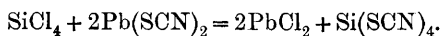


XLIV.—*Silicon Researches. Part X. Silicon Thiocyanate, its Properties and Constitution.*

By J. EMERSON REYNOLDS.

SILICON thiocyanate was obtained by Miquel in 1877 (*Ann. Chim. Phys.*, [v], II, 343) by heating to about 350° a mixture of lead thiocyanate and silicon tetrachloride, when a brown, oily liquid distilled over which quickly solidified to a crystalline mass. In this process, charring occurs even when small quantities of 10 or 12 grams are distilled, and an impure product results.

As I desired to attempt to settle the constitution of this substance, it was advisable to avoid a high temperature in its preparation, and, finding that silicon thiocyanate is soluble in perfectly dry benzene, it seemed probable that interaction between the materials could be effected in presence of that solvent and the compound be thus obtained at once in a pure state. This turned out to be the case, but it was also found that a much larger proportion of the lead salt must be used than is required by the equation :



The reason for this is that the lead salt is not converted into the simple chloride in the first instance, but that there is the intermediate production of the compound $\text{Pb}(\text{SCN})\text{Cl}$,* which latter is then converted very slowly and partially into the chloride by prolonged treatment; hence it is better to begin with a considerable excess of lead thiocyanate as in the following case.

One hundred grams of dehydrated and very finely-divided lead thiocyanate were diffused through about 400 c.c. of benzene contained in a flask provided with a reflux condenser; 17 grams of silicon chloride were then added and after brisk agitation for some time the mixture was heated on a water-bath. As the interaction proceeded, the lead salt assumed a pale yellow colour owing to the formation of the above-mentioned chlorothiocyanate. The treatment was continued until the whole of the silicon chloride had interacted, as evidenced by the cessation of fuming. The hot liquid was rapidly filtered into a distilling flask and much of the benzene thence removed by distillation; when the residual solution cooled, a fine crop of small, colourless crystals of pure silicon thiocyanate separated.

During this process it is necessary to exclude carefully any moisture

* A similar compound is easily produced by digesting lead thiocyanate with an alkaline chloride.

as the thiocyanate is easily decomposed and speedily becomes yellow owing to the separation of perthiocyanic acid, hence all the benzene is best removed by gentle heating in a current of dry hydrogen. Once free from benzene, however, the thiocyanate changes very slowly in nearly dry air.

Silicon thiocyanate prepared as above from its benzene solution forms small, apparently trimetric, prisms; it melts at $143\cdot8^{\circ}$ (corr.) and a clear, pale yellow-coloured liquid results. This liquid when further heated deepens in colour, becoming somewhat brown, and then distils, giving a distillate which quickly crystallises in the receiver. Miquel states (*loc. cit.*) that the thiocyanate boils "vers 300° degrés," but I find that the corrected boiling point is $314\cdot2^{\circ}$, and this result was checked by comparison with pure diphenylamine under exactly the same conditions. The crystals obtained by distillation were identical in composition with those from the benzene solution, as they afforded respectively 10.68 and 10.65 per cent. of silicon: $\text{Si}(\text{SCN})_4$ requires $\text{Si} = 10\cdot76$.

In the absence of moisture and oxygen, silicon thiocyanate is not so easily decomposed by heat as Miquel supposed. I passed the vapour from about 2 grams of substance very slowly through a long and narrow Jena glass tube which was heated to redness in a combustion furnace; nearly the whole of the substance passed through the tube unchanged and condensed at the cool end outside the furnace, a little carbon disulphide was given off, and at the hottest part of the tube some white silicon nitride was left. Very little further decomposition occurred even after passing the compound four times through the visibly red-hot tube. At the end of the treatment, the white crystals obtained on cooling the condensed liquid were compared with the original specimen of thiocyanate, and found to be identical in general properties and to melt at the same temperature.

