CCLXXXIV.—*Germanium. Part IX. The Action of Amines and of Certain Other Organic Bases on Germanium Tetrachloride. The Structure of Germanium Imide.**

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It has already been shown (Thomas and Pugh, this vol., p. 60) that the interaction of germanium tetrachloride with ammonia affords a mixture of one molecule of germanium imide with four molecules of ammonium chloride. The objects of the present investigation were (1) to determine to what extent substituted imides (or fully saturated amino-compounds) could be obtained by the action of amines and other organic bases, both aliphatic and cyclic, on germanium tetrachloride, and (2), by an examination of the properties of the substituted imides so obtained, to deduce their structure and hence, by inference, that of germanium imide itself.

On comparing the behaviour of the chlorides of other elements of the fourth group towards ammonia and organic bases with the results described in this paper, it is seen that germanium differs widely in this respect from all the other elements of this group, silicon excepted. An investigation of the interaction of titanium tetrachloride with ammonia and certain organic bases, carried out in this laboratory and shortly to be published, shows that germanium and titanium also closely resemble each other in this particular.

In contrast to the readiness with which germanium tetrachloride and ammonia interact, there appears to be no reaction between this gas and carbon tetrachloride and, although compounds of carbon tetrachloride with organic bases, *e.g.*, aniline, have been described (Hartung, J., 1918, **113**, 163), they are only formed extremely slowly except at high temperatures or in the presence of suitable catalysts. The tetrachlorides of tin and lead, on the other hand, react fairly readily both with ammonia and with organic bases, forming compounds of two types, *viz.*, $MCl_4,2NH_3$ and $MCl_4,4NH_3$, but Matthews, who has investigated the lead compounds (*J. Amer. Chem. Soc.*, 1898, **20**, 815), considers them to be true ammines. Germanium does not appear to form compounds of this type.

Silicon tetrachloride, however, when treated with ammonia and with organic bases, yields compounds which, whilst differing in some respects from those similarly obtained from germanium tetrachloride, resemble them closely in other important particulars. In both cases on treatment with ammonia the tetrachloride yields a

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stable di-imide. In the formation of silicon di-imide, however, clear evidence of the formation of an amide $Si(NH_2)_4$, stable below 0°, has been obtained (Lengfeld, *Amer. Chem. J.*, 1899, **21**, 531), whereas no analogous germanium compound has been prepared. Indeed, it has been shown (Thomas and Pugh, *loc. cit.*) that if such a compound exists it can only do so at temperatures below − 20°.

The action of silicon tetrachloride on primary amines is similar to that on ammonia. According to Lengfeld (*loc. cit.*), silicon tetraethylamide, $Si(NHEt)_4$, is obtained as the first product of its interaction with ethylamine, and a similar compound $Si(NHPh)_4$ was obtained by Reynolds (J., 1899, **75**, 474) by its action upon aniline. Both these compounds are stable, but they tend to decompose when warmed, giving off the free base. In this way, Reynolds obtained the silicon analogue of triphenylguanidine (J., 1900, **77**, 836), and, by heating this substance in a vacuum, the substituted di-imide, $Si(NPh)_2$. Germanium does not form an analogous stable fully-saturated compound.

On treating germanium tetrachloride with excess of ethylamine, a substance of composition $GeCl_4,6C_2H_5{\cdot}NH_2$ was obtained, analogous to that formed by the action of ammonia on the chloride. This was proved to be a mixture of one molecule of *germanium diethyldi-imide* (soluble in ether) with four molecules of ethylamine hydrochloride.

