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DERIVATIVES OF SILICON TETRACHLORIDE.¹

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GENERAL REMARKS UPON COMPOUNDS OF THE HIGHER HALOIDS OF THE ELEMENTS OF GROUP IV.

THE review of the reactions of these tetrachlorides furnishes some interesting data from which inferences of importance may be drawn. There are, however, numerous problems still unsolved, and many reactions that yet demand study, before any broad comparison of the behaviors of these elements can be definitely made, or any conclusion as to the influence of the atomic weight or metallic character on the reactivity of their tetrachlorides established. No general rule could be deduced from the data already collected, which would enable us by a logically drawn analogy, to predict their behaviors in certain uninvestigated reactions.

Carbon and silicon, the first two elements of the group, are by their position more or less isolated, and removed from too close a comparison with any of the sub-group elements, and their reactions are best studied with a view to determining or increasing their own already well developed similarities, without seeking to broaden to too great an extent their relation to other elements of the group. The chlorides of silicon and carbon may be said, however, in a general way, to possess in common with the other group members, a distinctly acid nature, and to exhibit the power of combining with bases to form stable, well defined compounds. This behavior may be predicted for even the unstudied chlorides of germanium, lead and thorium, since every element thus far investigated has in its tetrachloride form thus deported itself. Ammonia, the substituted ammonia derivatives, such as methylamine, toluidine, urea and amido bodies of a distinctly basic character, may here be said to react similarly with all. With acid amides and bodies of a distinctly acid nature, no such general rule may be adopted, and a series of reactions occur which seem to be conditioned by no rise or fall in atomic weight

¹ Thesis presented to the University of Pennsylvania for the degree of Doctor of Philosophy.

or by position and group relation of the elements. Titanium, one of the elements of the sub-group having a less metallic character, and tin of the opposite sub-group and of a distinctly metallic nature and a high atomic weight, represent the most reactive of the elements of Group IV, in their tetrachloride form. Other than this, there seems to be little relationship between them, being distinctly separated by such considerations as place them in opposite groups. Titanium, the element of lowest atomic weight of the first sub-group, is in its quadrivalent form most reactive. Its tetrahaloid forms derivatives with hydrocyanic acid, cyanogen chloride, and the oxides of nitrogen. It thus has the power of holding acid as well as basic compounds in combination. Zirconium, on the other hand, the element next in succession to titanium, exhibits no such reactions, and its combinations seem limited to compounds of a basic character, as work now in progress in this laboratory indicates. We might then assume the rule "that in the first sub-group the reactivity decreases with a rise in atomic weight, being highest in titanium," with more or less reason. In the case of the opposite sub-group, however, the paucity of data forbids the formulation of any such law. Tin we know to be exceedingly reactive in its quadrivalent haloids, but germanium, the element which precedes it in the sub-group, whose reactions, if studied, would make some such general statement possible, has been but little investigated with such an end in view.

The subsequent chlorides of thorium and lead are being studied at present, and the determination of their reactions will show the relevance of their weight relationship to their behaviors, and make possible a more comprehensive and thorough comparison of the actions of the tetrachlorides of the fourth periodic group. The accompanying table represents the behavior of the several tetrachlorides towards various reagents. The reactivity is indicated by the letter " r ," and the failure to form compounds with these reagents by the character " o ."

	Aniline, etc.	Fatty amines.	Urea, thiourea	Acid amides.	HCN.	Acetonitrile.	Benzonitrile.	Tolunitrile.	Succinonitrile.	Chlorocyanog'n	S ₂ Cl ₂ .	NO ₂ .	PCl ₅ .	PCl ₃ .	NH ₃ .
CCl ₄	r	r	.	.	r
SiCl ₄	r	r	r	o	o	o	o	o	o	o	o	o	o	o	r
TiCl ₄	r	.	.	.	r	r	r	r	r	r	r	.	r	.	r
GeCl ₄
ZrCl ₄	r	r	.	.	o	o	o	o	o	o	r
SnCl ₄	r	r	.	.	r	r	r	r	r	o	r	.	r	.	r
PbCl ₄	r	r
ThCl ₄	r	r

THE ACTION OF AROMATIC AMINES AND NITRILES ON SILICON TETRACHLORIDE.

