

June 16, 1870.

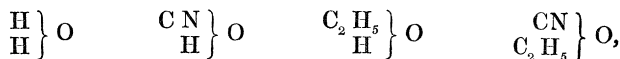
General Sir EDWARD SABINE, K.C.B., President, in the Chair.

Dr. E. H. Greenhow, Dr. J. Jago, Prof. N. S. Maskelyne, the Rev. Dr. Parkinson, Capt. R. M. Parsons, Dr. W. H. Ransom, Mr. R. H. Scott, Dr. A. Voelcker, and Dr. S. Wilks were admitted into the Society.

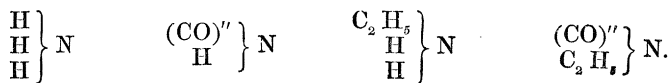
The following communications were read :—

I. "On Compounds Isomeric with the Cyanuric Ethers." By A. W. HOFMANN and OTTO OLSHAUSEN. Received April 29, 1870.

Some time ago M. Cloëz* described a remarkable body, which has the composition but none of the properties of ethylic cyanurate. This substance, which he called *cyanetholine*, is distinguished from cyanuric ether by its behaviour with alkalis, which, according to the observations of Cloëz, evolve from it ammonia and not ethylamine. Cyanetholine, according to Cloëz, combines with acids, forming crystallizable salts, none of which, however, up to the present time, has been more carefully investigated. It is rather strange how little the attention of chemists has been directed to this interesting compound. M. Cloëz contented himself with the discovery of cyanetholine and establishing its composition, but has not again reverted to the subject. Of the researches of other chemists who have touched upon cyanetholine, the only ones known to us are the few but rather important experiments of M. Gal†. According to his observations, cyanetholine is changed by treatment with potash solution into potassium cyanide and alcohol, and by the action of hydrochloric acid into cyanuric acid and ethylic chloride; and Gal and Cloëz, in consequence of these reactions, are of opinion that cyanetholine is the true ether of cyanuric acid constructed upon the water type—



whilst the earlier known ethylic cyanate of M. Würtz corresponds to the ammonia type—



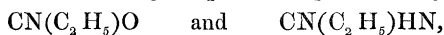
It need scarcely be mentioned how completely this view has been confirmed by the subsequent discovery of the isonitriles and of the series of mustard oils isomeric with the sulphocyanic ethers.

The formation of cyanetholine, which, as is known, is obtained by the action of chloride of cyanogen on sodium ethylate, proves a close connexion

* Compt. Rend. xliv. p. 482, and Ann. Chem. Pharm. cii. p. 354.

† Compt. Rend. lxi. p. 527, and Ann. Chem. Pharm. cxxxvii. p. 127.

between this body and the ethylecyanamide, discovered by Messrs. Cahours and Cloëz*, which is formed by treating ethylamine with chloride of cyanogen. The same reagent acting on ethylated water and ethylated ammonia causes in the one case the formation of ethylic cyanate, and in the other that of ethylecyanamide. The close analogy between cyanetholine and ethylecyanamide, which is, perhaps, best represented by the formulæ



cannot possibly be doubted, and accordingly the easy polymerization of ethylecyanamide, which is readily converted into triethylmelamine, naturally raised the question as to whether cyanetholine could not be polymerized in a similar manner; in other words, whether there might not exist a series of combinations isomeric with the known cyanuric ethers.

The experiments undertaken for the solution of this question have been performed in the methyl-, ethyl-, amyl-, and phenyl-series.

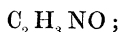
We begin the communication of our observations by a description of the experiments made in the methyl-series; for although in the first instance we had worked in the ethyl-series, it was the investigation of the methylic compounds which yielded at once results that could not be mistaken.

Experiments in the Methyl-series.

