XXI.—*Some Silicon Compounds and their Derivatives. I. The Action of Silicon Tetrabromide on Thiocarbamide.*

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ALTHOUGH a large number of silicon analogues of carbon compounds are known, it is remarkable that we do not find among them any well-defined representatives of cyanogen or its derivatives. This consideration led me some years ago to commence the investigation of reactions in which silicon and nitrogen take part. In the course of this work, a considerable number of new facts have been observed and reactions examined, especially those in which the silicon haloids and organic nitrogen compounds are concerned.

Several of the compounds obtained have been exhibited from time to time at meetings of the Royal Dublin Society, and those especially referred to in this communication were shown at the conversazione of the Royal Society in June last. These bodies were chiefly derived from compounds which include ammonia residues such as amines, amides, and amidic acids, thus the interesting work just published by Mr. Harden touches at one point (the action of a silicon chloride on aniline), that in which I have been engaged.

Early in the course of the general investigation, it was found that silicon tetrabromide is a more manageable reagent than the corresponding chloride. The former is much less volatile—boiling at 153°, the boiling point of the chloride being only 59°—and the bromide is not so rapidly decomposed by water.

Even with the bromide, some of the reactions above referred to are very complicated, particularly when oxygen is present; but the change which I propose to describe in the present paper is a tolerably simple one, and is that which takes place when silicon tetrabromide

acts on thiocarbamide, a substance which I obtained in the course of a former research (*J. Chem. Soc.*, 1869, **22**, 1).

I. *The Action of Silicon Tetrabromide on Thiocarbamide.*

When pure dry thiocarbamide in very fine powder is gently warmed with a solution of silicon tetrabromide in crystallisable benzene* combination takes place slowly. At first the particles of thiocarbamide adhere, and after some time a slightly yellowish semi-fused mass is obtained, which becomes a thick liquid at the temperature of the boiling benzene.

The composition of the product—which like thiocarbamide itself is scarcely soluble in benzene—was found by successive analyses to vary with the length of time during which the mixture was heated. The products contained the elements of silicon tetrabromide and thiocarbamide, and the proportion of the former to the amide rose until the ratio was reached of—

This ratio was not exceeded even when the amide was heated with a considerable excess of the bromide for several hours at the boiling point of the benzene mixture.

After several trials the following mode of operating was found to afford a satisfactory product when using comparatively large quantities of the materials.

100 grams of pure and perfectly dry thiocarbamide in very fine powder was added gradually and with frequent agitation to a mixture of 28 c.c. of silicon tetrabromide with 250 c.c. of crystallisable benzene contained in a flask. The volume of liquid is sufficient to form a thin cream when the powder is evenly diffused through it. The mixture, carefully protected from moisture, was allowed to stand over night, when slight action took place, and a partially coherent mass was obtained in the morning. The flask was now connected with a long reflux condenser, and heated on the water-bath nearly to the boiling point of benzene. The thiocarbamide became pasty† as combination proceeded, and could then be diffused through the hot liquid in droplets when the contents of the flask were agitated. Three hours' heating of the above quantities at the boiling point of benzene proved to be sufficient. At the end of the operation, the product subsided as a heavy, rather viscid mass, which gradually solidified on cooling.

The benzene poured off from the product had a somewhat alliaceous

* The benzene solution was found to act more regularly than the undiluted tetrabromide.

† The melting point of thiocarbamide is 149° , so that liquefaction in presence of tetrabromide of silicon takes place at a temperature 65° lower.

odour, and contained some silicon and bromine. The ratio of silicon to bromine in this residual solution was found to be—

therefore it contains the excess of tetrabromide left by the 100 grams of thiocarbamide, in addition to small quantities of secondary products. This residual benzene solution proved useful in future experiments.

The solid product obtained in such an operation was well washed with cold benzene, and then boiled with a fresh quantity for some time in order to remove excess of tetrabromide: when cold, it was rapidly broken up, again washed with benzene, and dried by a gentle heat: in all these operations, contact with moisture was carefully avoided.

The body which results from this treatment is, when freshly prepared, a somewhat translucent brittle substance without distinct crystalline structure. It is yellowish, and the colour deepens considerably on exposure to air owing to evident decomposition. It is readily decomposed by moisture, and gives off fumes of hydrobromic acid as well as a sulphuretted odour. It becomes pasty below 100° , but begins to decompose when the temperature is raised much above that point.

Good solvents of silicon tetrabromide, such as benzene, chloroform, carbon bisulphide, and ethyl bromide, failed to extract sensible quantities of silicon bromide from the compound in question. Thiocarbamide itself is not dissolved by any of the above-named liquids. On the other hand, solvents of thiocarbamide such as water and anhydrous alcohol, especially the latter, did not dissolve out the unchanged amide when the material was properly prepared, but the alcoholic solution contained derivatives of thiocarbamide and of silicon tetrabromide, which were in part due to the chemical action of the alcohol. These products will be again referred to. I may add that no solvent for the compound was found which did not at the same time obviously decompose it.

A portion of a freshly prepared specimen which had been very carefully washed with benzene, was dried and powdered for analysis. Care was taken to expose it as little as possible to the air during the treatment. It was found to contain the elements of thiocarbamide and of silicon bromide.

The following data were obtained :—

- I. 1.022 grams of substance gave 0.242 gram of N, = 23.67 per cent. of N = 64.24 per cent. of CSN_2H_4 .
- II. 1.001 grams gave 0.0634 of SiO_2 = 2.95 per cent. of Si = 36.66 per cent. of SiBr_4 .

And 1.96 gram $\text{BaSO}_4 = 63.96$ per cent. of CSN_2H_4 .