The work was entered upon chiefly with a view to developing some new analogies between the behavior of silicon tetrachloride and that of the tetrachlorides of the other members of Group IV, or any characteristic differences which might prove noteworthy. The hope of the investigation was, that by some well defined series of reactions observed therein, a new means might be found of isolating the members of the group, in their higher forms of combination, from one another or from members of other groups.

The investigation is all the more demanded, since but little work has been done in this field, the action of nitriles having been studied only with the tetrachlorides of titanium and tin.¹ The action, therefore, of nitriles on silicon tetrachloride was a needed expansion of the subject, and this, together with the actions of the chlorides of sulphur and phosphorus, cyanogen and chloride of cyanogen, nitrogen dioxide and nitroxyl chloride, upon silicon tetrachloride, constitute the experimental part of the present research, while the demonstration of the inactivity of the latter, as compared with the behaviors of tin and titanium tetrachlorides, determines its scope.

The second part of this article deals with the reactions between silicon tetrachloride and amines of the benzene series. The behavior of these bodies towards higher haloids of the fourth group has been investigated only in the silicon derivatives, and

¹ Henke : *Ann. Chem.* (Liebig), 106, 281; Shinn : Thesis, University of Pennsylvania, 1895.

here the reaction cannot be said to be determined, since the investigators in this field are at odds in their results, and it is hoped that this work will aid in fixing the exact constitution of the products of the reaction of silicon tetrachloride and aromatic amines.

The silicon tetrachloride was made by the action of dry chlorine on silicon, at a low heat, the resulting vapors being collected in chilled condensers. Any free chlorine was removed from the product by shaking with mercury, and the silicon tetrachloride further purified by fractional distillation, till it exhibited the constant boiling-point, 57° - 59° . The silicon used in this preparation was made by the reduction of very fine sand, free from iron, by magnesium powder, according to the method recommended by Gattermann.

THE ACTION OF FORMONITRILE ON SILICON TETRACHLORIDE.

Dry hydrocyanic acid gas conducted into cooled silicon tetrachloride produces no change; no product is formed and the silicon tetrachloride boils at the usual temperature. Wöhler¹ had prepared the compound $TiCl_4 \cdot 2HCN$, while Klein² got a corresponding tin derivative, as did also Shinn.³ These results led to the attempt to combine formonitrile and silicon tetrachloride with the result above indicated.

ACETONITRILE.

Henke⁴ had shown that methyl cyanide combined with titanium and tin tetrachlorides, to form derivatives of the type $SnCl_4 \cdot 2CH_3CN$. Anhydrous acetonitrile, made by the distillation of acetamide and phosphorus pentasulphide, and further purification of the product, was added to silicon tetrachloride chilled in ice; no action was apparent or heat generated. The precaution of chilling in ice was taken, because in the case of tin derivatives the amount of heat produced in the reaction was sufficient to decompose the products. Here, however, even when the ordinary temperature was resumed, no combination was effected. The slightest trace of moisture, however, serves

¹ *Ann. Chem.* (Liebig), 73, 226.

² *Ann. Chem.* (Liebig), 74, 86.

³ Thesis, University of Pennsylvania, 1896.

⁴ *Ann. Chem.* (Liebig), 106, 281.

to precipitate a silica compound which retains the nitrile tenaciously. Its analysis, however, indicates no definite constitution, and it is probably nothing more than a mixture of silicic acid and methyl cyanide.

PROPIONITRILE.

This was made by the distillation of potassium cyanide with potassium ethyl sulphate; the isopropionitrile formed at the same time, being removed by a small quantity of concentrated hydrochloric acid. As with acetonitrile, the anhydrous liquid gives no compound with silicon tetrachloride, while the tetrachlorides of tin and titanium afford derivatives of a constitution similar to the acetonitrile bodies. (See above references.)

SUCCINONITRILE.

The nitrile of succinic acid was made by digesting ethylene dibromide with an alcoholic solution of potassium cyanide, and after being rendered absolutely anhydrous was added to silicon tetrachloride. It gave no derivative, being in this distinguished from tin, which forms the compound $\text{SnCl}_4 \cdot 2(\text{CH}_2\text{CN})_2$.¹

AROMATIC NITRILES. BENZONITRILES.

