by an imido group. Because of this similarity of structure it may well be expected to dearrange in an analogous manner to that of nitrobiuret. This has been found to be true, and a detailed discussion will be made later.

Nitro Derivatives of the Urea Series.

The nitro compounds of the urea series are nitramides and contain the typical structure $-NH-NO_2$. The general procedure for their preparation consists in treating the parent compound, at temperatures close to $0^{\circ}C$. with either (a) fuming nitric acid, or (b) a mixture of concentrated sulfuric and nitric acids, or (c) treating the nitrate salt of the derivative with concentrated sulfuric acid.

The evident mechanism through which nitration occurs, would appear to be that of the urea derivative first forming a nitrate salt, which, through the dehydrating action of concentrated sulfuric acid (or fuming nitric acid) would lose a molecule of water, forming the nitro derivative; this has been the generally accepted, though erroneous picture.

The introduction of an alkyl group into the guanidine (or urea) molecule would be expected to increase the basicity of the nitrogen (or amino group) to which it is attached, and hence to impart greater basicity to the molecule as a whole. In a salt of such an alkyl derivative it would be expected that the nitric acid would be in combination with the alkylated nitrogen atom (or amino group). If now, the nitrate is formed into an alkyl-nitroguanidine (or urea) derivative, the nitro group would then be attached to the nitrogen atom which carries the alkyl group. This however, has been found not to be so. Davis states (62) that only NN'N"-trialkylguanidines are as strong bases as guanidine itself, monoalkylguanidines and NN-dimethylguanidine are slightly weaker, whereas NN'-dialkylguanidines are weak bases. Pauling has been able to explain this (63) through resonance, a property of the urea series which is becoming more evident and important in the appreciation of their properties.

Further investigations of alkylated ureas, guanidines and biurets (64)(65)(66) have shown that when a nitro derivative of these compounds is formed by direct nitration, the nitro group enters not the alkylated, but the nonalkylated amino group. There is one exception and that is methylurea, which forms N-nitro-N-methylurea (67). Where the amino group is entirely alkylated, that is, in NN-dialkyl-ureas, guanidines and biurets, (unsymmetrical disubstituted derivatives) the nitro group enters on the unsubstituted amino group. It would appear then, that the nitro group may enter only on the non-alkylated amino group. This is further substantiated by the fact that NN'-dialkyl-ureas and guanidines (symmetrical disubstituted derivatives) cannot be nitrated at all. Davis, therefore, concludes that the mechanism of nitration in this series is not the dehydration of the nitrate salt, and suggests that the basicity of urea, guanidine and biuret, and their alkyl derivatives is not confined to any one nitrogen atom, but is distributed through the molecule as a whole. These facts show that the mechanism of nitramide formation in this series remains relatively obscure and no detailed explanation can be offered at this time. However, studies such as those discussed by Pauling (63), on the bond distances and spatial structures involved in these compounds, show promise of shedding much light on the mechanisms of these reactions.

The industrially important nitramides of the urea series are nitrourea and nitroguanidine; those of theoretical interest are nitrocarbamic acid (68), its methyl (69) and ethyl (70) esters and biuret. To this group is now added guanyl-nitrourea, the properties of which indicate the possibility of its becoming an industrially important explosive.

Nitrourea today, is used as the intermediate compound in the preparation of semi-carbazide. It is formed from its nitrate salt by the action of cold, concentrated sulfuric acid (71)(72)(73) and is reasonably stable, but explodes violently when detonated with a fulminate cap (74). The reduction to semi-carbazide takes place quite readily and is carried out industrially by means of an electrolytic process (75).

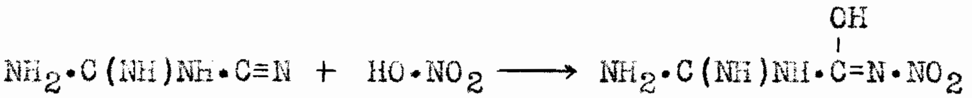
Nitroguanidine is an explosive of singular quality, having the property of exploding with no visible flash, and with a cool flame, whose reported temperature is 907°C. (1). It is prepared by treating guanidine nitrate with concentrated sulfuric acid in the cold (76)(77)(78)(79)(80)(81)(82)(83). On reduction (catalytically or electrolytically) it goes through the steps nitroguanidine ⟶ nitrosoguanidine ⟶ aminoguanidine, a process which has been studied by Smith (84)(85)(86). Nitrosoguanidine possesses some explosive properties (1)(87), and has been studied along dearrangement lines by Davis (88). Aminoguanidine as a sulfanyl derivative has bactericidal properties in intestinal infections and may become an important "sulfa" drug (89).

Nitrobiuret, important to this study because of its similarity to guanyl-nitrourea, is prepared from biuret by the action of mixed acids (90). It is the lone member of this "nitro" series which forms a dinitro derivative (NN'-dinitrobiuret) by the treatment of nitrobiuret with fuming nitric acid (90).

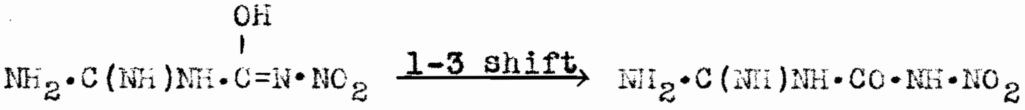
CHEMISTRY OF GUANYL-NITROUREA

Preparation of Guanyl-nitrourea.