As the thiocyanate was thus proved to be able to withstand a temperature far beyond its boiling point without suffering material decomposition, it appeared probable that its vapour density could be obtained with sufficient accuracy to serve as a control of the molecular weight.

A Victor Meyer tube of Jena glass was filled with dry nitrogen and heated to 413° in a constant temperature air-bath provided with Callendar's excellent electrical thermometer; the substance used in the determination was that which had been passed in the state of vapour through a strongly heated tube as described above. The following are the data obtained:

Weight taken, 0.1671 gram. Gas expelled, 16.2 c.c. T. $18\cdot5^{\circ}$. Bar. 763 mm. The vapour density is therefore 129.5 ($H = 1$), consequently the molecular weight is 259. Theory for $\text{Si}(\text{SCN})_4 = 260$.

It is obvious that so good an agreement with theory could not have

been obtained if any decomposition occurred at 413° , some 99° above the boiling point of the compound.

Silicon thiocyanate is stated by Miquel to be insoluble in ether, carbon disulphide, chloroform, benzene, and petroleum, and that its best solvent is "l'acide sulphocyanique en solution benzénique"; in my experience, benzene alone is a sufficiently good solvent, even in the absence of thiocyanic acid, to render the preparation of silicon thiocyanate described above quite easy and satisfactory.

Ten c.c. of a cold saturated benzene solution from which a crop of crystals of the thiocyanate had separated gave, after decomposition with water, oxidation by nitric acid, and ignition of the residue, 0.288 gram of silica; 100 c.c. of this benzene solution therefore contained 12.5 grams of silicon thiocyanate.

Again, I find that carbon disulphide, chloroform, and even light petroleum dissolve the compound in small but sensible proportions, contrary to Miquel's experience. It is difficult for anyone not accustomed to work with silicon compounds to realise the care necessary in the removal of all traces of moisture from all solvents used with them; a very slight hydration leads to superficial decomposition of the solid and the formation of a slight layer of a silicic acid, which much impedes the action of a solvent. In this consideration is probably to be found the explanation of the differences between the two sets of observations, as all my solvents had been specially dehydrated. Ether, free from alcohol as well as moisture, does not dissolve the thiocyanate, but gradually decomposes it, and alcohol acts rapidly. It is scarcely necessary to add that acids and alkalis readily break up the compound.

The constitution of silicon thiocyanate is the question of chief interest connected with this very curious substance, as Augustus E. Dixon has shown (Trans., 1901, 79, 541) that the somewhat analogous phosphorus "trithiocyanate" acts as if it were a tautomeric compound. Dixon's admirable and extensive work in the difficult department of organic chemistry which he has studied so successfully entitles his opinion to great weight, and I therefore readily accept his view that phosphorus trithiocyanate exhibits a marked tendency to act not only as $\text{P}(\text{SCN})_3$, but in certain cases as $\text{P}(\text{NCS})_3$. It was therefore a matter of considerable interest to ascertain whether silicon thiocyanate acts under favourable conditions as $\text{Si}(\text{NCS})_4$ rather than as $\text{Si}(\text{SCN})_4$.

The elements silicon and phosphorus, although near to each other in atomic weight, belong to two very distinct periodic groups, and their compounds even when of the same general class do not necessarily undergo similar changes; therefore, silicon tetrathiocyanate and phosphorus trithiocyanate are not so closely related that the tautomerism which the latter substance exhibits is to be presumed to exist in the

case of the silicon compound. On the contrary, the following considerations leave little, if any, doubt that silicon and sulphur are directly united in silicon thiocyanate, and that it does not afford any real evidence of thiocarbimide structure under the conditions to which it has been subjected.

The fact that silicon thiocyanate which has been prepared at a temperature not exceeding 80° can be vaporised and heated in that state to quite 500° without undergoing isomeric change, and without decomposition, is good evidence that nitrogen is not directly united to silicon as in $\text{Si}(\text{NCS})_4$; for all other silicon compounds which are known to include four atoms of nitrogen lose two atoms of it at temperatures below 200° .