This reagent was made by distilling benzoic acid and dry potassium thiocyanate, adding ammonia to the semi-solid distillate and extracting with ether. With this nitrile the behavior of tin and titanium chlorides had been investigated by Henke,² who obtained the compounds $\text{C}_6\text{H}_5\text{CN} \cdot \text{TiCl}_4$ and also $\text{C}_6\text{H}_5\text{CN} \cdot \text{SnCl}_4$. With silicon tetrachloride, however, it gives no derivative under ordinary conditions or by the action of heat and pressure. Silicon tetrafluoride also exhibits no reaction with this nitrile.

TOLUNITRILE.

The tetrachloride here gives a compound, but neither the chloride nor fluoride of quadrivalent silicon unite with it. No variation in the result was noticed when the silicon tetrachloride was heated under pressure with the nitrile, these compounds remaining uncombined as before.

¹ Shinn: University of Pennsylvania, Thesis, 1896.

² *Ann. Chem.* (Liebig), 106, 181.

The *nitriles* of *mandelic* and *lactic acids* gave no derivatives with silicon tetrachloride under ordinary conditions, but when heated under pressure, silicic acid and complex tarry decomposition products resulted, which did not attract analysis. In all the above cases the mediums of interaction were benzene and ether, the latter being preferable, because it was thought the more easily dried.

NITROGEN DIOXIDE.

Marignac¹ obtained the derivative of carbon tetrachloride, to which he assigned the formula $\text{CCl}_4 \cdot 2\text{NO}_2$. Later, Kuhlmann² prepared derivatives of silicon tetrachloride with every oxide of nitrogen. On passing NO_2 , prepared by heating lead nitrate, into silicon tetrachloride, no heat development was noticed. The latter dissolves the gas and becomes colored by the same, but a single distillation, during which the boiling-point showed no change, sufficed to completely decolorize the liquid and remove the nitrogen dioxide from it.

THE MIXED VAPORS OF NO_2 AND CHLORINE.

These were conducted into cooled silicon tetrachloride, as in the former instance. There was no liberation of heat, the liquid becoming merely colored by the gases and giving them up freely on distillation, the boiling-point remaining normal, thus indicating that no compound had been formed and that simply an absorption of the vapors had taken place. This is all the more remarkable, since the derivatives $3\text{TiCl}_4 \cdot 2\text{NO}_2 \cdot \text{Cl}$ and $3\text{SnCl}_4 \cdot 2\text{NO}_2 \cdot \text{Cl}$ had been readily prepared by Hampe.³

THE CHLORIDES OF PHOSPHORUS.

Phosphorus trichloride, under ordinary conditions, or heated under pressure with silicon tetrachloride, gives no derivative; the liquids merely commingle to a solution from which both constituents may be isolated by fractional distillation. Phosphorus in solid condition remains insoluble in silicon tetrachloride, but when its vapors, partly dissociated, are conducted into the same, they are absorbed and dissolved. Upon subsequent distillation

¹ *Ann. Chem.* (Liebig), 38, 17.

² *Ann. Chem.* (Liebig), 39, 320.

³ *Ann. Chem.* (Liebig), 126, 43.

the liquid, for the greater part, boils at 58° – 60° , leaving a liquid residue, which is driven over only at the boiling-point of phosphorus trichloride. The only effect of the phosphorus pentachloride seems to be a slight elevation of the boiling-point of the silicon compound, while the latter serves to completely dissociate the pentachloride into the lower chloride and free chlorine. Casselmann¹ had prepared a compound of tin and phosphorus chloride, of the formula $(\text{SnCl}_4)_2 \cdot \text{PCl}_5$. Here again the analogy between tin and silicon fails.

SULPHUR MONOCHLORIDE.

The liquids were mixed in all proportions, and on boiling the mixture, the silicon tetrachloride being in excess, the greater part came over between 57° – 59° . The temperature rises gradually and then suddenly is elevated to 139° , the boiling-point of sulphur monochloride, thus showing that no compound had been formed. H. Rose,² however, obtained the compound $\text{SnCl}_4 \cdot 2\text{S}_2\text{Cl}_2$.

CYANOGEN CHLORIDE.