Unlike the other nitro derivatives of this series, guanyl-nitrourea (nitrodicyandiamidine)(IX) has not been prepared by the usual method of direct nitration of guanylurea. It was first prepared by Thiele and Uhlfelder (2) by the action of concentrated sulfuric and nitric acids on dicyandiamide. Although these authors did not propose a mechanism for this somewhat unorthodox reaction, they implied that it consisted of the addition of nitric acid in its pseudo form to the cyano group (i), followed by rearrangement to the nitrourea form (ii).



$$NH_2\cdot C(NH)NH\cdot C{\equiv}N + HO\cdot NO_2 \longrightarrow NH_2\cdot C(NH)NH\cdot \overset{OH}{\overset{|}{C}}{=}N\cdot NO_2 \qquad (i)$$



$$NH_2\cdot C(NH)NH\cdot \overset{OH}{\overset{|}{C}}{=}N\cdot NO_2 \xrightarrow{\text{1-3 shift}} NH_2\cdot C(NH)NH\cdot CO\cdot NH\cdot NO_2 \qquad (ii)$$

IX

There is the possibility of the dicyandiamide first hydrolyzing to guanylurea, and the mixed acids then acting, not on the primary product, but on the intermediate guanylurea, although under the conditions of Thiele's reaction (temperature below 0°C.) it is not likely that this occurs. However, guanyl-nitrourea has been prepared from dicyandiamide by Cheetham (91) under conditions (in dilute solution and at temperatures as high as 65°C.) where there is great possibility of hydrolysis to guanylurea (92)(93). An attempt was made by the author to verify this, by nitrating guanylurea directly, under Thiele's conditions. A product, identical in physical properties with guanyl-nitrourea, was obtained, which on decomposing in boiling water yielded guanidine carbonate, the main decomposition product of that compound. Because of the insolubility and unreactivity of guanyl-nitrourea, no further identification of the product was possible. It was therefore, concluded that the nitration of guanylurea yielded the same compound as that prepared from dicyandiamide.

Guanyl-nitrourea has also been prepared from dicyandiamide, by the action of cold, fuming nitric acid. This reaction, however, adds no light to the mechanism of formation, since in this case, it may consist of simple addition of $HO{\cdot}NO_2$, or it may take place through the dehydrating action of the fuming acid.

Properties of Guanyl-nitrourea.

Guanyl-nitrourea is a colorless, micro-crystalline material which when slowly heated, does not melt, but appears to decompose at 415°C.; when heated rapidly it explodes with an evolution of white fumes, but no flame. Its most important property is that when it is mixed with nitrocellulose and nitroglycerine, it lowers the explosion temperature to a point where thedetonation becomes flashless.

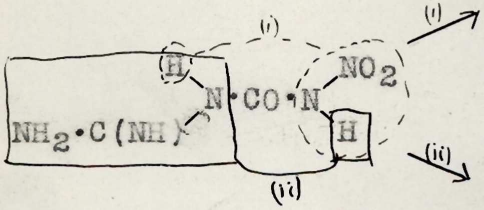
The main characteristic of guanyl-nitrourea, from the chemical point of view, is its insolubility and unreactivity. It is insoluble in all common organic solvents (2) and dissolves in water to the extent of only 0.06 gram in 100 ml. of boiling water, but at the same time slowly decomposes. Guanyl-nitrourea dissolves only in concentrated mineral acids, in a large excess of ammonium hydroxide and in equimolecular amounts of sodium and potassium hydroxide solutions. From these solutions it may be reprecipitated by neutralization (2). The neutralization of alkaline solutions with carbon dioxide gas may be used as a method of purification, because guanyl-nitrourea is insoluble in cold alkaline carbonate solution, although it dissolves to some extent in warm (94).

The dissolution of guanyl-nitrourea in mineral acid is due at least in the case of nitric acid, to the formation of an acid salt. This salt is somewhat unstable, and on dilution with water or ethanol, it immediately decomposes, and regenerates the original guanyl-nitrourea. This compound forms an explosive silver derivative when its alkaline solution is treated with silver nitrate. Like the other nitramides of this series, it is reduced by zinc and hydrochloric acid to guanyl-aminourea (amido-dicyandiamidine) a hydrazine type of compound which reacts readily with ketones and aldehydes to form hydrazides (2).

The introduction of the nitro group into the molecule produces a drastic effect on the properties of guanylurea. Whereas the latter forms colored precipitates withsalts of copper (95)(96) and nickel (97)(98)(99) reactions which are used as qualitative and quantative methods of determining these metals, guanyl-nitrourea does not. The contrast is quite evident in the comparison of solubility, guanylurea and its salts being quite soluble in common organic solvents, in which guanyl-nitrourea is completely insoluble, only going into solution as it decomposes.

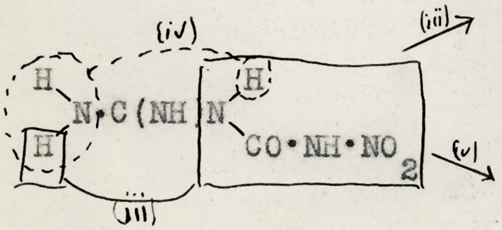
Dearrangement of Guanyl-nitrourea.

Guanyl-nitrourea might be expected to dearrange in four possible manners indicated below:



$$NH_2\cdot C(NH)NCO + NH_2\cdot NO_2 \rightarrow H_2O + N_2O \qquad (i)$$

$$NH_2\cdot C(NH)NH_2 + O{=}C{=}N\cdot NO_2 \rightarrow N_2O + CO_2 \qquad (ii)$$



$$HN{=}C{=}NH + NH_2\cdot CO\cdot NH\cdot NO_2 \rightarrow HNCO + N_2O + CO_2 \qquad (iii)$$

$$HN{=}C{=}NH \downarrow NH_2\cdot CN$$

$$NH_3 + NO_2\cdot NH\cdot CO\cdot N{=}C{=}NH \rightarrow HN{=}C{=}NH + N_2O + CO_2 \qquad (iv)$$

$$HN{=}C{=}NH \downarrow NH_2\cdot CN$$

The two modes indicated in (i) and (ii) suggest that the urea portion of the molecule, being symmetrically disubstituted, undergoes dearrangement, leaving the guanidine portion intact. Modes (iii) and (iv) suggest that the guanidine portion, acting like a mono-substituted derivative dearranges and leaves the nitrourea portion intact, to dearrange in its own right.