When a stream of gaseous chloride of cyanogen is passed through a dilute solution of sodium methylate in methylic alcohol (we have generally dissolved 20 grms. of sodium in about 400 grms. of anhydrous methylic alcohol), a considerable quantity of common salt is separated. If the current of gas be continued until the solution smells of chloride of cyanogen, and the excess of methyl alcohol then distilled off, a brown oil remains behind, similar to that which Cloëz obtained by the corresponding experiment in the ethyl-series, and which he described as cyanetholine. This oil sometimes remains fluid for a long time, but generally solidifies on standing. Frequently, however, little or no oil is formed, and when the methyl alcohol is distilled off, there remains a residue which solidifies to a brown crystalline mass. The purification of this substance offers no difficulties; one or two crystallizations from boiling water, in which it is easily soluble, whilst it dissolves but slightly in cold water, and a final treatment with animal charcoal remove the colour. But these crystals, though perfectly colourless, prove, under the microscope, to be a mixture of two compounds, of which the one, crystallizing in fine needles, is the more easily soluble, whilst the other, consisting of rhombic tables, dissolves with greater difficulty. If an intermediate mixed product be sacrificed, they may, by repeated crystallizations from boiling water, be both obtained in a pure state. They are, however, better separated by the extraordinary difference of their solubility in ether, which dissolves the needles and leaves the rhombic tables behind.

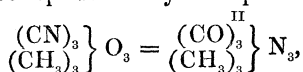
* Ann. Chem. Pharm. xc. p. 91.

Methylic Cyanurate.—When the ether which has been poured off the crystals is evaporated, a crystalline mass is left, which may be recrystallized from alcohol, or, better, from hot water. The needles thus obtained possess the characters of a pure substance. Determination of the carbon, hydrogen, and nitrogen, the latter of which can easily be weighed as ammonia, yields as the simplest atomic expression for this body the formula

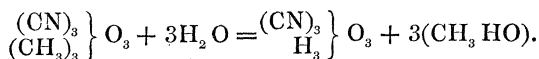


but it only required a somewhat closer examination to prove that this is not the methylic cyanate but the methylic cyanurate, not the monomolecular but the trimolecular combination. The melting-point of the crystals is 132° , the boiling-point (we were only in possession of a moderate quantity) between 160° and 170° . These properties unmistakably characterize the trimolecular compound, the cyanurate.

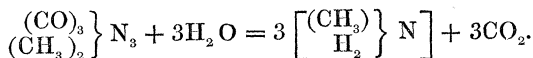
It would have, nevertheless, been desirable experimentally to confirm these indications by the vapour-density determination; but this was prevented by a peculiar comportment of the new body, which, however, furnished evidence almost as conclusive as the vapour-density for the molecular weight of the compound. When the new cyanurate is heated in a retort, it distils without leaving an appreciable residue, the distillate solidifying to a white crystalline mass. But these crystals are no longer the unchanged body; their melting-point has risen from 132° to 175° , and their crystalline form is entirely changed; in the place of fine needles we have now short, thick prisms with sharply defined summits. It is easily perceived that the new cyanuric ether, by an atomic migration within the molecule, which may be represented by the equation



has become converted into the long known ether. If the careful investigation of the physical properties were not deemed sufficient proof of this transformation, it would suffice to compare the reactions of the body *before* and *after* distillation. Before being distilled, it yields cyanuric acid and methyl alcohol when heated with potash,—



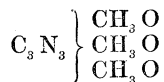
If submitted to the same treatment after distillation, methylamine and carbonic acid are obtained,—



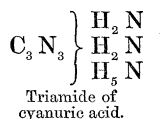
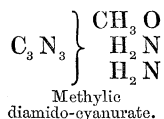
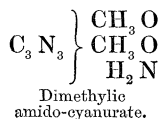
These experiments are sufficient to establish the nature of the new cyanuric ether. In order to obtain further data as to the constitution of this body, the changes which it undergoes by the action of ammonia had to be examined.

Whilst the ether of a monobasic acid, when treated with ammonia gas,

by an interchange of the primary alcohol fragment with the primary ammonia fragment, is directly converted into the amide, whilst, on the other hand, the ether of a bibasic acid yields, in the first instance, the ether of an amidic acid, the production of the true amide of a tribasic acid must necessarily be preceded by the formation of the ethers of a first and of a second amidic acid. According to this view, the action of ammonia on the methylic cyanurate



may be expected to give rise to the formation of the following bodies :—

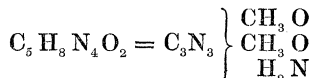


not to speak of the possibility of alcohol fragments being simultaneously exchanged for water fragments.