A saturated solution of mercuric cyanide was made, and an excess of the salt was added to this in a finely divided condition. Chlorine was then conducted into this liquid, until it was completely saturated by the gas, and the product was set aside in a dark place in a flask, filling the space above the liquid with chlorine. After a time the excess of mercuric cyanide had dissolved and the chlorine was completely absorbed. Uncombined chlorine was then removed by shaking with mercury, and the solution was poured into a flask provided with a calcium chloride tube. On gently heating the solution, the cyanogen was evolved, and led through a tube filled with copper turnings, to remove the last traces of chlorine, into silicon tetrachloride chilled in ice and salt. Silicon in its behavior here was found to ally itself with tin, both Wöhler³ and Klein⁴ having failed to obtain chlorocyanogen compounds with the higher chlorides of the latter, while Wöhler had however succeeded in preparing a titanium derivative of the composition $\text{TiCl}_4(\text{CNCl})_4$.

¹ *Ann. Chem. (Liebig)*, 83, 258.

² *Pogg. Annalen*, 42, 517.

³ *Ann. Chem. (Liebig)*, 74, 86.

⁴ *Ann. Chem. (Liebig)*, 73, 221.

SILICON TETRACHLORIDE AND AROMATIC AMINES.

Kuop¹ obtained derivatives from silicon tetrafluoride with urea and aniline. With the latter a white crystalline compound was prepared, to which he assigned the formula $\text{Si}_2\text{H}_3\text{F}_{10}\cdot 3\text{Cl}_2\text{H}_7\text{N}$. This constitutes the first work investigating the action of the aromatic amines on the tetrahaloids of the fourth group. As, however, the medium here used is anhydrous alcohol which decomposes the silicon tetrafluoride, the resulting compound cannot be said to be a derivative of it. Laurent and Delbos² obtained a compound of aniline and silicon tetrafluoride, whose constitution they expressed as $3\text{C}_6\text{H}_5\text{NH}_2\cdot 2\text{SiF}_4$, but did not establish. Jackson and Comey³ obtained also this compound, proved its constitution, and described its properties. They prepared in a similar manner, derivatives from ortho- and para-toluidine, diphenylamine and dibenzylamine, while dimethyl-aniline and quinoline gave no product.

Girard and Pabst⁴ investigated the action of the tetrachlorides of carbon, tin, and silicon on aniline at increased temperatures. With carbon tetrachloride and aniline, they obtained the derivatives, triphenylguanidine and rosaniline. With the chloride of tin under the same conditions, violaniline, mauvaniline (phenyl-safranine), and, it seems, rosaniline were obtained. Silicon tetrachloride also forms violaniline, together with the production of triphenylamine blue.

The only investigations on these reactions which are established by exact analyses are those of Harden⁵ and Reynolds⁶; the latter is a repetition of the work of the former experimenter, in which results are obtained which vary from it. Unaware of any conflict of results, or, indeed, of any precedence in the field, the present investigation was begun; and it was not until its results were complete that any divergence in previous work on the subject was encountered. The work was then found to agree entirely with that of the earlier of these investigators, and to establish by new methods of procedure his results.

¹ *Chem. Centrbl.*, 1853, 388; *Jsb. d. chem.*, 1853, 148; *J. prakt. Chem.*, 74, 41.

² *Ann. chim. phys.*, 22, 101.

³ *Ber. d. chem. Ges.*, 19, 3194.

⁴ *Bull. Soc. Chim.*, 34, 38.

⁵ *J. Chem. Soc.*, 51, 49.

⁶ *J. Chem. Soc.*, 55, 474.

SILICON TETRACHLORIDE AND ANILINE.

When aniline is added to silicon tetrachloride, there is a great evolution of heat, with the coincident precipitation of a white compound completely insoluble in ether. Owing to the violence of the reaction, anhydrous ether, and afterwards benzene, was used as a diluent and medium of interaction. The complete combination of the silicon tetrachloride was evidenced by the loss of the odor of that body when sufficient aniline had been added. With this as a means of indication, the synthetic proportions were found to be one molecule of silicon tetrachloride to four molecules of aniline.

Three and five-tenths grams silicon tetrachloride required 7.50 grams aniline. Calculated, 7.65 grams aniline.