From aniline, a solid of composition $GeCl_4,4C_6H_5{\cdot}NH_2$ was always obtained whether chloride or base was in excess. This, too, was separated by means of ether into aniline hydrochloride and a soluble portion, which yielded only primary amine on hydrolysis and contained germanium, chlorine, and nitrogen in the ratio 1 : 2 : 2; it was thought to be the hydrochloride of the di-imide, $Ge(NPh,HCl)_2$, but, as Harold (*J. Amer. Chem. Soc.*, 1898, **20**, 1329) has described a compound $SiCl_2(NHPh)_2$, obtained by the action of one molecular proportion of silicon tetrachloride on four of aniline, the possibility that our compound might be dichlorogermanium dianilide had to be considered. This alternative was rejected when it was found that germanium diethyldi-imide reacts with ethylamine hydrochloride, liberating ethylamine. It is more probable that the interaction of germanium tetrachloride with aniline takes place according to the equations

$$(1)\quad GeCl_4 + 6Ph{\cdot}NH_2 = Ge(NPh)_2 + 4Ph{\cdot}NH_2,HCl$$

$$(2)\quad Ge(NPh)_2 + 2Ph{\cdot}NH_2,HCl = Ge(NPh,HCl)_2 + 2Ph{\cdot}NH_2$$

In no case was it possible to prepare fully saturated compounds by the action of primary amines on germanium tetrachloride, though, from the nature of the reaction between piperidine and the tetrachloride, it seems probable that unstable saturated compounds are actually first formed. Germanium tetrachloride reacts with eight molecular proportions of the base: $GeCl_4 + 8C_5H_{10}NH = Ge(NC_5H_{10})_4 + 4C_5H_{10}NH,HCl$. The stability of this saturated compound is readily explained by the fact that its nitrogen atoms are an integral part of the cyclic piperidine radicals, and are combined externally with germanium only, so that the formation of an unsaturated compound would involve rupture of the stable piperidine ring. Should such saturated compounds be formed, however, by the interaction of the chloride with bases such as primary amines, internal condensation can readily occur. It is presumed that this is the course actually taken by the reaction, and in the case of aniline the complete reaction would be represented by the equations

(3) $GeCl_4 + 8Ph{\cdot}NH_2 = Ge(NHPh)_4 + 4Ph{\cdot}NH_2,HCl$
(4) $Ge(NHPh)_4 = Ge(NPh)_2 + 2Ph{\cdot}NH_2$

followed by reaction (2).

Of the many compounds which might theoretically be expected from the interaction of germanium tetrachloride with ammonia and primary amines, only the imides and their salts and the compound, germanam, have actually been isolated.

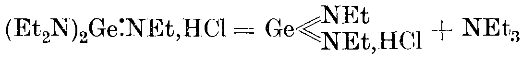
The difference in behaviour between silicon and germanium is more pronounced when the interaction of their chlorides with secondary amines is considered. According to Michaelis and Luxembourg (*Ber.*, 1896, **29**, 711), a silicon compound of the composition Et_2NSiCl_3 is thus obtained from diethylamine, but the reaction in the case of germanium does not proceed in this way and appears to be more complicated than is the case when primary amines are used. The solid final product obtained by the interaction of these substances in the gaseous state was found to contain 5—6 mols. of base per mol. of germanium tetrachloride, the lower value for this ratio being obtained when the product was heated at 90° in a current of air for several hours. When the reaction was carried out in ether, the ratio chloride : base was very nearly 1 : 6, but here again, prolonged heating in a current of air increased the value to 1 : 5. By using ether as solvent, the product of the reaction could be separated into a soluble and an insoluble portion. The latter consisted of a mixture of diethylamine and triethylamine hydrochlorides. In the ether-soluble fraction the Ge : Cl ratio was invariably 1 : 1, but the Cl : N ratio varied between 1 : 2 and 1 : 3, the former value being obtained when all traces of free base had been removed by heating in a vacuum or in a current of air at about 85°. On hydrolysis, the ether-soluble portion yielded primary amine only; no trace of ammonia or of secondary amine could be detected.