The action of aniline on phosphorus thiocyanate is, however, that which has afforded Dixon the chief evidence in favour of the view that the compound is tautomeric; consequently I have examined the action of the same substance on silicon thiocyanate with care in order to ascertain whether under the influence of the strong base it would act as $\text{Si}(\text{NCS})_4$. The test was carried out in the following manner.

Ten grams of pure silicon thiocyanate dissolved in 85 c.c. of benzene were mixed with 28 grams (8 mols.) of pure aniline; the mixture became warm, indicating that chemical action had taken place, but no solid matter separated, as aniline thiocyanate is freely soluble in benzene. No external heat was applied, and the solution was allowed to stand at the ordinary temperature for ten days in order that the action might be completed; at the end of that time, the liquid was still perfectly clear, and a drop of it when shaken up with ferric chloride gave the red thiocyanate reaction very strongly. The solution was now diluted with about three volumes of benzene and boiled in a reflux apparatus; after a short time, a little of the liquid was removed and cooled, but nothing separated. If any material quantity of a phenylthiourea had been formed, it must have separated at this stage owing to its low solubility in cold benzene. The boiling was continued and a white substance began to form; the process was prolonged until no further separation of the white substance took place; the latter was then quickly filtered off, thoroughly washed with boiling benzene, and dried. The filtered solution gave a good crop of crystals on cooling; much of the benzene was distilled off and two more crops of similar crystals were obtained. The mother liquor from the last crop contained some free aniline. The crystals, which were mixed and recrystallised from alcohol and ultimately from boiling water, presented all the characters of monophenylthiourea; they gave the lead reaction strongly; when heated in a test-tube, they gave much ammonia and a thiocarbamine, and the melting point was $153\text{--}154^{\circ}$.

0.3994 gave 0.6036 BaSO₄. S = 21.17.

CS(NH·C₆H₅)·NH₂ requires S = 21.5 per cent.

The white substance which separated on prolonged heating included all the silicon and gave a very strong thiocyanic reaction with ferric chloride; it slowly dissolved in caustic alkali with separation of aniline.

0.4478 gave 0.748 SiO₂. Si = 7.78.

0.5404 ,, 0.0905 SiO₂ and 0.38 BaSO₄. Si = 7.78; S = 9.65.

Si(N·C₆H₅)₂·NH₂·C₆H₅, HSCN requires Si = 7.73; S = 8.83 per cent.

The sulphur is high, as usual, in these cases owing to the imidothiocyanate precipitate carrying down with it a little of the perthiocyanic acid which is inevitably formed in small quantity on long-continued heating of the benzene solution.

The interpretation of these facts presents but little difficulty in view of the known habits of certain of the silicon compounds described in former papers of this series. Silicon thiocyanate evidently interacts with excess of aniline very much as the chloride does, although not quite so energetically, and the following equation doubtless represents the first stage:



Prior to diluting and boiling the solution, no phenylated thiourea was detected, but further changes proceeded *pari passu* on heating the diluted liquid. Probably the first to begin is the gradual molecular rearrangement of aniline thiocyanate* into the more stable isomeric form of monophenylthiourea, which most of it ultimately assumes. Under the same conditions, the silicophenylamide parts with two molecules of aniline and is reduced to the di-imide, a change which has been shown in previous papers to take place easily, and the imide carries down with it a molecule of aniline thiocyanate, with which it appears to form an additive compound similar to those obtained in other cases.

Under all the conditions specified, there is therefore no doubt that silicon thiocyanate is correctly represented by the expression Si(SCN)₄.

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* This change takes place much more easily than is commonly supposed. Strong alcoholic solutions of aniline hydrochloride and ammonium thiocyanate, if mixed in the cold, precipitate ammonium chloride, and aniline thiocyanate is retained in solution and remains unchanged for a considerable time. When the solution is boiled and then poured into cold water, an abundant precipitate of monophenylthiourea can be obtained, so that boiling in alcoholic or even aqueous solution determines the molecular change:

