

Citation:

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$$pv_{A_0} = 1 - B_{A_0} - C_{A_0} + \frac{B_{A_0}}{v_{A_0}} + \frac{C_{A_0}}{v_{A_0}^2}$$

And seeing on the other hand that the densities attained are not sufficiently great to allow of the calculation of the last coefficients, values of E_A and F_A and sometimes too of D_A (insofar as they had to be allowed for) were obtained by combining the critical constants published a short time ago with the set of reduced virial coefficients VII. 1. Solutions for the other coefficients were then obtained for each isotherm from a number of suitable chosen points, and were tested with the observed results. Finally, correspondence was made as satisfactory as possible either by least squares or by the method of E. F. VAN DE SANDE BAKHUYZEN¹⁾.

In this way the individual coefficients for each isotherm given in table II were obtained. Numbers borrowed from the reduced coefficients VII. 1., are printed in italics.

With these coefficients values of pv_A were calculated; table III gives percentage deviations of calculated results from observed ones. In this table [] and ' have the same significance as before. Deviations placed between () are so treated because the observations to which they belong were not used in the adjustment of coefficients; this was done from consideration of the difficulty of obtaining agreement with a formula of whose constants only three are derived from observations in that neighbourhood.

Chemistry. — "*On the reaction products of potassium isocyanate and diaminoacetone hydrochloride. Amino- and ureopropylene-ureine.*" By Prof. A. P. N. FRANCHIMONT and Dr. J. V. DUBSKY.

(Communicated in the meeting of November 26, 1910).

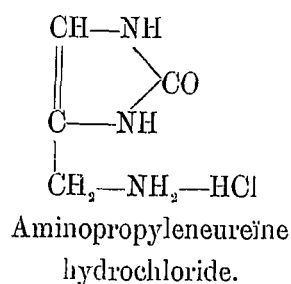
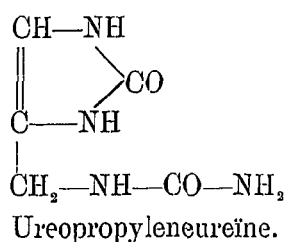
More than three years ago (February 23 1907) I called attention to the importance which the knowledge of acetoneureine would have in answering the question as to the action of nitric acid on heterocyclic compounds consisting of two CO-, two NH- and two CH₂ groups. Of the eleven theoretically possible isomers, there are two which are urea derivatives, namely hydro-uracil and acetoneureine. The first has been investigated as to its behaviour with nitric acid by myself and FRIEDMANN, the second has not been obtained as yet.

¹⁾ Proc. July 1906, Comm. No. 95a.

Attempts with Dr. FRIEDMANN to prepare it from diaminoacetone hydrochloride, although not having led to the desired result, still showed that a substance obtained by RÜGHEIMER in 1892 by the action of chloroformic ester on diaminoacetone and which he supposed to be acetone-ureine, although no analysis of it was made, can have been nothing else than acetonediuurethane.

We have now continued these investigations and have succeeded in elucidating the reaction with potassium isocyanate, although this also has not led to the desired result. RÜGHEIMER had pretended in 1892 that a *diureo-acetone* would form which, however, was so unstable that he could not isolate the same and that it was converted at the ordinary temperature with loss of ammonia into a substance which he called *acetonylbiiuret*¹⁾, in which he determined the carbon and hydrogen but not the nitrogen; at least he does not give the percentage. Had he done so, he would probably have found that it possesses quite a different composition, not $C_5H_7O_3N_3$ as he states, but $C_5H_8O_2N_4$ which we have found for the compound formed by the action of two mols. of potassium isocyanate on one mol. of diaminoacetone hydrochloride in aqueous solution. By the action of one mol. of isocyanate, a chlorinated substance, having the composition $C_4H_8ON_3Cl$, is formed, which on being treated with a second mol. of isocyanate, yields the first product. In consequence of the analogy with a number of other well-known reactions we take it for granted that as soon as a ureo-group has formed, this acts with its NH_2 -group on the CO of the acetone residue, when a cyclic compound is generated with formation of water.

The following formulae will have to be assigned to the two compounds obtained; although other ones might be proposed, they are amply confirmed by the derivatives obtained.



1) To which he assigned the formula

$$\begin{array}{c}
 \text{CH}_2, \text{NH}, \text{CO} \\
 \diagdown \quad \diagup \\
 \text{CO} \quad \text{NH} \\
 \diagup \quad \diagdown \\
 \text{CH}_2, \text{NH}, \text{CO}
 \end{array}$$

The name chosen is in agreement with the one formerly used by myself and others.