If it be assumed that an unstable fully-saturated compound is first formed, the course of the reaction could be represented by the following series of equations :

(1) $GeCl_4 + 8Et_2NH = 4Et_2NH,HCl + Ge(NEt_2)_4$
(2) $Ge(NEt_2)_4 = Ge(:NEt)(NEt_2)_2 + NEt_3$
(3) $NHEt_2,HCl + NEt_3 = NHEt_2 + NEt_3,HCl$
(4) $Ge(:NEt)(NEt_2)_2 + NHEt_2,HCl = Ge(NEt_2)_2:NEt,HCl + NHEt_2$

When moderated by cooling, or when carried out in ethereal solution, the reaction stops at this point, and the product contains, besides the germanium compound, a mixture of the hydrochlorides of di- and tri-ethylamine, the Ge : Cl : N ratio in the whole mass being 1 : 4 : 6. When this mixture is heated for some time under reduced pressure at about 85°, however, a further molecule of base is lost and the ratio becomes 1 : 4 : 5. This loss of base may occur in two ways; either

(5) $(Et_2N)_2Ge:NEt,HCl = Et_2N{\cdot}GeCl:NEt + NHEt_2$

or (6) 
$$(Et_2N)_2Ge:NEt,HCl = Ge\begin{cases} NEt \\ NEt,HCl \end{cases} + NEt_3$$

On hydrolysis, the product of (5) should yield a mixture of primary and secondary amines, whereas primary amine only was actually obtained; hence, taking into account all the available evidence, we are of opinion that the last stage of the reaction is represented by equation (6). The variation in the Cl : N ratio between 1 : 2 and 1 : 3 is easily explained by the comparatively high b. p. of triethylamine (89°) and its strongly basic character. Except after prolonged heating, the following equilibrium would be set up :

$$Ge(NEt)_2,HCl + NEt_3 \rightleftharpoons Ge(NEt)_2 + NEt_3,HCl$$

In order to investigate the behaviour of tertiary bases, experiments were made with diethylaniline. No reaction could be detected between this and germanium tetrachloride, either at the ordinary temperature or when the substances were heated together at 160°. This is not surprising : in diethylaniline no hydrogen is directly attached to the nitrogen atom of the base and this seems to be a necessary condition for the interaction of germanium tetrachloride with organic bases.

In general, except when the base used had a cyclic structure, the final product of the interaction was a compound containing germanium and nitrogen in the atomic ratio 1 : 2. Various structures may be assigned to these compounds; for example, the ammonia derivative may be symmetrical, $HN:Ge:NH$, or unsymmetrical, $N{:}Ge{\cdot}NH_2$. When ethylamine is the base used, in addition to these possibilities, the product may have any of the following structures : (1) $N{:}Ge{\cdot}NEt_2$; (2) $HN:Ge:NEt$; (3) $EtN:Ge:NEt$.

When the product contains no alkyl groups, it is difficult to distinguish between the symmetrical and the unsymmetrical form, but when alkyl groups are present, the structure can be ascertained by examining the products of hydrolysis : a compound of structure (1) would yield one molecule each of ammonia and secondary amine; structure (2) would yield one molecule each of ammonia and primary amine; and structure (3), two molecules of primary amine only.

The ether-soluble products of the interaction of germanium tetrachloride and ethylamine, diethylamine, and aniline were examined along these lines. In every case the base produced by hydrolysis consisted of primary amine only : no ammonia and no secondary amine could be detected. The compounds under discussion must, therefore, have the symmetrical structure $RN{:}Ge{:}NR$, and it may be concluded that germanium di-imide itself also has a symmetrical structure.

Ethylamine and diethylamine thus react with germanium tetrachloride to form the same substituted imide, which is symmetrical in structure and forms both mono- and di-hydrochlorides. From aniline, the dihydrochloride only was isolated.

EXPERIMENTAL.

The germanium chloride used was prepared by the method of Thomas and Pugh (J., 1926, 105). The redistilled material was stored in bulbs of about 1 c.c. capacity provided with a fine capillary tube 6—7 inches long. By means of this tube, the liquid could readily be introduced through a small opening into the reaction vessel without taking up moisture from the air. The estimation of germanium was carried out by precipitating the element as sulphide from solution in 6*N*-sulphuric acid. The sulphide was then dissolved in fairly concentrated ammonia and oxidised by means of 6% hydrogen peroxide in a platinum dish to the dioxide, which was finally ignited to constant weight.

