

LECTURES

ON

ORGANIC CHEMISTRY :

DELIVERED DURING THE WINTER SESSION, 1844, IN THE  
University of Giessen.

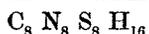
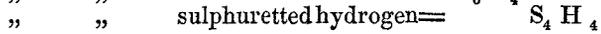
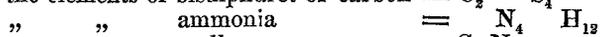
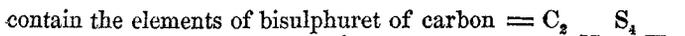
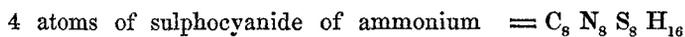
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CYANOGEN AND ITS COMPOUNDS, CONTINUED—PRODUCTS RESULTING FROM THE DECOMPOSITION OF SULPHOCYANIDE OF AMMONIUM—MELAM—MELAMINE—AMELINE—AMELIDE.

GENTLEMEN,—Having in my last lecture concluded my observations on mellon, I will now proceed to the examination of certain substances resulting from the decomposition of one of the sulphocyanides—viz., sulphocyanide of ammonium. The composition of sulphocyanide of ammonium corresponds to that of cyanate of ammonia, or urea, with this difference, that the oxygen of the cyanate is replaced by sulphur in the sulphocyanide. It was to be expected, therefore, that sulphocyanide of ammonia would, upon distillation, yield products bearing a certain relation to the products obtained from sulphocyanogen by the action of heat, on the one hand, and to those resulting from the decomposition of urea, on the other.

We have in sulphocyanide of ammonium, hydrosulphocyanic acid in combination with ammonia, and therefore we have the elements of bisulphuret of carbon, ammonia, mellon, and sulphuretted hydrogen, in the following proportions:—



This arrangement of the elements composing sulphocyanide of ammonium will at once readily explain the decomposition of this substance by the action of heat, and account for the resulting products. Upon submitting sulphocyanide of ammonium to the action of heat, bisulphuret of carbon, ammonia, and sulphuretted hydrogen, are evolved, or sulphuretted hydrogen is evolved in combination with the ammonia—i. e., as hydrosulphuret of ammonia—and there remains in the residue a yellow substance, exhibiting the same deportment as mellon, inasmuch as upon being heated to redness, it yields nitrogen gas and cyanogen gas; or if only a moderate degree of heat is made to act upon the sulphocyanide of ammonium, there remains in the residue compounds containing the elements of mellon and of ammonia; and thus we see that this residue is, at all events, convertible into the product which urea yields under the same circumstances—viz., cyanuric acid. To understand this readily, you need only recollect that mellon is converted into cyanuric acid by the action of acids and alkalis. The action of heat upon sulphocyanide of ammonium yields, as I just now stated, a residue containing either mellon or combinations of mellon with the elements of ammonia; the residue must therefore be convertible, in either case, into cyanuric acid, or into cyanuric acid and ammonia.

The residuary powder which remains upon submitting sulphocyanide of ammonium to a moderate degree of heat, is of a dirty-grey colour; its composition varies exceedingly, according to the lower or higher degree of heat applied for the decomposition of the sulphocyanide of ammonium; it dissolves almost completely when gently heated in concentrated sulphuric acid, only a very inconsiderable portion remaining undissolved. The simple addition of water to this solution does not disturb it; but if the solution be diluted with water and then kept boiling for a few hours, and afterwards allowed to cool, a copious amount of crystals of cyanuric acid is obtained, and in the solution there remains sulphate of ammonia. It is easy to ascertain the exact moment when this transformation of the residue into cyanuric acid is completed. The test employed for this purpose is carbonate of ammonia. Upon adding this substance to the solution of the residue in sulphuric acid, after its dilution with water, a white precipitate is obtained, which is insoluble in water. After the solution has been kept boiling for some time, the addition of this re-agent causes it simply to become turbid, and subsequently produces not the slightest alteration in its appearance. When this is

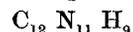
the case, the residue we are speaking of has become completely converted into cyanuric acid.