Aminopropylencureïne hydrochloride which, as already stated, is obtained from one mol. of potassium isocyanate and one mol. of diaminoacetone hydrochloride in aqueous solution crystallises in beautiful small needles which are very soluble in water. Up to the present we have not isolated from it the free aminopropyleneureïne but have prepared a few of its compounds with other acids and also a number of other derivatives.

With the calculated amount of silver nitrate in aqueous solution, in the cold, the *nitric compound* was formed which may be precipitated by addition of alcohol; this also forms beautiful small needles.

The *acid sulphuric compound* was obtained by treating the hydrochloride, in the cold, with sulphuric acid and removing the hydrogen chloride in a vacuum and freeing the residue from the excess of acid by means of alcohol and ether. The *neutral sulphuric compound* was prepared from lead isocyanate and diaminoacetone sulphate and was purified by precipitation with alcohol.

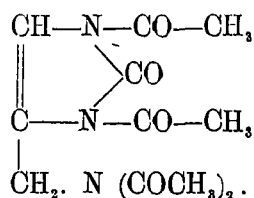
The four compounds, which have all been analysed, form delicate colourless small needles, which have no real melting point, but are decomposed on heating at various temperatures.

When boiled with acetic anhydride and sodium acetate for five minutes the hydrochloride yielded a *triacetyl derivative*, which if recrystallised from benzene forms small delicate needles melting at 141°.

On further boiling, a *tetracetyl derivative* was obtained, which crystallised from alcohol containing a little acetic acid in small, beautiful, square plates melting at 163°—164°.

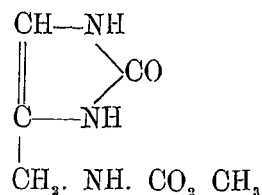
The composition of these acetyl derivatives is derived from the results of the elementary analysis, because acetyl determinations, even those according to PERKIN, did not yield good results.

The composition of the tetracetyl compound in which, presumably, two acetyl groups have entered into the NH_2 group, and two into the NH groups of the ureïne, and which then has this formula :



is a peculiar one.

With methyl chloro-formate and sodium carbonate in aqueous solution, aminopropylene ureine hydrochloride yields a *carboxymethyl derivative* (a urethane), which, when recrystallised from alcohol, forms glittering leaflets, which melt at 238° with decomposition. From this was



prepared, by five minutes boiling with acetic anhydride, a *monoacetyl derivative* which crystallises from ethyl acetate in splendid needles, melts at 215°, and is decomposed when heated a trifle above that temperature.

A *diacetyl derivative* was obtained by boiling for an hour with acetic anhydride; this yields also splendid needles and melts at 125°—126°.

The two acetyl groups will, therefore, most probably be attached to the nitrogen atoms of the ureine, and no acetyl has arrived at the urethane function.

The corresponding *carboacetyl derivative* was also prepared; this crystallises from boiling alcohol in small very glittering crystals melting at 208°. In the same manner as in the case of carboxymethyl derivative, a *monoacetyl compound* was obtained therefrom, which crystallises from acetic acid in beautiful, silky needles, melting at 218°—219°, and also a *diacetyl compound*, melting at 101°—102°.

Ureopropyleneureine was obtained, not only from diaminoacetone hydrochloride with two mols. of potassium isocyanate in aqueous solution, but also from aminopropyleneureine hydrochloride with one mol. of isocyanate. When crystallised from boiling water (it is but little soluble in cold water), it forms snow-white leaflets, which have no melting point, but are decomposed with change of colour at a little over 220°. It is soluble without decomposition in boiling acetic acid, and in this solvent the molecular weight was determined.

In aqueous solutions it gives no precipitates with silver nitrate and mercuric chloride unless ammonia is added, but it is precipitated by mercuric nitrate and therefore, behaves in this respect like urea.

On being boiled with acetic anhydride the bulk remained at first unaltered and it took ten hours to effect the change. The tetracetyl compound of aminopropyleneureine was thus obtained and recognised by its form and melting point: the urea residue has, therefore, been broken up.

Finally, it should be mentioned that diacetylaminacetone is also converted on prolonged boiling with an excess of acetic anhydride into tetracetyldiaminoacetone. When crystallised from boiling benzene, or from alcohol, it forms long, very lustrous needles which cake at 98° and melt at 103°.