In view of Davis' previous work on nitroguanidine and particularly nitrobiuret, dearrangement would be more likely to occur by the first two modes, since the breakdown of the nitrourea portion may be promoted by the nitro group. This has been found to be true.

Thiele (2) has reported that guanyl-nitrourea in boiling water, slowly goes into solution, evolving carbon dioxide and nitrous oxide, and forming guanidine, which can be recovered in the form of the carbonate salt, by evaporation of the solution to dryness. This indicates that dearrangement according to mode (ii) occurs, the nitroisocyanic acid produced, breaking down to the two gaseous products as suggested by Davis.

A more detailed study of the decomposition in water, by the author, has shown that isocyanic acid is formed during the process, and that the final residue, after evaporation of the solution, contains small amounts of ammeline.

If isocyanic acid were formed by dearrangement in mode (iii), it would be accompanied by the formation of nitrourea; but tests for this compound were negative. Furthermore, the presence of nitrourea, with its nitro group intact, is highly improbable since evolution of nitrous oxide has been found to precede a positive isocyanic acid test. The fourth mode may be ruled out because ammonia has not been detected, nor has urea, which could be formed by the combination of ammonia and isocyanic acid. It was then concluded, that the first mode of dearrangement does occur, forming nitramide which decomposes to nitrous oxide and water, and forming guanylisocyanate, the presence of which has been proven by its reaction with ammonia to form guanylurea. This reaction takes place when guanyl-nitrourea is dearranged in the presence of ammonium carbonate.

$$NH_2{\cdot}C(NH)NCO \ + \ NH_3 \longrightarrow NH_2{\cdot}C(NH)NH{\cdot}CO{\cdot}NH_2$$

Guanylisocyanate may partially decompose to cyanamide and isocyanic acid. The undecomposed portion of the guanylisocyanate can then react with cyanamide to form the small amounts of ammeline (see page 9) which were detected; cyanamide also may arise from the dearrangement of a small portion of guanidine.

When guanyl-nitrourea is dearranged in concentrated ammonium hydroxide, in which it is partially soluble, carbon dioxide, nitrous oxide, urea and guanidine carbonate are formed. The fairly large amount of urea may be explained in two ways. First the dearrangement takes place in the second mode. The guanidine then dearranges to cyanamide, which in alkaline solution is

$$NH_2\cdot C(NH)NH\cdot CO\cdot NH\cdot NO_2 \rightleftharpoons NH_2\cdot C(NH)NH_2 + NO_2\cdot NCO \tag{ii}$$

$$NH_2\cdot C(NH)NH_2 \rightleftharpoons HN{=}C{=}NH + NH_3$$

$$HN{=}C{=}NH \xrightarrow{H_2O} HNCO + NH_3$$

$$HNCO + NH_3 \longrightarrow NH_2\cdot CO\cdot NH_2$$

hydrolyzed to isocyanic acid (13)(14), and this reacts with ammonia to form urea. The other explanation is that dearrangement takes place preferentially in the first mode, caused by the mass action of the ammonia (see page 21). The guanylurea then immediately dearranges to guanidine, ammonia and isocyanic acid, which then reacting with the excess of ammonia, forms urea.

$$NH_2\cdot C(NH)NH\cdot CO\cdot NH\cdot NO_2 \longrightarrow NH_2\ C(NH)NCO + NH_2\cdot NO_2 \tag{i}$$

$$NH_2\cdot C(NH)NCO + NH_3 \longrightarrow NH_2\cdot C(NH)NH\cdot CO\cdot NH_2$$

$$NH_2\cdot C(NH)NH\cdot CO\cdot NH_2 \rightleftharpoons NH_2\cdot C(NH)NH_2 + CO_2 + HNCO$$

$$HNCO + NH_3 \longrightarrow NH_2\cdot CO\cdot NH_2$$

Guanyl-nitrourea, in warm sodium hydroxide solution, very readily yields carbon dioxide, nitrous oxide, guanidine carbonate, isocyanic acid and ammonia. However, no urea is formed. This discredits the first explanation given above for the formation of urea, since the hydrolysis of cyanamide is determined not by the ammonium hydroxide present, but rather by the pH of the solution (13)(14). If this hydrolysis does occur, there would be present sufficient ammonia (formed by dearrangement of guanidine) to react with isocyanic acid to form at least traces of urea ; since this is not the case it may be concluded that isocyanic acid remains inactive, in the form of its sodium salt.

Dearrangement in warm dilute sulfuric acid solution takes place more readily than in water, but less readily than in alkaline solution. The products are the same as those of the water dearrangement except that melamine, along with ammeline, is formed. The formation of melamine may be explained by the fact that cyanamide (formed from guanylisocyanate or guanidine) at the low pH of the solution (13)(14), polymerizes to dicyandiamide, which with another molecule of cyanamide, cyclizes to the trimer melamine (see page 9).