	Theory.		Experiment.	
	I.	II.	I.	II.
SiBr_4	348	36.41	—	36.66
$8(\text{CSN}_2\text{H}_4)$	608	63.59	64.24	63.96

The results agree fairly with the formula—

If this substance were a mixture of excess of thiocarbamide with a compound of the amide with silicon tetrabromide, it should be capable of taking up more of the bromide by continued action, but that was not found to be the case. Another preparation was made in which a larger excess of tetrabromide was used (as the fresh 27 c.c. of tetrabromide were dissolved in the benzene solution left from a former operation), and the mixture was finally heated to the boiling point of benzene for rather more than five and a half hours, or for nearly double the time given in the former operation. The product obtained was more yellowish and rather less translucent, but was found to contain a *less* proportion of silicon tetrabromide than before. In order to trace the cause of this difference, a more detailed analysis of the product was made than seemed necessary in the former case.

The following data were obtained :—

I.	1.312 grams	gave 0.0716 SiO_2 and 2.4128 BaSO_4 .
II.	1.0012	„ 1.8706 BaSO_4 .
III.	0.8099	„ 0.2044 N.
IV.	0.483	„ 0.1204 N.
V.	0.8966	„ 0.6833 AgBr.
VI.	0.5004	„ 0.2197 CO_2 .†

	Theory.		Experiment.					
	I.	II.	I.	II.	III.	IV.	V.	VI.
Si. . .	28	2.77	2.53	—	—	—	—	—
Br_4 ..	320	31.76	—	—	—	—	32.40	—
C_{10} . .	120	11.91	—	—	—	—	—	11.88
N_{18} . .	252	25.00	—	—	25.23	24.92	—	—
S_8 . . .	256	25.39	25.25	25.65	—	—	—	—
H_{32} ..	32	3.17	—	—	—	—	—	—
	1008	100.00						

* Experiments are in progress in my laboratory on the action of bromides of carbon and tin on thiocarbamide.

† Calcium chloride tube spoiled.

The difficulty experienced in separating the bromide of silver in a perfectly pure state sufficiently accounts for the slight excess of bromine; but the data generally lead to the conclusion that the substance includes the octothiocarbamide compound already obtained, together with an excess of carbon and nitrogen, doubtless resulting from the decomposition of another portion of the amide by the long-continued action of excess of silicon bromide at the boiling point of benzene. It is of interest to note that the expression,

closely agrees with the numbers obtained.

It seems probable that the product is a mixture, but that point will be investigated later on, as my immediate purpose was served when it was found that continued heating under the conditions stated led to decomposition, and not to increase in the proportion of silicon tetrabromide combined with the amide.

As there was some reason to suppose that slight access of air during the operation facilitated the decomposition just referred to, another experiment was made in a pressure tube with 6.1 grams of thiocarbamide, and silicon bromide and benzene in proportion. Air was expelled, the tube sealed, and then heated for 36 hours at 100°. At the end of this prolonged heating, and when the contents of the tube were cold, the solid product seemed perfectly homogeneous and closely resembled that already obtained. It was removed, broken up, washed with benzene, and the ratio of sulphur to nitrogen and carbon determined.

The ratio of sulphur to nitrogen was—

$$\text{S} : \text{N}_{1.976}.$$

and sensibly equal volumes of carbon dioxide and nitrogen were obtained on combustion with chromate of lead, therefore no such decomposition of thiocarbamide took place in the formation of this product, as occurred in a shorter time and at a lower temperature when air had access to the mixture.

The evidence obtained is conclusive as to the fact that 8 mols. of thiocarbamide withdraw but 1 mol. of silicon tetrabromide from a large excess of the latter when presented in benzene solution under the conditions specified above; and further, that the product is the result of chemical union between the compounds concerned. Whether the product is a single compound or a mixture must of course be determined by other means.

Mechanical solvents having failed to break up the substance, the action of anhydrous alcohol on it was next examined. When a quantity of the freshly prepared compound was boiled with carefully

dehydrated ethyl alcohol almost complete solution took place, and only a minute quantity of a siliceous body separated. On cooling the solution in a well-closed flask, beautiful stellate groups or tufts of fine silky crystals separated. These groups of crystals sometimes resembled sea anemones in appearance; they were easily purified by several recrystallisations from alcohol. Although this compound gave the galena reaction with alkaline lead tartrate solution, which I recently described (*Trans.*, 1884, p. 162), it did not possess any of the other characters of thiocarbamide.

On analysis, this substance proved to be a monobromo-compound of pentathiocarbamide, and its production is evidence that silicon tetrabromide, when made to act as described on the thiocarbamide, determines condensation of the latter to an extent which greatly exceeds that which we already know bromine alone can induce.

When the alcoholic solution from which the above-mentioned pentathiocarbamide derivative separated was distilled, a further crop was obtained, the mother-liquor from which when shaken up with two volumes of anhydrous ether separated into two layers. The heavier liquid, on standing, deposited crystals of the compound of ethyl bromide with thiocarbamide, and some of the bromethyl dithiocarbamide. The lighter layer was found to contain some of the bromethyl compounds and ethylic silicates.

A full account of the compounds obtained by the alcoholic treatment will shortly be laid before the Society; but the outline already given serves to explain the unexpected results obtained by the action of silicon tetrabromide on thiocarbamide, as it is evident that the silicon compound determines the condensation of the amide and then unites with the product. Any further discussion of the constitution of the octothiocarbamide compound with silicon tetrabromide must obviously be reserved until the results of the examination of the products of its action with alcohol have been stated in detail.

I have to thank my friend and former pupil, Mr. R. E. Doran, F.C.S., for much assistance in this work.

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