Five and eight-tenths grams silicon tetrachloride required 12.4 grams aniline. Calculated, 12.68 grams aniline.

That the silicon tetrachloride united with the aniline in the proportion of one to four molecules, was further proved by weighing the resultants of the action of quantities of these substances united according to the above ratio. Ether was used as a medium.

To three and five-tenths grams of silicon tetrachloride, dissolved in ether, a slight excess of four molecules of aniline was added, stirring vigorously during the addition of the latter substance. The white precipitate thus obtained was placed on a tared filter and washed with anhydrous ether, in a current of dry air, until the washings showed no trace of aniline. The precipitate was then dried in a desiccator, the filter and precipitate placed in a weighing bottle and its weight found.

From three and five-tenths grams silicon tetrachloride were obtained 11.16 grams product. Calculated for three and five-tenths grams silicon tetrachloride, and 7.66 grams, or four molecules of aniline, gave 11.3 grams product.

In a second experiment the following figures were obtained:

Four and six-tenths grams of silicon tetrachloride gave 14.8 grams product. Calculated for 4.60 grams silicon tetrachloride and 10.06 grams, or four molecules of aniline, 14.66 grams product.

The additional weight of the precipitate was here probably due

to some small quantities of aniline retained by it. Portions of this substance which had been placed in the cup of a Soxhlet apparatus and washed with ether for three hours, were taken for analysis. The exit tube of the Soxhlet apparatus was, in this instance, connected with a drying apparatus, and the precipitate during the washing thus protected from the action of moist air. All precautions were taken to remove every trace of free aniline, the washings of the precipitate being constantly examined for the same, till they failed to give reactions of that body. The compound was placed in a desiccator and portions taken for analysis.

I. 0.1135 gram gave 0.0122 gram silica, or 5.052 per cent. silicon.

II. 0.3739 gram gave 0.0280 gram silica, or 4.80 per cent. silicon.

III. 0.0965 gram gave 0.0103 gram silica, or 5.01 per cent. silicon.

IV. 0.1432 gram gave 0.2805 gram carbon dioxide, or 53.42 per cent. carbon; and 0.0684 gram water, or 5.31 per cent. hydrogen.

V. 0.2153 gram gave 0.1572 gram Pt, or 10.47 per cent. nitrogen.

VI. 0.2034 gram gave by Dumas' method 0.02166 gram nitrogen, or 10.65 per cent. nitrogen.

VII. 0.3467 gram gave 0.3710 gram silver chloride, or 26.46 per cent. chlorine.

VIII. 0.2972 gram gave 0.3130 gram silver chloride, or 26.05 per cent. chlorine.

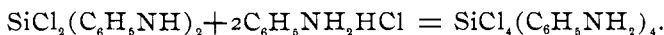
	Calculated for (C ₆ H ₅ NH ₂) ₄ SiCl ₄ .	I.	Found. II.	III.
Silicon.....	5.16	5.05	4.80	5.01
Carbon.....	53.13	53.42
Hydrogen.....	5.16	5.31
Nitrogen.....	10.32	10.47	10.65
Chlorine.....	26.19	26.46	26.05

These analyses further substantiate the proportions of combination which had been indicated by the synthetic experiments. As the compounds thus produced possess the formula

$\text{SiCl}_4(\text{C}_6\text{H}_5\text{NH}_2)_4$, the reaction may be written as follows :



This was regarded as a single molecular compound, and the reaction was thus written until the use of a medium other than benzene, in the combination of these bodies, gave results that pointed to the conclusion that the above compound was a mixture of the compounds $\text{SiCl}_2(\text{C}_6\text{H}_5\text{NH})_2$ and $2\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$, so formed by the combination of one molecule of silicon tetrachloride and four of aniline. The resulting dichlorosilicon diphenylamide and the aniline hydrochloride, being both insoluble in ether, would be combined in such proportions as to give a mixture whose total composition would correspond to the formula deduced from the above analysis :



The results that led to the inference that the latter compound was not simple are below detailed. When instead of ether as a medium, anhydrous benzene is used, all of the products are not precipitated, but it was found on washing the precipitate thus obtained with benzene in a dry Soxhlet apparatus, a white compound was left, which gave the following proportions on analysis :

I. 0.3401 gram gave 0.3751 gram silver chloride, or 26.99 per cent. chlorine.

II. 0.2266 gram gave 0.2506 gram silver chloride, or 27.07 per cent. chlorine.

The compound thus obtained did not show any silica content.