The amines were supplied by Merck and were redistilled from freshly burnt lime before use. They were free from ammonia, and the primary and the secondary amine were also uncontaminated with each other. The aliphatic amines were estimated by distilling them into *N*/2-sulphuric acid and then titrating the excess of acid with *N*/2-sodium hydroxide, methyl-red being used as indicator. Aniline was estimated by Koppeschaar's method (Sutton, " Volumetric Analysis," 1914, p. 367). Check experiments on pure material showed that this method gives trustworthy results.

The Action of Aniline on Germanium Tetrachloride.

Experiments were made using excess of each of the reactants in turn. Owing to its greater volatility, excess of germanium chloride

(b. p. 86°) is more readily removed than excess of aniline (b. p. 184·4°), and the results obtained when the former was in excess are, therefore, the more trustworthy.

The reaction vessel consisted of a weighing bottle of about 75 c.c. capacity, for which a special stopper carrying two tubes had been made. The vertical inlet tube reached nearly to the bottom of the vessel, and to it, at a point about 1″ above the stopper, a side tube was sealed. The inlet tube was fitted with a movable glass rod, held in position by a short piece of tightly fitting but flexible rubber tube. The purpose of this was to allow of the inlet tube being kept clear of the solid formed during the reaction. The side tube was sealed to the outlet of a small wash-bottle of about 20 c.c. capacity. After the apparatus had been thoroughly dried, the tip of a sealed bulb of germanium chloride was broken and the liquid was rapidly transferred to the wash-bottle, the inlet tube being then immediately connected with drying vessels containing concentrated sulphuric acid. The exit tube from the reaction vessel was similarly connected with a drying train. In the reaction vessel, 30 c.c. of ether dried over sodium were placed, a known weight of dry aniline was added from a Lunge pipette, and the vessel attached to its stopper. The wash-bottle was then gently warmed in a water-bath, and a slow stream of dry air drawn through the apparatus. As the germanium chloride vapour came into contact with the aniline solution a thick white precipitate formed. As soon as all the germanium chloride had passed over, the ether was slowly evaporated, and the reaction vessel was then heated to 80° for 2 hours in a slow stream of dry air. In this way the excess of germanium chloride was removed. The reaction vessel was disconnected, quickly stoppered and weighed, and the composition of the product determined.

In a typical experiment of this series 0·48 g. of germanium tetrachloride and 0·74 g. of aniline were taken, and the solid product, a white powder almost insoluble in water but slowly soluble in dilute sulphuric acid, weighed 1·074 g. (Found : Ge, 12·6 ; Cl, 24·1 ; $C_6H_5{\cdot}NH_2$, 63·1% ; Ge : Cl : $C_6H_5{\cdot}NH_2$ = 1 : 3·92 : 3·91). It is clear that under these conditions 1 mol. of germanium tetrachloride reacts with 4 mols. of aniline.