In attempting to hydrolyze guanyl-nitrourea to nitrobiuret as indicated below, it was found that at temperatures as low as 65^{o}C., this compound underwent dearrangement evolving nitrous oxide quantitatively before any hydrolysis

$$NH_2\cdot C(NH)NH\cdot CO\cdot NH\cdot NO_2 + H_2O \xrightarrow{Ba(OH)_2} NH_2\cdot CO\cdot NH\cdot CO\cdot NH\cdot NO_2 + NH_3$$

took place. Guanidine carbonate and urea, were recovered by evaporation of the solution. Evidently it was guanidine, the product of the dearrangement, rather than the guanyl-nitrourea that was hydrolyzed. This experiment clearly shows that guanyl-nitrourea is essentially an unreactive compound, being capable of reaction only through the smaller compounds to which it dearranges. This is the characteristic property of the urea series, which is the basis of Davis' theory of Urea Dearrangement.

EXPERIMENTAL PART

Preparation of Guanyl-nitrourea (Thiele's Method).

In a typical experiment, a mixture of 500 ml. of concentrated sulfuric acid and 200 ml. of concentrated nitric acid was cooled to about -4°C. in an ice-salt bath. One hundred and twenty five grams of dicyandiamide (obtained from American Cyanamide Co.) were added in small portions over a period of three hours, during which the mixture was mechanically stirred and the temperature maintained below 0°C.. After an additional one hour of stirring, the thick mixture was poured onto approximately 5 kilograms of cracked ice and allowed to stand overnight. The white product which separated was then filtered on a large Buchner funnel and washed several times with water until the washings were neutral to litmus paper*. The product was then washed with acetone or ethanol and dried at 100°C.; it weighed 208 grams, corresponding to a yield

---

* During the washing on the funnel, the finely crystalline form of guanyl-nitrourea caused channelling, if it were allowed to dry. This could only be overcome by keeping the funnel continually filled with water.

of 95%. Persistently high yields were obtained in a series of similar preparations.

A sample of the product was purified by dissolving it in a solution containing 10% in excess of the required amount of sodium hydroxide, and then passing a current of carbon dioxide until no more precipitate formed. Analysis, calculated for $C_2H_5O_3N_5$: N, 47.64%. Found N, 47.33, 47.92.

2. Nitration of Dicyandiamide with Fuming Nitric Acid.

Eight and four-tenths grams of dicyandiamide in small portions were added with stirring, over a period of one hour, to 26.2 ml. of fuming nitric acid, previously cooled in an ice-salt bath. The resulting solution, which was slightly turbid, was allowed to stand in the bath for an additional hour, after which it was poured through glass wool into 200 ml. of cold (-20°C.) methanol, and let stand in the ice-box overnight. The white product which separated was filtered, washed with methanol until free from acid, and dried. Weight, 8.6 grams, corresponding to a yield of 58%.

This material was found to explode flashlessly without melting; insoluble in water and methanol, it dissolved in 5% sodium hydroxide solution, from which it was reprecipitated with hydrochloric acid. It was presumed to be guanyl-nitrourea.

3. Decomposition Temperature of Guanyl-nitrourea.

A sample of guanyl-nitrourea was heated in a copper block, by means of a bunsen flame. If the temperature were allowed to rise rapidly, decomposition occurred at about 165°C.. If the temperature were raised slowly, decomposition took place at 415°C..

4. Dearrangement of Guanyl-nitrourea in Water.

Fifteen grams of guanyl-nitrourea were heated with 300 ml. of water to about 90°C.. As the solid went into solution, vigorous evolution of gas occurred, but subsided when all had dissolved. A small portion of the solution was removed and cooled, pyridine was added. On adding a few drops of copper sulfate solution, a deep blue complex was formed, which dissolved in chloroform, forming an azure-blue solution; this is Werner's sensitive test for the isocyanate radicle (103). Heating was continued for an additional fifteen minutes in order to complete the reaction, and the solution was then evaporated to dryness on the water-bath. The dried residue weighing 8.7 grams, was then partially dissolved in 12-15 ml. of water and filtered.

The insoluble portion weighing 0.1 gram (1.3%) did not melt, and was found to be insoluble in boiling water (different from melamine, cyanuric acid), insoluble in sodium carbonate solution (different from ammelide) but soluble in potassium hydroxide. Precipitated by acetic acid, it was identified as ammeline. Analysis, calculated for $C_3H_5O_1N_5$: N, 55.11%. Found N, 54.72, 54.92. The picrate was formed according to Ostragovich's directions (100) and melted at 264°C. (reported melting point 266°C.).

The water soluble portion was found to consist entirely of guanidine carbonate, insoluble in alcohol, and decomposing without melting at 197-199°C., weight 8.6 grams or 98.7%.

5. Guanyl-nitrourea and Ammonia.

A mixture of 450 ml. of 15% ammonium hydroxide solution and 15 grams of guanyl-nitrourea was heated on the water-bath for two hours. When the evolution of gas had ceased, a small portion of the solution was removed and cooled, and found to give a negative test for guanylurea. On evaporating the solution to dryness, a somewhat hygroscopic residue, weighing 10 grams, was obtained. This, on extraction with ethanol, left 8.5 grams of an insoluble, carbon dioxide containing compound, whose melting point corresponded to that of guanidine carbonate. This was further identified by the melting point of its nitrate and by a mixed melting point determination with a known sample of guanidine nitrate.

The ethanol solution, on evaporation yielded 1.0 gram of urea, melting point 129-131°C.. Urea was identified by the melting point of its nitrate and by mixed melting point with a known sample of urea nitrate.

6. Dearrangement of Guanyl-nitrourea in Alkaline Solution.

Twenty-five grams of guanyl-nitrourea were dissolved in 175 ml. of 5% sodium hydroxide solution and slowly heated. Evolution of gas began as the temperature rose to 60°C. and abated after about one hour. After a further forty-five minutes of heating, during which ammonia was evolved, a sample, removed from the solution, gave a strongly positive test for isocyanic acid and a negative test for guanylurea. On evaporation guanidine carbonate was recovered from the residue, but no urea.

7. Dearrangement of Guanyl-nitrourea in Acid Solution.

To a solution of 60 ml. of concentrated sulfuric acid in 400 ml. of water, 25 grams of guanyl-nitrourea were added, and the mixture heated to 90-95°C.. A portion of the solution was removed, neutralized and tested for isocyanic acid and guanylurea - both tests were negative. After eighty minutes the solution was cooled, and 330 grams of hydrated barium hydroxide were added. After allowing the mixture to stand for some time, during which it was occasionally stirred, the precipitated barium sulfate was removed by filtration on a Buchner funnel and washed. The filtrate was saturated with carbon dioxide to remove any dissolved barium, filtered and evaporated to dryness. The residue, extracted with about 20 ml. of water, yielded a white insoluble powder, (weight 0.5 gram) which was found to consist of equal amounts of melamine and ammeline.

Separation of these two was made by treating the mixture with boiling water and filtering rapidly. On cooling the filtrate, there settled out a colorless compound, which was alkaline to litmus, and which dissolved in dilute nitric acid (different from cyanuric acid). This was presumed to be melamine. The ammeline portion, insoluble in boiling water, was also insoluble in sodium carbonate solution (different from ammelide) but dissolved in potassium hydroxide solution from which it was reprecipitated with acetic acid. The picrate was formed, and melted at 262-264°C..

The water soluble portion of the original residue, was found to consist of 7.3 grams of guanidine carbonate, melting point 197-199°C.. This was identified by its carbon dioxide content, and the melting point of its nitrate.

8. Guanyl-nitrourea and Ammonium Carbonate.

One and four-tenths grams of guanyl-nitrourea were added to a solution of 25 grams of ammonium carbonate in 150 ml. of water. The mixture was boiled until all the solid had dissolved, and evolution of gas had ceased. The solution was then diluted to a volume of 250 ml. and an aliquot of 5.0 ml. was neutralized with dilute sulfuric acid to this solution 1.0 ml. of 10% copper sulfate was added, and then 1.0 ml. of 10% sodium hydroxide. The resulting blue-pink colored solution was then compared with the colored solutions produced by known quantities of guanylurea, and was found to contain 0.008 gram of guanylurea. The total amount of guanylurea formed was therefore, approximately 0.4 gram or 36% of the original material.

9. Guanyl-nitrourea and Baryta.

Sixty-two grams of hydrated barium hydroxide, dissolved in 500 ml. of carbon dioxide-free water, and 29.4 grams (0.2 mole) of guanyl-nitrourea were placed in a flask equipped with a reflux condenser. The flask was connected through the condenser to a bubbler containing 125 ml. of normal hydrochloric acid and then to a container in which nitrous oxide could be collected by displacement of water. The flask was heated and maintained at 60°C.* for twelve hours. During this time approximately 4.5 liters (about 0.2 mole) of nitrous oxide were evolved, and 0.07 gram (.004 mole) of ammonia collected in the

---

* the decomposition temperature of nitrobiuret is 65°C..

hydrochloric acid trap. The barium carbonate, formed in the reaction flask was filtered, washed with water, and then extracted with 10% sodium hydroxide solution. On filtration and acidification of this solution, no guanyl-nitrourea was found.

The reaction solution was saturated with carbon dioxide toremove the barium, filtered and evaporated to dryness under reduced pressure, the temperature being maintained below 60°C.. The residue weighing 13 grams, was found to contain 9.1 grams of urea, determined by its solubility in hot ethanol, and identified by its melting point, that of the nitrate, and by a mixed melting point of the latter with a known sample of urea nitrate. The other portion of the residue consisted of 3.9 grams of guanidine carbonate. There was no evidence of nitrobiuret.

10. Solubility of Guanyl-nitrourea.

One gram of guanyl-nitrourea and 100 ml. of water were heated to boiling for three minutes, and filtered rapidly through a hot Büchner funnel. The filtrate on cooling in ice-water deposited a white material, which, filtered and dried, weighed 0.065 gram. This was identified as guanyl-nitrourea by its dissolution in alkali and precipitation with carbon dioxide, and by the manner in which it exploded on heating.

Further studies have shown Guanyl-nitrourea to be insoluble in methanol, ethanol, ether, benzene, carbon disulfide, carbon tetrachloride, chloroform, petroleum ether, acetone, acetic acid, aniline, pyridine, dioxane and ethyl acetate.

11. Attempted Reaction of Guanyl-nitrourea and Nitrous Acid.

Several attempts to introduce a nitroso group into the guanyl-nitrourea molecule were made. In all cases there was no reaction, the compound being recovered quantitatively from the reaction mixture.

12. Attempted Formation of Guanyl-nitrourea Complexes and Colored salts.

a) Phosphate.

The preparation of a phosphate salt of guanyl-nitrourea was attempted, by means of the method described for that of guanylurea and dicyandiamide (101), by dissolving it in concentrated hydrochloric acid and slowly adding syrupy phosphoric acid. No reaction took place.

b) Mercuric cyanide and potassium iodide complex.

Although guanidine and guanylurea, dissolved in mineral acids, gave flaky, colorless crystals when potassium iodide and mercuric cyanide solutions were successively added (102), a similar precipitate could not be obtained with guanyl-nitrourea, dissolved in either concentrated hydrochloric, nitric or sulfuric acids.

c) Copper derivative.