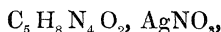
Hitherto we have met only with one of the above-mentioned bodies, viz. :—

Dimethylic Amido-cyanurate.—This compound is formed by the action of ammonia on the new methylic cyanurate; but it is not easy to obtain it pure by this means, as the reaction generally goes further, and a mixture of substances is produced, the separation of which we have not hitherto been able to effect. The compound in question, however, is always formed in larger or smaller quantity as a by-product in the preparation of the trimethylic cyanurate; it is, in fact, the substance insoluble in ether mentioned above, and as no other product is formed but these two bodies, it is easy to obtain the dimethylated amidic acid in a pure state.

The new compound crystallizes from hot water in fine rhombic tables, odourless and tasteless, and melting at 212° . It is much more difficultly soluble in cold water than the cyanuric ether, soluble with difficulty in cold alcohol, more easily in hot, almost insoluble in cold ether. The composition



was established by a determination of the carbon, hydrogen, and nitrogen, and also by the analysis of a silver-salt,



which, crystallizing in fine needles, is obtained by adding silver nitrate to the nitric solution of the amido-ether and recrystallization of the precipitate.

By treatment with aqueous ammonia in sealed tubes, the same products are obtained as are furnished by the original ether when submitted to the

action of ammonia. They have not yet been investigated, but it has been ascertained that methyl alcohol is liberated, as might have been expected.

Finally, as regards the formation of the amido-ether by the action of chloride of cyanogen upon sodium methylate, this is obviously due to the presence of traces of water, which could scarcely be avoided in this process. Water causes first the formation of hydrochloric and cyanic acids, the latter of which splits up into carbonic acid and ammonia; ammonia and methylic cyanurate coming together in the nascent state form methyl alcohol and the amido-ether.

In fact the common salt which separates during the reaction contains a considerable quantity of cyanate and carbonate.

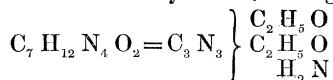
Experiments in the Ethyl-series.

Our first experiments were conducted in this series, and we have actually worked more in it than in the methyl group. We have, however, not yet been able to obtain the ethylic cyanurate in a pure state; on the other hand, we have succeeded in obtaining the ethers of both amidic acids.

The action of chloride of cyanogen upon sodium ethylate present the same phenomena as the analogous treatment of the methylate, and which moreover have been well described by M. Cloëz. We have sometimes obtained at once a solid body; but generally there is formed an oil, which after some time deposits crystals, the quantity of which in different operations varies exceedingly. The idea naturally suggested itself that they were the trimolecular modification of cyanetholine; but analysis showed that these crystals, in spite of their beauty, were but a mixture containing the desired cyanurate, when at all, only in small quantity. They contain, as numerous analyses have proved, the ethylic ethers of the two amidic acids, the separation of which has cost indeed very considerable trouble.

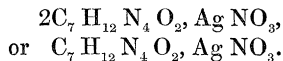
Diethylic Amido-cyanurate.—By treatment with animal charcoal and numerous recrystallizations of considerable quantities of the crystals obtained from the crude cyanetholine, we succeeded in obtaining thin white prismatic crystals melting at 97° ; this melting-point remained unchanged after several recrystallizations from water, a sign of the purity of the substance. The same body was obtained when crude cyanetholine was heated for some hours with aqueous ammonia in a sealed tube. The digestion, however, must not be carried too far, as then other products are formed, amongst these an amorphous substance quite insoluble in water.

The analysis of the crystals, which are soluble both in alcohol and ether, especially when warm, has proved them to be the ethylic compound corresponding to amido-ether of the methyl series, having the composition



The diethylic amido-cyanurate combines in two proportions with silver

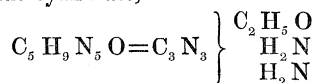
nitrate. According as the substance dissolved in nitric acid or the silver nitrate is in excess, we obtain the compounds—



Both salts crystallize in needles; the latter can be recrystallized from boiling water without appreciable change, but the former is decomposed, being converted into the second salt.