Sulphocyanide of ammonium contains no oxygen, nor does the residue remaining upon its distillation, whilst cyanuric acid is an oxygen compound. It is evident, therefore, that this acid must owe its formation to double decomposition. It is not easy to designate positively the ultimate link in the chain of this decomposition—i. e., the precise substance from which its formation proceeds immediately, since the residue in question is obviously a mixture of several compounds, which hardly admit of isolation by solvents, without undergoing alteration.

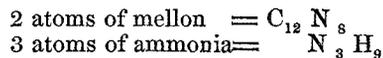
If the residue remaining upon the distillation of sulphocyanide of ammonium is treated with boiling potass lye, the solution speedily filtered from off the portion remaining undissolved, and the filtrate made to cool quickly, a white heavy powder precipitates, which, upon being washed with cold water, exhibits only slight traces of alkali. This pulverulent substance seems to be the principal product of the decomposition of the sulphocyanide of ammonium; but if the residue in question is kept boiling for some time with the potass lye, it becomes completely dissolved, and the solution, upon cooling, yields no longer any precipitate, and contains now only the products of the decomposition of that precipitate. The name of *mellam* has been assigned to this substance.

MELAM.

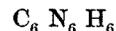
From its analysis the following formula is deduced:—



According to this, it contains the elements of two atoms of mellon, and of three atoms of ammonia.



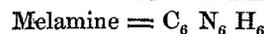
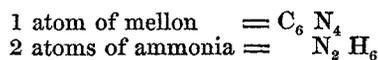
It is only after long protracted boiling that the residue remaining upon the distillation of sulphocyanide of ammonium (which residue we will designate by the term *crude* and *impure mellam*) dissolves completely in dilute solution of caustic potass with evolution of ammonia. If this solution is concentrated at a high temperature, and, from time to time, allowed to cool, it deposits lustrous, hard, rhomboidal octahedrons, possessing all the properties of a salifiable base, but without alkaline reaction. The name of *mellamine* has been assigned to this substance. It is free from oxygen, and its composition is expressed by the following formula:—



This formula indicates the proportion of this substance combining with one equivalent of acid, to form a neutral salt.

MELAMINE.

You perceive that melamine contains the elements of one atom of mellon and two atoms of ammonia—



All the salts of melamine are crystallizable. Melamine combines directly with the hydracids and with the so-called hydrates of the oxygen acids. Solution of melamine in water precipitates hydrated magnesia from solutions of salt of magnesia, upon boiling; from salts of ammonia it evolves ammonia at a high temperature; with perchloride of platinum, melamine forms a crystalline compound, and also with nitrate of silver it forms a basic double salt.

If the alkaline solution from which the melamine has been deposited is supersaturated with acetic acid, a shining-white, somewhat gelatinous, precipitate is obtained. This is another base, to which the name of *ameline* has been assigned.

AMELINE.

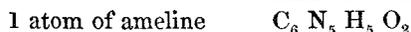
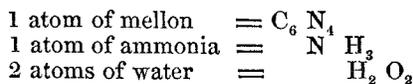
In order to obtain this base perfectly pure, the precipitate procured upon supersaturating the alkaline solution of the crude and impure mellam, after the crystallization of melamine, is washed, and, whilst still moist, projected into dilute and hot nitric acid until the acid is saturated; the solution thus obtained is filtered, and evaporated at a gentle heat. When the solution has thus become somewhat concentrated, nitrate of ameline crystallizes in fine, white, transparent prisms, which are then re-dissolved in very dilute nitric acid, and the solution treated with carbonate of ammonia, when the pure ameline precipitates. This precipitate of pure ameline has a silky lustre, and exhibits under the microscope the form of fine transparent needles. Ameline is a very weak base, which, like melamine, combines with acids, but without destroying their acid reaction; with perchloride of platinum it forms a neutral double

compound, and with nitrate of silver a basic double compound. The formula—



expresses its composition.

