

bromide at the temperature of boiling alcohol, viz.: methyl-, ethyl-, allyl-, phenyl-, diphenyl-, and acetyl-phenyl-thiocarbamides.

3. Thiocarbamide combines with tetrethylammonium bromide and iodide, and forms well-defined crystalline compounds of the type $(H_4N_2CS)_2Et_4NR'$. But no well-defined substance could be isolated under any of the experimental conditions containing more than 2 mols. of the amide and 1 mol. of the tetrethylammonium salt.

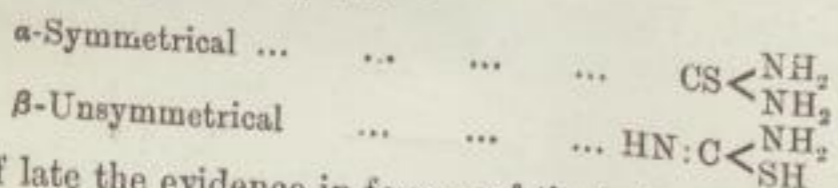
4. Thiocarbamide combines with diethylammonium bromide, and the well-crystallised compound $(H_4N_2CS)_3Et_2H_2NBr$ was separated. If a tetra-compound be formed in solution, it is certainly broken up on slow crystallisation.

5. Thiocarbamide also unites with triethylammonium bromide, and in presence of excess of amide a somewhat felted mass is obtained, which on recrystallisation affords two distinct crystals, namely, $(H_3N_2CS)_3Et_3HNBr$ and $(H_4N_2CS)_2Et_3HNBr$.

6. With methylammonium bromide, thiocarbamide afforded the compound $(H_4N_2CS)_4MeH_3NBr$, which resembles the corresponding ammonium bromide compound in appearance, but melts at a temperature 34° lower. On the other hand, with ethylammonium bromide no combination whatever could be effected, and when 4 : 1 mols. of the amide and salt were heated in a pressure tube with alcohol at 135° , ethyl oxide and tetrathiocarbamidammonium bromide were the products.

Bearing of the Results on the Question of the Constitution of Thiocarbamide.

Unless thiocarbamide is held to be a tautomeric substance, its constitution may be represented by either of the following formulæ, viz:—



Of late the evidence in favour of the latter constitution has been considerably strengthened, more especially by the careful work of Mr. Emil A. Werner carried on in my laboratory (see Trans., 1890, 57, 283). I shall now proceed to show that the facts recorded in the present paper supply evidence of a new kind, and altogether in favour of the β or unsymmetrical structure—at least under the conditions of my experiments.

The readiness with which ammonium bromide, iodide, and chloride form tolerably stable tetrathiocarbamide compounds—and only these—is evidently connected with the number of atoms of hydrogen in the ammonium haloid, that is, with the valency of its nitrogen. This necessarily involves the idea of something in the nature of substitution. Moreover, the tendency to form complete and comparatively simple compounds of the order in question must be strong, since we have seen that ethyl is displaced by hydrogen when ethylammonium bromide and 4 mols. of thiocarbamide are heated to 135° , the stable ammonium bromide compound being then formed.

The fact that none of the mono- or di-substituted thiocarbamides combine with ammonium bromide under the usual conditions goes far to prove that neither the carbon nor sulphur of thiocarbamide are concerned in the linkage with the ammonium haloid. It is admitted that alkylic or other radicles of substituted thiocarbamides of the types used are directly united with nitrogen; there is, therefore, no reason why the carbon or sulphur of the primary should be materially affected by such substitution. And further, in regard to sulphur, neither the di- nor tri-ethylammonium

bromide compounds formed with thiocarbamide afforded mercaptan or alkylic sulphide, or their products, when heated to 100° with alkalis and alkaline lead solution, in these particulars differing materially from the action of addition compounds of thiocarbamides of the sulphine class.

On the other hand, the loss of power of combination with ammonium bromide when but one atom of hydrogen in thiocarbamide is displaced by a more positive radicle, such as ethyl or phenyl, is inconsistent with the symmetrical constitution of thiocarbamide, which should still have an NH_2 group unaffected and available for union; but is quite consistent with its unsymmetrical structure.* In the latter case, the two nitrogen atoms are differently engaged, and the genesis of a monosubstituted thiocarbamide from $R \cdot N : CS$, and ammonia, points to the structure $R \cdot N : C < \begin{matrix} NH_2 \\ SH \end{matrix}$

rather than $HN : C < \begin{matrix} NHR \\ SH \end{matrix}$ for the product. Now the fact that combination takes place with facility between thiocarbamide and ammonium bromide, but not at all with ethyl- or phenyl-thiocarbamide, accords with the structure $RN : C < \begin{matrix} NH_2 \\ SH \end{matrix}$, where the presence of the positive radicle in the imidic group paralyses the power of combination, which appears in consequence to be exclusively due to the NH of the substance we have been accustomed to term thio-carbamide. The ammonium bromide compound would therefore become $[NH_2(SH)CNH_2]_4NBr$; but whether union is effected by breaking the double linkage of carbon and NH , or the change of valency of the latter, remains for determination.

In the ammonium bromide compound, the attraction of the components seems to be at a maximum; but whilst substitution in thiocarbamide reduces it to zero, similar substitution in ammonium bromide (save in the case of the ethylammonium salt†) only lessens the power of forming tetra-compounds without destroying it. These facts seem to point to the development of quinquavalence in one of the nitrogen atoms of thiocarbamide in the course of combination.

I think the true "thiocarbamide" is yet to be discovered, and that we must revert to the name "sulphurea" or "thiourea" as the correct designation of the primary substance from which the above compounds have been obtained.

BRUSSELS EXHIBITION.

The following is a list of the awards to the British exhibitors at the Brussels Exhibition:—

Grand Diploma of Honour to J. Pattison Gibson, Hexham.

Silver gilt medals to F. P. Cembrano, Richmond; Lyd. Sawyer, Newcastle-on-Tyne; Col. Waterhouse, Calcutta; Walter Colls, and Window and Grove, London.

Silver medals to Wilson and Son, Aberdeen; Werner and Son, Dublin; W. Clement Williams, Halifax.

Bronze medals to J. Carpenter, London; J. Martin Harding, Shrewsbury; Morgan and Kidd, London; W. Winter, Derby; York and Sons, London; J. Luders, Cape Town; J. W. Ross, Cape Town; A. Hendrey, Godmanchester.

* From a somewhat similar point of view, the production of a tetra- rather than a di-thiocarbamide compound is inconsistent with the symmetrical structure.

† Whose non-combination may be more apparent than real if formed and decomposed at nearly the same temperature level.