

Citation:

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Chemistry. — “*On nitrogen (or nitrilo)-trimethylnitraminomethylene*”.

By Prof. A. P. N. FRANCHIMONT.

(Communicated in the meeting of October 29, 1910).

Many times I have pointed out the analogy, and also the difference in behaviour between hydrogen cyanide and methylnitramine. The analogy renders it probable that the nitramine reacts as $\text{CH}_3 \cdot \text{NH} \cdot \text{NO}_2$. The following is a striking instance.

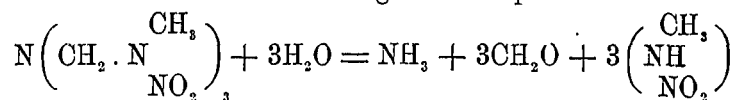
ESCHWEILER has allowed hydrogen cyanide in aqueous solution to act on hexamethylenetetramine (urotropine) and on using six mols. of CNH for one of urotropine, he obtained iminodiacetonitrile. He advises the addition now and then of a little hydrochloric acid to neutralise the ammonia which is also formed and yields brown coloured products with the hydrogen cyanide. On using a larger quantity of hydrochloric acid he obtained nitrogen-triacetonitrile.

If methylnitramine and urotropine in aqueous solution are allowed to react on each other in the same proportion nothing happens apparently, but, on warming, formaldehyde is at once liberated. If the solution is exposed to the air (not in a desiccator over sulphuric acid) there are formed after some time splendid pillar-shaped crystals melting at 116° . If these are removed when they no longer increase but actually seem to be disappearing and are then pressed dry, or recrystallised from boiling chloroform, which is the best solvent, their

analysis agrees with the formula $\text{N} \left(\text{CH}_2 \cdot \text{N} \begin{array}{c} \text{CH}_3 \\ \text{NO}_2 \end{array} \right)_3$ which is nitrogen

(or nitrilo)-trimethylnitraminomethylene.

This formula is confirmed by a molecular weight determination and by determining the products of decomposition by acids and alkalis which are formed according to the equation.



On boiling with solution of barium hydroxide barium methylnitramine could be obtained, but the two other decomposition products could not be isolated quantitatively, as a portion of the formaldehyde and the ammonia recombined to form urotropine, which is not decomposed by the alkali. On boiling with dilute sulphuric acid the formaldehyde could be distilled off and determined as such while the methylnitramine is decomposed into methylalcohol and nitrous oxide, which latter was measured; the ammonia is retained by the acid from which it is afterwards liberated by alkali and collected in standard acid.

The result of these three determinations agrees with the formula and the above equation of decomposition.

The yield, however, was very bad and, therefore, it was endeavoured in the first place not only to effect an improvement, but also to gain an insight into the progressive change of the reaction.

It appeared that the addition of hydrochloric acid, at least if care was taken to avoid an excess, caused each time the formation of the nitrilo-derivative, provided the product formed was removed each day before the addition of a little more acid; in this manner the yield finally amounted to about 70%.

If one took less than six mols. of nitramine for one of urotropine, the latter crystallised from the solution. If eight mols. were taken a little more of the nitrilo-derivative was formed but only a trifling amount. If the solution is placed in a desiccator over sulphuric acid crystals of ammonium sulphate are noticed on the wall of the desiccator when this has been moistened with sulphuric acid; the liquid has an odour of ammonia, although it is acid to litmus, but yields no nitrilo-derivative.

When urotropine and methylnitramine are mixed in the dry state, the mixture, after a few moments, turns liquid and becomes very cold but nothing further takes place; on addition of water, however, a little separation of crystals may sometimes occur.

Obviously, urotropine in aqueous solution is decomposed by the feebly acid methylnitramine, but the compound of nitramine with ammonia is strongly hydrolysed in water and, therefore, the addition of a little hydrochloric acid to fix the ammonia promotes the formation of the nitrilo-derivative, which is decomposed by ammonia in aqueous solution, in which the latter acts as a base.

The nitrilo-derivative which is not soluble in water is, however, decomposed by water after some time, and the products of decomposition pass into solution which has a distinct odour of formaldehyde. If that solution is allowed to evaporate spontaneously, the nitrilo-derivative is reformed when the three components are present in the exact proportion.

As in the decomposition of urotropine, four mols. of ammonia are formed for six mols. of formaldehyde, two more than required, I therefore added to the urotropine solution another six mols. of formaldehyde and twelve mols. of nitramine. After half an hour, the nitrilo-derivative commenced to crystallise and after 24 hours 94% of the theoretical yield was already obtained; further crystals were obtained from the mother liquor, so that the final yield was a quantitative one.