This substance therefore contains the elements of one atom of mellon, one atom of ammonia, and two atoms of water—



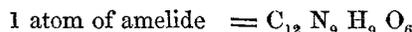
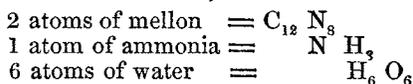
If melam is dissolved in concentrated nitric acid, or melamine and ameline in concentrated sulphuric acid, and the solutions obtained are mixed, in the first place, with double their volume of water, and afterwards with four times their volume of alcohol, another white substance separates, which contains all the carbon of the melam, or of the melamine and ameline, and exhibits in its physical properties a great resemblance to ameline, but differs essentially from this last substance in its composition and chemical properties. Upon being heated in moderately concentrated nitric acid, it dissolves in this menstruum; the solution thus obtained solidifies at a low temperature, forming a crystalline mass, which, upon being washed with water, loses every trace of nitric acid, and leaves the original substance in a state of perfect purity and with all its original properties. The name of *amelide* has been assigned to this substance.

#### AMELIDE.

Its formula is—

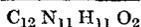
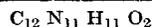
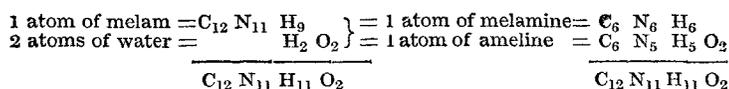


According to this formula, it contains the elements of two atoms of mellon, one atom of ammonia, and six atoms of water—



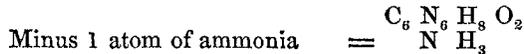
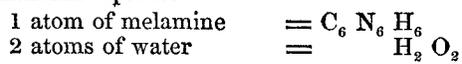
According to Knapp, who has investigated this substance, amelide, when dissolved in dilute nitric acid and mixed with nitrate of silver, yields, upon the addition of ammonia, a white crystalline precipitate: this consists of an amelide compound, analogous to salts, in which one atom of oxide of silver has displaced and replaced one atom of water of the amelide. In this respect, amelide differs totally from ameline and melamine: both these latter substances yield white precipitates, upon their solution in nitric acid being mixed with nitrate of silver, but these precipitates contain one atom of oxide of silver to one atom of anhydrous nitrate of ameline or melamine; they are compounds in which the water of hydration of the nitric acid in the nitrate of ameline or melamine is replaced by one atom of oxide of silver. Many organic bases enter into combinations of this kind, and differ essentially, in this respect, from the acids, or from those bodies which comport themselves like acids, such as amelide. It is evident that ameline and melamine possess the character of organic bases, whilst amelide approaches that of the acids. Amelide, in this respect, occupies a kind of medium position between a base and an acid; for if the above-mentioned compound of amelide and oxide of silver is dissolved in nitric acid, and the solution gently evaporated, it yields a double compound containing amelide and nitrate of silver.

The four substances which we have just now considered stand evidently in very definite relation to each other. No melamine is obtained by treating the crude and impure melam simply with boiling water; melamine seems, therefore, to be produced by the action of caustic potass upon melam. If we add to one atom of melam the elements of two atoms of water, we have exactly the elements of one atom of melamine and one atom of ameline—



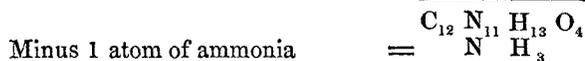
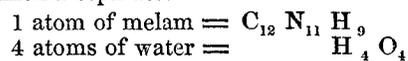
According to this it would appear as if melamine and ameline are formed from melam, without any evolution of ammonia, and yet evolution of ammonia is invariably observed upon the solution of the crude and impure melam in caustic potass, and this evolution of ammonia increases in amount proportionally to the concentration of the potass lye employed. It is highly probable that part of this ammonia owes its origin to the decomposition of melamine, since this substance is easily convertible into ameline and ammonia. I stated that melamine comports itself to acids, like a base. If to a boiling and saturated solution of melamine in water, dilute hydrochloric acid, nitric acid, or sulphuric acid, be added, and the fluid then allowed to cool, it solidifies, forming a mass of crystalline needles of hydrochlorate, nitrate, or sul-

phate of melamine. But upon dissolving melamine at a high temperature, in moderately concentrated hydrochloric acid, this substance disappears completely, and the hydrochloric solution contains ameline and ammonia instead. This decomposition is readily explained: two atoms of water join the elements of one atom of melamine, whilst, on the other hand, the elements of one atom of ammonia separate



There remains 1 atom of ameline  $C_6 N_5 H_5 O_2$

It is doubtless owing to this decomposition that the crude and impure melam, when treated with concentrated hydrochloric acid, in the same manner as melamine, yields as the principal product of the ensuing decomposition, simply ameline; one atom of melam and four atoms of water yield two atoms of ameline, whilst one atom of ammonia separates

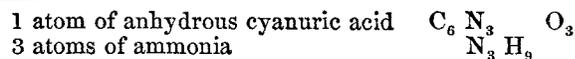


There remain 2 atoms of ameline }  
= 2 (C<sub>6</sub> N<sub>5</sub> H<sub>5</sub> O<sub>2</sub>) ..... } = C<sub>12</sub> N<sub>10</sub> H<sub>10</sub> O<sub>4</sub>

I have already told you that melam, as well as melamine and ameline, is convertible into amelide; it is this last substance which, upon being boiled with any dilute acid, or with an alkali, yields cyanuric acid, with absorption of water and evolution of ammonia.

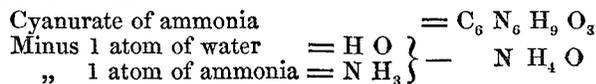
All these substances (melam, melamine, ameline, and amelide) yield, upon being submitted to dry distillation, ammonia and hydrated cyanuric acid, leaving a yellow residue, which, upon the application of a red heat, affords cyanogen gas and nitrogen gas. Therefore, to judge from the mode of their formation, as well as from the results of their decomposition by dry distillation, we may consider them as mellon compounds.

With respect to their department with acids and alkalies, and their transformation into cyanuric acid, we may assume that every one of these four compounds corresponds to a cyanurate of ammonia from which the elements of water have separated. Let us subtract three atoms of water from the elements of an hypothetical anhydrous tribasic cyanurate of ammonia, and there remains melamine.



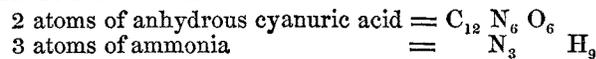
There remains melamine = C<sub>6</sub> N<sub>6</sub> H<sub>6</sub>

If we take the same cyanurate of ammonia and subtract from it one atom of water and one atom of ammonia, there remain the elements of ameline.



There remains 1 atom of ameline = C<sub>6</sub> N<sub>5</sub> H<sub>5</sub> O<sub>2</sub>

Amelide may be considered as a combination of two atoms of cyanuric acid with three atoms of ammonia.



1 atom of amelide = C<sub>12</sub> N<sub>9</sub> O<sub>6</sub> H<sub>9</sub>

This view of the composition of these substances—viz., assuming them to be cyanurates of ammonia, from which the elements of water (or, as would be the case with ameline, the elements of water and ammonia) have separated, points out very clearly and positively the relations which these substances bear to cyanuric acid, and accordingly it did not seem by any means improbable, but that one or the other of these substances might be formed artificially from cyanuric acid and ammonia. Experiments made with this view have indeed shewn that in the distillation of urea a substance is formed which bears the closest resemblance to amelide, and thus it has been proved that there exists a compound which may be said to intervene between amelide and cyanuric acid.

The further consideration of this subject we must, however, defer until the next lecture.