Ethylic diamido-cyanurate.—White crystals were deposited from a solution of the above-described but not fully purified compound, which had been standing for a long time with concentrated solution of ammonia.

These melted between 190° and 200° , and were much more difficultly soluble in alcohol. Numbers were obtained by the analysis of these crystals (carbon, hydrogen, and nitrogen determinations) which indicated it to be the ethylic diamido-cyanurate,—



This compound also, when dissolved in nitric acid, gives fine crystalline needles on the addition of silver nitrate. These, however, have not yet been analyzed.

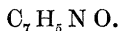
Experiments in the Amyl-series.

Up to the present time we have only worked qualitatively in this series. The product of the action of chloride of cyanogen on sodium amylate is oily; it distils at about 200° , but not, as it would appear, without being thoroughly altered. The last portions of the distillate solidify to a mass of white lustrous crystals, which can easily be obtained pure by solution and recrystallization. We are inclined to consider this substance as amylic cyanurate, but at present we have no numbers to confirm this opinion.

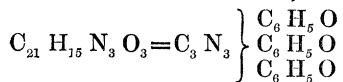
Experiments in the Phenyl-series.

Lastly, we may here mention some experiments which were made in the phenyl-series. Chloride of cyanogen acts with the same energy upon sodium phenylate (which in this case was dissolved in absolute alcohol) as on the other sodium compounds. The solution poured off from the common salt which had separated gave, on the addition of water, an oil heavier than water, which was submitted to distillation. What first came over was almost pure phenol; the distillation was interrupted as soon as a drop of the residue solidified to a crystalline mass. The residue in the retort was then mixed with cold alcohol, thrown on a filter and washed for some time with the same liquid. The white crystalline mass thus obtained was then recrystallized from a very large quantity of boiling alcohol. When the solution was allowed to cool slowly, long thin needles separated which were almost insoluble in alcohol and ether, but were found to dissolve, though sparingly, in benzol.

The analysis of these crystals leads to the formula



But from their formation as well as their general properties we are convinced that they are the trimolecular combination, the phenylic cyanurate,



which corresponds to the methyl compound described in the beginning of this note.

The melting-point of the crystals was found to be 224° , somewhat lower than that of the isomeric compound (264°) which one of us* has lately examined.

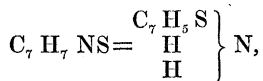
The latter, which must now be regarded as the phenylic isocyanurate, is easily distinguished from the new cyanurate, both by its crystalline form and behaviour with solvents. It has yet to be determined whether the phenyl compound, like the methyl one, is changed under the influence of heat into the cyanurate already known.

We cannot close this communication without thanking Messrs. R. Bensemann and K. Sarnow for the assistance they have rendered us in carrying out these experiments.

II. "Contributions towards the History of Thiobenzamide."

By A. W. HOFMANN, LL.D., F.R.S. Received May 27, 1870.

When a stream of sulphuretted hydrogen is passed through a solution of benzonitrile in alcoholic ammonia, the liquid, after the lapse of a few hours, deposits fine yellow needles, which are the thiobenzamide,



discovered by M. Cahours. It can be obtained in a pure state by recrystallization from boiling water.

When a cold saturated alcoholic solution of this body is mixed with an alcoholic solution of iodine, the latter is immediately decolorized with separation of sulphur. If the addition of iodine solution be continued until even after a short boiling free iodine remains, which can readily be detected by starch-paste, the solution filtered from the sulphur, and poured into water, solidifies to a mass of white interlaced needles, which can readily be freed from adhering hydriodic acid by washing with cold water.

This substance can be obtained pure by repeated crystallization from boiling alcohol. In this state it forms long shining snow-white needles, which melt at 90° , and distil without decomposition at a very high temperature. The compound also dissolves in ether, chloroform, and benzol. At first I believed it to be free from sulphur. Its alcoholic solution can be

* Hofmann, *Berichte der Chem. Gesellsch. z. Berlin*, III. 268.