

- II. "Report of Researches on Silicon Compounds and their Derivatives. Part I." By J. EMERSON REYNOLDS, M.D., F.R.S., Professor of Chemistry, University of Dublin. Received September 27, 1888.

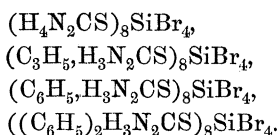
The present investigation was undertaken some years ago with a view to examine the action of the silicon haloids—but more especially of silicon tetrabromide—on various compounds containing nitrogen, as our knowledge of the relations of silicon and nitrogen is extremely limited.

It was ascertained at an early stage of the inquiry that the bromide of silicon is much superior to the chloride as a reagent with nitrogenised compounds, but since the bromide had apparently not been obtained in any quantity even by its discoverer, Serullas, considerable time had to be devoted to working out a method for the production of a sufficiently large supply of this material.

In the purification of the crude tetrabromide a new *chlorobromide** of silicon was discovered, which boils at 141° C. This proved to be the compound SiClBr_3 , which was required to complete the series of possible chlorobromides of silicon.

The first group of nitrogen compounds subjected to the action of silicon tetrabromide included the primary thiocarbamide or sulphur urea, obtained by the author in 1869, and the allyl-, phenyl-, and diphenyl-thiocarbamides.

All these are shown to unite with silicon tetrabromide and afford the highly condensed compounds—

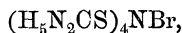


These are more or less vitreous solids, with the exception of the allylic compound, which is a transparent and singularly viscous liquid. All are dissolved and decomposed by water and by alcohol.

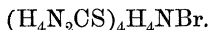
The action of alcohol on the compound $(\text{H}_4\text{N}_2\text{CS})_8\text{SiBr}_4$, was studied in detail, and it is shown that not only do ethyl bromide, thiocyanate, and diethylic silicate result, but that the representatives of two new classes of thiocarbamide derivatives are formed.

* The chlorine required for the production of this compound was derived from the crude bromine (which always contains chloride of bromine) used in preparing the tetrabromide.

The first of these is a beautiful *tetrathiocarbamide* compound, whose formula proved to be

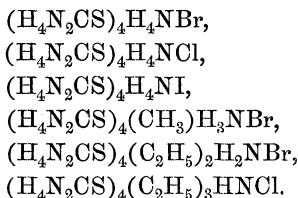


which may obviously be written

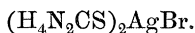


This body separates from alcohol in fine masses of crystals resembling sea anemones in appearance, which melt at $173-174^\circ$, and begin to decompose at $178-180^\circ$. The synthesis of this substance was effected by heating ammonium bromide with thiocarbamide.

Several homologues of the above *tetrathiocarbamidammonium bromide* were produced by synthetic methods; some of these contain chlorine or iodine instead of bromine. The following are examples of the compounds formed in the course of this part of the investigation:—



By the action of silver nitrate on the *tetrathiocarbamidammonium bromide* the crystalline *dithiocarbamide* compound with silver bromide was obtained—

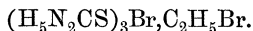


This was subsequently produced by the direct union of thiocarbamide with the pure silver haloid. The compound—



was also obtained in fine crystals, as were other similar substances.

A *trithiocarbamide* compound is also formed during the action of ethyl alcohol on $(\text{H}_4\text{N}_2\text{CS})_3\text{SiBr}_4$, but it is much more soluble than that which first separates. It is also crystalline, and its analysis and reactions lead to the formula—

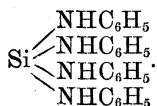


Hitherto only mono- and di-thiocarbamide derivatives have been known; but the results above stated in outline prove that tri- and tetra-thiocarbamide compounds are formed in presence of silicon tetrabromide and certain other agents, which latter form addition products with the condensed amide.

So far, cases were only dealt with in which silicon tetrabromide combined with nitrogenised groups without loss of its halogen. The next stage of the inquiry involved the investigation of certain interactions in which the tetrabromide loses *all* its halogen. One of the chief results obtained in that direction forms the subject of a separate communication which accompanies this Report.

III. "Preliminary Note on a Silico-organic Compound of a New Type." By J. EMERSON REYNOLDS, M.D., F.R.S., Professor of Chemistry, University of Dublin. Received September 27, 1888.

The subject of this note is a fine crystalline substance, and is the first well-defined compound yet known in which we have reason to believe that silicon is in direct and exclusive union with the nitrogen of amidic groups. Its analysis and mode of formation lead to the conclusion that it is *silicotetraphenylamide*,



This body is produced when silicon tetrabromide (or the tetrachloride) is added to excess of aniline, diluted with three or four volumes of benzene. Aniline hydrobromate (or hydrochlorate) is a secondary product of interaction and separates, being insoluble in benzene. If aniline be in excess throughout the operation, the whole of the halogen precipitates as aniline salt, and there remains in solution impure silicotetraphenylamide. If aniline be not in excess, a bromo-compound is obtained analogous to Harden's rather ill-defined chlorinated product.

Distillation from a water-bath readily removes benzene from the solution, and a liquid remains which solidifies after some time to a yellowish mass. The latter dissolves in warm carbon disulphide leaving a residue containing some thiocarbanilide, and cautious evaporation of the solution leads to the separation of magnificent crystals of the silicon compound. These form chiefly at the surface of the liquid, as they are specifically lighter than the solution.

When twice recrystallised from carbon disulphide, the substance is obtained in a state of purity.*

* A large quantity was prepared in June last, and about 50 grams of the pure compound were exhibited on September 11th, in Section B, during the meeting of the British Association at Bath.