	Calculated for aniline hydrochloride.	I.	Found. II.
Chlorine.....	27.13	26.99	27.07

It was further noticed that the total weight of this precipitate was only about half that calculated for the complete precipitation of the compound of silica, expressed in the reaction with ether as a medium.

I. Three and five-tenths grams silicon tetrachloride and four molecules of aniline gave 5.29 grams of product insoluble in benzene ; with ether as a medium obtained 11.3 grams of product insoluble in ether.

II. Three and nine-tenths grams silicon tetrachloride gave 5.06 grams of product insoluble in benzene; calculated for $(C_6H_5NH_2)_4SiCl_4$, 12.43 grams.

As the aniline hydrochloride was entirely free from silica, the silicon compound produced in the reaction was looked for in the clear filtrate from the aniline hydrochloride. This solution was not allowed to evaporate, to yield in this manner the dissolved derivative, as it was known, since the aniline was originally in slight excess, that any compound so produced would be saturated with aniline, the last traces of which it would be difficult to remove. To the solution was therefore added ether, which precipitated a white compound containing silicon, carbon, hydrogen, nitrogen and chlorine, and whose analyses gave the following results:

I. 0.2461 gram substance gave 0.4602 gram carbon dioxide, or 50.95 per cent. carbon; and 0.0860 gram water, or 3.88 per cent. hydrogen.

II. 0.2840 gram gave 0.0589 gram silica, or 9.69 per cent. silicon.

III. 0.2131 gram gave 0.0442 gram silica, or 9.74 per cent. silicon.

IV. 0.2761 gram gave 0.2788 gram silver chloride, or 24.70 per cent. chlorine.

V. 0.3013 gram gave 0.2014 gram Pt, by method of Varrentrapp and Will, or 9.59 per cent. nitrogen.

	Calculated for $SiCl_4(C_6H_5NH_2)_4$	I.	Found. II.
Carbon.....	50.88	50.95	...
Hydrogen.....	4.24	3.88
Nitrogen.....	9.87	9.59
Silicon.....	9.87	9.69	9.74
Chlorine.....	25.08	24.70

This is the compound which had been obtained by Harden¹. On weighing the amount of this produced from definite amounts of silicon tetrachloride, and adding to it the quantity of aniline hydrochloride produced at the same time, the total weight both of the silicon tetrachloride and the aniline are united and found in the products described above.

¹ *J. Chem. Soc.*, 51, 40.

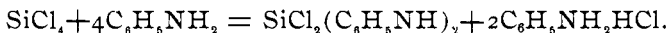
Three and five-tenths grams of silicon tetrachloride and four molecules, or 7.65 grams, aniline gave :

	Grams.
Dichlorosilicon diphenylamide.....	5.83
Aniline hydrochloride.....	5.29
	<hr/>
Total found	11.12
Calculated for three and five-tenths grams silicon tetra- chloride and 7.65 aniline.....	11.15

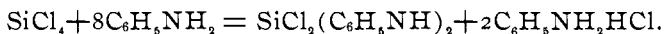
Three and nine-tenths grams silicon tetrachloride and 8.55 grams aniline gave :

	Grams.
Dichlorosilicon diphenylamide.....	6.52
Aniline hydrochloride.....	5.96
	<hr/>
Total found.....	12.58
Calculated for three and nine-tenths grams silicon tetrachloride and 8.53 grams aniline.....	12.43

These bodies are almost quantitatively produced, as the above results have indicated, and no amount of any secondary products can be believed to be present. The reaction may, therefore, be written as follows :



Both these products were obtained, and only these, although the aniline was always in excess ; while Reynolds writes the reaction thus :

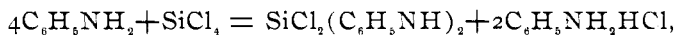


The silicon tetraphenylamide prepared by him is a well crystallized body, and the careful methods of analysis pursued place its exact constitution beyond doubt. The cause of the divergence in the results is, therefore, due to the variation in procedure. In the work of Harden in the present investigation, smaller quantities of material are used (only a slight excess of four molecules of aniline are employed), and the diluents of the action were not present in such great amount as in the work of Reynolds, where the benzene is double the value of the reagents. In his work, 100 grams of silicon tetrachloride are added to 438 grams of aniline, or in the proportion of one to eight molecules.

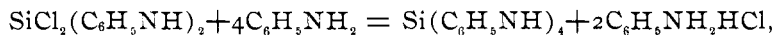
In the use of such a quantity of benzene, the purpose is to keep the larger amount of the silicon compound in solution, so that the precipitate will consist almost wholly of aniline hydrochloride, retaining but little of the silicon derivative. The precipitate, according to the method of this investigator, is quickly filtered from the solution, washed often with benzene and the filtrate distilled free from the greater part of the benzene in a current of hydrogen. The syrupy liquid thus obtained was poured into an excess of carbon disulphide, which served to precipitate a little aniline hydrochloride which had continued in solution. The filtrate was then concentrated and allowed to crystallize, when the compound described by him was obtained.

It will be here observed that the work is less direct than that of the methods of procedure before described, and that more chance of secondary reactions is encountered in the manipulation than in the first instance, and that the reaction which requires four molecules of aniline with one of silicon tetrachloride, represents the normal behavior of these two substances.

It is believed that the use of ether in lieu of benzene, furnishes a far preferable medium for determining the proportions of the reaction, though preventing an analysis of the two products, which are equally insoluble in it. It renders possible, however, a weighing of the total products of the reaction and a comparison of their quantity, with the amount of silicon tetrachloride and aniline used, since it exerts no solvent action on either product, while both reagents are soluble in it. The possibility of secondary reactions, or of the solvent playing the rôle of a reagent, was thus avoided. The readiness of weighing the total product of the reaction, and the determination of the synthetic proportions of the same, seem to establish that it proceeds as follows :



and that the compound without chlorine, $\text{Si}(\text{C}_6\text{H}_5\text{NH})_2$, and the reaction which Reynolds writes, does not represent the immediate action of the reagents, but that the time-consuming method of the latter introduces a second phase into the reaction, during which the following may take place :



which would explain the formation of both silicon derivatives and the contradiction of the reactions.

It might here be noticed that the names "Dichlorosilicon diphenylamide" for $\text{SiCl}_2(\text{C}_6\text{H}_5\text{NH})_2$, and "Silicon tetraphenylamide" for $\text{Si}(\text{C}_6\text{H}_5\text{NH})_4$, are cumbersome and not sufficiently clear; "Chlorsilicon dianilide," for the first, and "Silicon tetranilide" for the latter, are suggested as briefer and more expressive names.

SILICON TETRACHLORIDE AND ORTHOTOLUIDINE.

The methods employed in the preparation of the toluidine derivatives were similar to those made use of in the production of the aniline compound. A greater reactivity was, however, noticed on the part of the toluidine, as it was found to combine with the silicon tetrachloride at the temperature of ice and salt, while aniline was inert under these conditions. The precaution was taken to remove all paratoluidine from the liquid variety, by means of their acetyl derivatives, and the pure orthotoluidine thus formed was used in the reactions.

The white compound insoluble in benzene was washed with ether, dried, and analyzed.

I. 0.3146 gram gave 0.3126 gram silver chloride, or 24.32 per cent. chlorine.

II. 0.4012 gram gave 0.4006 gram silver chloride, or 24.43 per cent. chlorine.

Calculated for $\text{C}_6\text{H}_4\text{CH}_3\text{NH}_2\text{HCl}$, 24.73 per cent. chlorine.

The compound is, therefore, toluidine hydrochloride and its production similar to that of the aniline body.