Several attempts were made to apply the sensitive copper test for guanylurea (96) to guanyl-nitrourea and were unsuccessful, no reaction taking place.

d) Nickel derivative.

Similar negative results were also obtained on applying the nickel test for guanylurea (99) to this compound.

13. Attempted Preparation of Dinitroguanylurea.

Several attempts to introduce a second nitro group into the guanylurea molecule were made and all were unsuccessful. The procedure used was that of Thiele for dinitrobiuret (90), and consisted in dissolving guanyl-nitrourea in cold, fuming nitric acid. This solution was subjected to varied methods of treatment, and in all cases, unchanged guanyl-nitrourea was quantitatively recovered.

The only compound isolated in these experiments, was obtained by allowing the nitric acid solution to evaporate to dryness under vacuum. The needle-like crystals thus obtained, were found to explode sharply, in a manner different from that of guanyl-nitrourea. They gave a positive test for nitrate and were presumed to be nitrate salt of guanyl-nitrourea.

14. Nitration of Guanylurea.

A mixture of 13.5 ml. of concentrated sulfuric and 5.5 ml. of concentrated nitric acid was cooled in an ice-salt bath, and 5.4 grams of guanylurea, prepared by the method of Söll and Stutzer (93), were added in small portions over a period of an hour, during which the mixture was vigorously stirred by hand, and the temperature maintained below 0°C.. After allowing the mixture to remain in the ice-salt bath for twenty minutes, it was poured into a beaker containing 400 grams of cracked ice, and let stand overnight. The white compound which settled to the bottom of the beaker was filtered on a Buchner funnel, washed until free from acid and dried in an oven at 100°C.. Weight 4.0 grams.

The product was found to be insoluble in water, methanol, ethanol, acetone, ether, chloroform, pyridine and carbon tetrachloride. On heating it exploded without melting, and with no flash. It dissolved in 10% sodium hydroxide, from which it was precipitated by neutralization with carbon dioxide or mineral acids, and was also soluble in concentrated sulfuric and hydrochloric acids.

One gram of the nitrated compound was heated in 75 ml. of boiling water. During the dissolution, gas was evolved, part of which was found to be carbon dioxide. After evolution of gas had ceased, the solution was evaporated to dryness and yielded a residue which appeared to consist mainly of guanidine carbonate, melting point 195-197°C.. This was identified by its insolubility in ethanol, carbon dioxide content, and the melting point of its nitrate. No evidence of urea, guanylurea, or biuret was found. This compound, by its solubility properties and its dearrangement products, is evidently identical with guanyl-nitrourea.

GUANYL-NITROUREA AS A COMPONENT OF FLASHLESS PROPELLENTS.

When the explosive properties of Picrite (nitroguanidine) were discovered, just after the last Great War, the idea of flashless propellents was conceived by the United States Army (1). The present war has increased the interest in this type of propellent, and for the first time, the industrial preparation of Picrite has been undertaken, this, in Canada, within the last two years.

Picrite, and the cordite made from it, possess certain technical disadvantages which have stimulated investigations bent on eliminating, or at least bettering these undesirable properties. During the course of such a study, the compound guanyl-nitrourea (named Rossite) was found, and its properties, both chemical and ballistic, strongly indicate the possibility of it replacing Picrite in these propellents.

Rossite is prepared from dicyandiamide by a simple, one-step reaction, as compared with the two-step process involved in the preparation of

Picrite (dicyandiamide + ammonium nitrate → guanidine nitrate (104), guanidine nitrate + sulfuric acid → nitroguanidine (83)).

A large batch of Rossite, prepared on a pilot-plant scale, was incorporated with nitrocellulose and nitroglycerine and made into a special cordite. Several shells were charged with this and fired from a 3.74 inch, high velocity anti-aircraft gun. The propellent explosion was found to be that desired, completely flashless. This is an improvement over the Picrite-cordite, which has a small, but yet visible flash. The only shortcoming of the Rossite-cordite was the fact that the muzzle velocity of the shell was decreased to 2620 feet per second, as compared to 2706 feet per second of ordinary flashless cordite, a point which can easily be remedied by further ballistic studies.

Several other advantages of Rossite have been pointed out to the author, one of which is its micro-crystalline form. Picrite crystals are bulky, and besides presenting an important shipping problem, cause considerable difficulty in the kneading process in which Picrite, nitrocellulose, nitroglycerine and other compounds are incorporated into a dough. This dough is then extruded through a small hole and drawn into a cord, which on drying is found to be brittle.

This incorporation consists mainly of the dispersion of the flashless component in nitrocellulose, nitroglycerine acting as the dispersing agent. When Rossite is used, the dough is very easily made, and the resulting cordite is decidedly flexible. The experimental Rossite-cordite made in this way, and used in the actual firing tests, had the following composition:

	%
Rossite	55.0
nitrocellulose	21.5
nitroglycerine	21.5
centralite	2.0
chalk	0.15 to 0.10
cryolite	0.3 to 0.1

The industrial advantages of Rossite, which are perhaps, its greatest feature, are the low cost of production (less than one third the cost of Picrite) and the lack of danger involved in its preparation. These two weigh heavily in favor of its replacement of Picrite in the explosive industry. The safety of Rossite is mentioned because two explosions, involving several death, have occurred in the production of Picrite.

Although still in the experimental stage, the use of Rossite in flashless cordite nevertheless shows promise of being a step forward in the bettering of these very valuable propellents.

SUMMARY

The compound N-guanyl-N'-nitrourea has been prepared in two new manners,

a) from dicyandiamide, by the action of fuming nitric acid, and

b) from guanylurea, by the action of concentrated nitric and sulfuric acids.