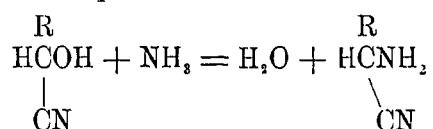
A still simpler procedure was to add to commercial formaldehyde solution as much ammonia as corresponded with one mol. to three mols. of formaldehyde, to cool the solution in water and then to add three mols. of nitramine which caused a strong cooling. A quarter of an hour after the liquid had been brought to the ordinary temperature by warming with the hand crystallisation set in. The yield, in this case, was also a quantitative one.

The reaction is, therefore, analogous to the one which I communicated in 1897 for piperidinomethyl alcohol with methylnitramine and to which I have recently added another viz. piperazine formaldehyde and methylnitramine. Like some other aldehydes, formaldehyde yields with ammonia and some amines amino-alcohols 1.1 which behave like bases and on which methylnitramine acts as an acid, so that a kind of salt (or ester) is produced with formation of water. These compounds are all decomposed by water, owing to hydrolysis.

The reaction of methylnitramine is quite analogous to that of hydrogen cyanide; the aminonitriles 1.1, however, are very permanent, because in them the carbon is linked to carbon, as in the case of the esters of hydrogen cyanide.

Usually, however, the aminonitriles are prepared from the oxynitriles 1.1. with ammonia or amines; this has not been found to apply to the nitramines for attempts to obtain compounds of aldehydes with nitramines have proved unsuccessful up to now.

It appears to me, however, that one goes too far when looking on the process of the formation of aminonitriles, -- as often happens -- as represented by the equation



as if a double decomposition between the oxynitrile and the ammonia, with formation of water, took place. For, if we wish to consider the oxynitriles 1.1. (cyanhydrins) as alcohols, that reaction with ammonia in aqueous solution is very strange and hardly probable. The acid character of the OH-group of the cyanhydrins must have been strengthened by the adjacency of the cyano-group, so that they may be rather looked upon as feeble acids. One might then expect the formation of an ammonium salt which will be strongly hydrolysed or dissociated in water, but not so much the elimination of water and the formation of an amide-like substance in the aqueous solution.

If we consider, however, that the cyanhydrins, like their analogous halogen compounds, are readily decomposed by bases with loss of hydrogen cyanide and formation of the aldehyde, and that ammonia, not only in aqueous solution reacts as a base, but even without the presence of water can, like amines, abstract the acid, the reaction of ammonia (and amines) on the cyanhydrins may be reduced to that of hydrogen cyanide on the amino alcohols 1.1.

The equation then certainly indicates the endproducts, but the progressive change of the reaction, considering the properties of the substances, would be that NH_3 removes CNH from the cyanhydrins to form ammonium cyanide, which is for the greater part hydrolysed, while with NH_3 the liberated aldehyde yields the amino alcohol, which then reacts with CNH .

Geophysics. — “On the application of DARWIN’S method to some compound tides.” By M. H. VAN BERESTEYN. (Communicated by Dr. J. P. VAN DER STOK).

(Communicated in the meeting of October 29, 1910).

Sir G. H. DARWIN has given a method for reduction of tidal observations, which in the case of 24 hourly daily observations has been fully described in his “Scientific Papers” Vol. I, p.p. 216—257.

Briefly the method consists of evaluating a special hour corresponding to 12^h m. s. time of any day; taking the speed of the tide equal to $15^\circ p$ ($p = 1.2 \dots$) for the hours 12...0 and 12...23; summing the observations arranged under the same special hour; then by harmonic analysis from those sums (24) both components of the tide can be found.

It appears from the table on p. 241 l. c. that this method is also applied to the compound tides MS , $2SM$, and $2MS$. As no mention has been made of disturbing influences, which these tides may undergo from others, it is of some importance to show, that these tides, when calculated after DARWIN’S method, need a correction. Moreover as may appear from what follows, the two combining tides M_2, M_4 are in the same manner influenced resp. by MS , $2SM$ and $2MS$.

Suppose the speed per m. s. hour of a tide to be $= p.\sigma$.

Then the speed of a compound tide (R_1, ξ_{r1}) consisting of one of the tides of this series and one of the S series. ($S_{2.4.6}$) is generally:

$$\begin{aligned} \sigma_1 &= p\sigma + 15^\circ q \\ (p &= \pm 1 \pm 2 \dots \\ q &= \pm 1 \pm 2 \dots) \end{aligned}$$