On the addition of ether to the filtrate, a white voluminous precipitate appeared, which was washed with anhydrous ether, and dried in a desiccator. Of this substance:

I. 0.1722 gram gave 0.0319 gram silica, or 8.70 per cent. silicon.

II. 0.1650 gram gave 0.0313 gram silica, or 8.91 per cent. silicon.

III. 0.2160 gram gave 0.0403 gram silica, or 8.77 per cent. silicon.

IV. 0.1834 gram gave 0.1727 gram silver chloride, or 22.51 per cent. chlorine.

V. 0.2803 gram gave 0.2617 gram silver chloride, or 22.85 per cent. chlorine.

	Calculated for $\text{SiCl}_2(\text{C}_8\text{H}_4\text{CH}_3\text{NH})_2$.	I.	Found. II.	III.
Silicon	9.00	8.70	8.91	8.77
Chlorine	22.80	22.51	22.85

The behavior of orthotoluidine is, therefore, analogous to that of aniline. That four molecules of toluidine were required for the saturation of silicon tetrachloride was proved as in the former instance by determining the synthetic proportions of the compounds, and by the use of ether as a medium, determining the weight of the total product. It required :

	Toluidine. Grams.
For 3.0 grams silicon tetrachloride.....	7.7
Calculated.....	7.6
For 5.3 grams silicon tetrachloride.....	13.2
Calculated	13.2

The precipitate produced and washed in ether in the

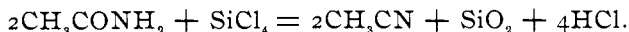
	Product. Grams.
First experiment gave.....	10.8
Calculated for 7.6 and 3.0	10.6
Second experiment gave.....	18.8
Calculated for 5.3 and 13.2	18.5

SILICON TETRACHLORIDE AND ACID AMIDES. BENZAMIDE.

The vapors of silicon tetrachloride, conducted into benzamide in the molten condition, gave rise to benzaldehyde, which was collected and recognized by the malachite green reaction. It was thought that the silicon tetrachloride would form a product with the benzamide, as with the aromatic amines, but it is probable that the benzamide is not sufficiently basic in character to so act.

SILICON TETRACHLORIDE AND ACETAMIDE.

With the latter compound no derivative is obtained, but on conducting the vapors into acetamide, acetonitrile was produced. Possibly according to the following :



The present investigation on the behavior of silicon tetrachloride is but one in a series which has for its scope the determination of the reactions also of lead and tin tetrachlorides with amine bodies. Work is also in progress in this laboratory on the conduct of thorium and zirconium tetrachlorides with the same reagents. The results thus obtained will afford a wider study of the fourth group elements, and furnish data for a broader comparison of the reactions of its members.

SOME NEW RUTHENOCYANIDES AND THE DOUBLE FERROCYANIDE OF BARIUM AND POTASSIUM.

BY JAS. LEWIS HOWE AND E. D. CAMPBELL.¹

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THE resemblance between the double cyanides of iron, ruthenium, and osmium, was first pointed out by Claus,² and further developed by Martius,³ who formed a number of the double osmocyanoïdes. More recently Dufet⁴ has described the crystals of potassium ruthenocyanide and osmocyanoïde and shown their close crystallographic resemblance to the ferrocyanide. The chemistry and the crystallography of the ferrocyanides has been very exhaustively studied by Wyruboff,⁵ and his work affords a valuable starting point for any investigation of the isomorphous ruthenocyanides and osmocyanoïdes.

Since the publication of a recent paper by one of us (Howe)⁶ on the ruthenocyanides, several new salts have been prepared, and in all of them the analogy of the ruthenocyanides with the ferrocyanides is complete. The ruthenocyanides are decidedly more soluble than the ferrocyanides and correspondingly more difficult to crystallize. In one salt only have crystals been obtained which were perfect enough to measure.

Strontium Ruthenocyanide, $\text{Sr}_2\text{Ru}(\text{CN})_6, 15\text{H}_2\text{O}$.—Formed by treating lead ruthenocyanide with dilute sulphuric acid and neutralizing of the hydroruthenocyanic acid formed with strontium

¹ Contributed to the November meeting of the Cincinnati Section of the American Chemical Society, November 16, 1897.

² Beiträge zur Chemie der Platinmetalle. pp. 98 and ff.

³ Ueber die Cyanverbindungen der Platinmetalle. Inaug. Diss., Göttingen, 1860.

⁴ *Compt. rend.*, 120, 377.

⁵ *Ann. chim. phys.* [4], 16, 280: 21, 271.

⁶ This Journal, 18, 981.