Studied from the "Urea Dearrangement" point of view, this compound has been found to behave like a typical symmetrical disubstituted urea, dearranging to guanidine, nitroisocyanic acid, nitramide and guanylisocyanate.

N-guanyl-N'-nitrourea (named Rossite) explodes on heating with a cool flame and no visible flash. After many tests made by the Department of Munitions and Supply, its use, as the flashless component of flashless propellents has been strongly recommended.

BIBLIOGRAPHY

1. Davis, Army Ordnance 3, 193(1923); C.A. 17, 1143 (1923).
2. Thiele and Uhlfelder, Ann. 303, 108, (1898).
3. Davis, Proc. Am. Acad. Arts Sci., 11, 68 (1925).
4. Emil Werner, numerous papers on Carbamides, J.Chem. Soc., 1915 to 1924; Chemistry of Urea. Longmans & Green & Co., London (1923).
5. Goubeau, Ber. 68B, 895 (1935).
6. Linhard, Betz, Ber. 73B, 177 (1940); C.A. 34, 4005(1940).
7. Wöhler, Pogg. Ann. Physik 12, 253 (1828).
8. Reference 4.
9. Davis, J.A.C.S. 51,1806 (1929).
10. Kohlrauch Z. physik. Chem. B37, 421 (1937); C.A. 32, 428 (1938).
11. Smolka and Friedreich, Monatsh. 9, 701 (1888).
12. Blair and Smith, J.A.C.S. 56, 907 (1934).
13. Hetherington and Braham, J.A.C.S. 45, 828 (1923).
14. Buchanan and Barsky, J.A.C.S. 52, 195 (1930).
15. Chastellain, Helv. Chim. Acta. 18, 1287 (1935).
16. Bamberger, Ber. 16, 1074 (1883).
17. Strecker, Lehrbuch der organischen Chemie, (5 Aufl., S. 637).
18. Davis, J.A.C.S. 44, 2600 (1922).
19. Hughes, J.A.C.S. 62, 1258 (1940).

20. Pohl, J. prakt. Chem. (2) 77, 533 (1908).

21. Drechsel, J. prakt. Chem. (2) 11, 202 (1837), ibid. 13, 331 (1838).

22. Cloez and Cannizzaro, Compt. rend. 32, 63 (1851); Ann. 78, 229 (1851).

23. Lemoult, Ann. chim. (7) 16, 409 (1899).

24. Davis, J.A.C.S. 43, 2230 (1921).

25. American Cyanamid Co. Melmac plastics.

26. Smolka and Friedreich, Monatsh. 10, 95 (1889).

27. Emich, Monatsh. 4, 412 (1883).

28. Liebig, Ann. 95, 264 (1855).

29. von Ponomarew, Ber. 18, 3267 (1885).

30. Smolka and Friedreich, Monatsh. 9, 701 (1888); ibid. 10, 96 (1889); ibid. 11, 203 (1890).

31. Das Gupta, J. Indian Chem. Soc. 11, 207 (1934).

32. Davis, J.A.C.S. 47, 1063 (1925).

33. Hallwacks, Ann. 153, 293 (1870).

34. Blair and Smith, J.A.C.S. 56, 907 (1934).

35. Blair and Pinck, J.A.C.S. 49, 509 (1927).

36. Davis, J.A.C.S. 51, 1801 (1929).

37. Baumann, Ber. 19, 452 (1886).

38. Wurtz, Ann. chim. (3) 30, 460 (1850).

39. Wurtz, Compt. rend. 27, 242 (1848).

40. Volhard J. prakt. Chem. (2) 9, 21 (1874).

41. Fleischer, Ber. 9, 995 (1876)

42. Wöhler and Liebig, Ann. 26, 301 (1838).

43. Walker and Hambly, J. Chem. Soc. 67, 747 (1895).

44. Wöhler and Liebig, Ann. 26, 261 (1838).

45. Wöhler, Pogg. Ann. Physik 15, 622 (1829); Ann. chim. (2) 43, 67 (1830).

46. Davis, J.A.C.S. 44, 2595 (1923).

47. Werner, Chemistry of Urea, Longmans & Green & Co., London (1923).

48. Davis, Proc. Am. Acad. Arts Sci. 61, 437 (1926).

49. Hofmann, Ann. 74, 14 (1850).

50. Fleischer, Ber. 9, 995 (1876).

51. Schiff, Ann. 148, 338 (1868).

52. Clermont, Ber. 9, 446 (1876); ibid. 10, 494 (1877).

53. Davis, J.A.C.S. 51, 1790 (1929).

55. Hofmann, Ber. 4, 265 (1871).

54. Baeyer, Ann. 130, 155 (1863).

56. Finckh, Ann. 124, 335 (1862).

57. Werner, J. Chem. Soc. 103, 1014, 2278 (1913).

58. Emich, Monatsh. 4, 412 (1883); ibid. 13, 11 (1891).

59. Smolka and Friedreich, Monatsh. 10, 95 (1889); ibid. 11, 45 (1890); ibid. 11, 203 (1890).

60. E, Merck, German Patent 458,437 (1926).

61. Davis, Proc. Am. Nat. Acad. Arts Sci. 11, 68 (1925)

62. Davis, J.A.C.S. 54, 1499 (1932).

63. Pauling, Nature of the Chemical Bond, Cornell University Press, p. 214 (1940).

64. Davis J.A.C.S. 49, 2303 (1927).

65. Davis, J.A.C.S. 55, 731 (1933).

66. Davis, J.A.C.S. 58, 1800 (1936).

67. Degner and von Pechmann Ber. 30, 652 (1897).

68. Thiele and Lachman, Ann. 288, 295 (1895).

69. Thiele and Dent, Ann. 302, 249 (1898).

70. Thiele and Lachmann, Ber. 27, 1520 (1894).

71. Thiele and Lachman, Ann. 288, 281 (1895).

72. Baeker, Rec. 31, 21 (1912).

73. Willstätter and Pfannesteil, Ber. 59B, 1870 (1926).

74. Badische, German Patent 303,927; C.A. 14, 2713 (1920).

75. Org. Syntheses, Collective vol. 1, 472 (1932).

76. Jousselin, Compt. rend. 88, 1087 (1879).

77. Pellizzari, Gazz. chim. ital. (2) 21, 406 (1891).

78. Franchimont, Rec. 10, 231 (1891).

79. Thiele, Ann. 270, 17 (1892).

80. Ewan and Young, J. Soc. Chem. Ind. 40, 109T (1921).

81. Davis, J.A.C.S. 47, 1063 (1925).

82. Smith, Sabetta and Steinback, Ind. Eng. Chem. 23, 1124 (1931).

83. Org. Syntheses, Collective vol. 1, 392 (1932).

84. Smith and Sabetta, J.A.C.S. 54, 1034 (1932); ibid. 57, 2478, 2730 (1935).

85. Smith and Lieber, J.A.C.S. 57, 2479 (1935); ibid. 58, 1417, 2170 (1936); ibid. 59, 1150, 1834, 2283 (1937).

86. Smith and Lieber, Chem. Rev. 25, 213 (1939).

87. Kerone, U.S. Patent 2,146,188 (1939).

88. Davis, J.A.C.S. 59, 2112 (1937).

89. Winnek and Roblin, J.A.C.S. 64, 1682 (1942).

90. Thiele and Uhlfelder, Ann. 303, 95 (1898).

91. Cheetham, Dept. Munitions and Supply, private communication.

92. Haag, Ann. 122, 25 (1862).

93. Söll and Stutzer, Ber. 42, 4534 (1909).

94. Caro, Z. angew. Chem. 23, 2414 (1910).

95. Grossmann, Mannkeim, Chem. Zeit. 42, 17 (1918).

96. Haag, Ann. 133, 31 (1862).

97. Grossmann and Schuck, Z. angew. Chem. 20, 3844 (1907); Ber. 39, 3357 (1906); Chem. Zeit. 31, 335, 911 (1907).

98. Prettner and Grossmann, Chem. Zeit. 33, 411,841 (1909).

99. Cochet, Ann. fals. 18, 396, 468 (1925); C.A. 20, 258 (1926).

100. Ostragovich, Gazz. chim. ital. 60, 648 (1930).

101. Cochet, Compt. rend. 195, 324 (1932).

102. Ragni, Gazz. chim. ital. 63, 303 (1933).

TESTS ON PORPOISE-OIL.

The author was awarded a scholarship by the Bureau Provincial des Recherches Scientifiques in order to investigate, under the direction of Dr. W. H. Hatcher, the composition of porpoise-oil (huile de marsouin). The sample however did not arrive at McGill University until the last two weeks of the scholastic year 1940-41, and only the preliminary tests, listed below were carried out. In the meanwhile, the author was permitted to conduct the investigation which is the subject of this work under the direction of Dr. J. H. Ross and Dr. Raymond Boyer.

1. REFRACTIVE INDEX (Abbe Refractometer)

16.5°C	1.475
17.8°C	1.474
19.5°C	1.473
22.0°C	1.471

2. FREE FATTY ACID VALUE. (Procedure according to A.O.A.C. p. 436 (1940))

	I	II	III	IV
wt. of oil	7.050g.	7.064g.	7.135g.	7.188g.
ml. of 0.1n NaOH	3.2	3.3	3.2	3.35
ml. of .25n NaOH	1.28	1.32	1.28	1.34
%Free Fatty Acid	1.28	1.31	1.27	1.31

% Free Fatty Acid expressed as ml. .25n NaOH required for 7.05g. of oil.

Factor of .1n NaOH is 0.8692

3. SAPONIFICATION NUMBER (Procedure according to A.O.A.C. p. 432 (1940)

	I	II	III	IV
wt. of oil	2,569g.	2,522g.	2.477g.	2.596g.
ml. of 0.5n HCL	10.9	11.3	11.6	10.8
Saponification No.	192.5	190.7	191.5	190.5

blank requires 29.2 ml. of .5n HCL

Saponification No. expressed as milligrams of KOH required to saponify 1.0g. of oil.

Factor of .5n HCL o.9615.

4. IODINE NUMBER (Hans Method according to A.O.A.C. p. 429 (1940))

	I	II	III	IV
wt. of oil	0.250g.	0.252g.	0.255g.	0.246g.
ml. of 0.1n $Na_2S_2O_3$	22.0	20.9	21.6	22.05
Iodine Value	85.5	85.8	85.7	86.2

iodine value, expressed as mgm. of I_2 absorbed by 1g. of oil.

blank requires 39.5, 39.4 ml.

5. REICHERT/MEISSL AND POLENSKE VALUES (Procedure according to A.O.A.C. p. 433 (1940))

	I	II	III
wt. of oil	5.048g.	5.036g.	5.019g.
Soluble Acids			
ml. of 0.1n NaOH	21.7	21.4	20.8
Reichert-Meissal Value	18.15	18.00	18.10

blank requires 0.4 ml.

factor of 0.1n NaOH is 0.8692

	I	II	III
Insoluble Acids			
ml. of 0.1n NaOH	1.1	0.8	1.1
Polenske Value	0.94	0.68	0.95