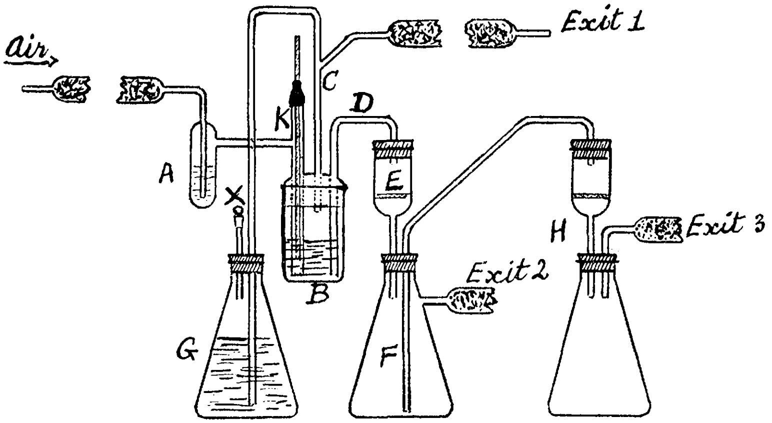
This product is not analogous to that obtained under all conditions by the action of ammonia under atmospheric pressure on germanium chloride, and further experiments were therefore carried out in the same apparatus but without a solvent. In a typical case, 1·2 g. of germanium chloride and 5·2 g. of aniline (app. 10 mols.) were taken. A white solid mass, smelling strongly of aniline, was obtained. Excess of base was removed by heating for several hours at 160° under 22 mm. The final product weighed 3·28 g. (Found : Ge, 12·6 ; Cl, 23·9 ; $C_6H_5{\cdot}NH_2$, 63·2% ; Ge : Cl : $C_6H_5{\cdot}NH_2$ = 1 : 3·89 : 3·92). It was dirty white in appearance, and a small quantity of white sublimate was observed in the reaction vessel just above the level of the liquid in the heating bath. When the main product of the reaction was treated with dilute sulphuric acid, it dissolved rapidly with the exception of a small pink residue. The product of the reaction thus appears to be the same no matter what proportions of the reacting substances are taken.

The sublimate just mentioned was next examined. The reactants in the molecular proportion 1 : 4 were introduced into the lower portion of a vertical tube constricted in the middle over a length of about $\frac{1}{2}''$. When the reaction was over, the pressure in the tube was reduced to 19 mm. and the lower portion was heated in a glycerol-bath at 140°. After 6 hours the whole of the solid, except a small residue weighing only 0·07 g., had sublimed into the upper portion of the tube, the constriction was sealed, and the sublimate analysed (Found : Cl, 25·5 ; $C_6H_5{\cdot}NH_2$, 64·3% ; Cl : $C_6H_5{\cdot}NH_2$ = 1 : 0·96). Though the analytical figures are rather high, the product appears to sublime practically unchanged. It is clear, however, that no separation of the product into its constituents can be effected by sublimation.

The experiments in which excess of aniline was used were not conclusive, inasmuch as any higher compound, if formed, might easily be decomposed at the high temperature required for the removal of the excess of base. Attempts were therefore made to remove this excess by the use of volatile solvents, *e.g.*, ether. These attempts failed because it was found that, in addition to the excess of base, the solvent also dissolves a compound containing all the germanium that had taken part in the reaction, leaving practically pure aniline hydrochloride undissolved.

The nature of this soluble product was next investigated. Because of the danger of the final product being contaminated with grease, an apparatus was constructed which contained no stopcocks (Fig. 1). The small wash-bottle A and the reaction vessel B were the same as those previously used, except that the exit tube C was modified as shown to allow of the introduction of fresh solvent from the reservoir G for washing the precipitated material, and a third tube D was added. This tube passed to the bottom of the reaction vessel and, by means of it, the products of the reaction could be transferred to the filter of sintered glass E. The filtrate was collected in the conical flask F, which was connected to a second filtering device H. The air inlet and the various exits were all protected from moisture by drying tubes. The wash-bottle A having been charged with a known weight of germanium tetrachloride, and B with aniline dissolved in dry ether, the stopper X was inserted, exits 2 and 3 were closed, and a slow stream of dry air was drawn through the apparatus by means of a pump attached to exit 1, A being meanwhile warmed in a water-bath. When all the germanium chloride had distilled over, exit 1 was closed and, by attaching the pump to exit 2, the contents of B were transferred to the filter. After filtration, the stopper X was removed, and the solid retained in the filter was washed several times with small quantities of fresh solvent drawn over from G. Stopper X was then replaced, exit 1 opened, and a current of dry air drawn over the insoluble material for several hours in order to remove the last traces of solvent. The dry solid, pure white and readily soluble in water, was then weighed and analysed. In a typical experiment, 1·80 g. of aniline and 1·539 g. of germanium chloride yielded 1·21 g. of this solid (Found : Cl, 26·6 ; $C_6H_5{\cdot}NH_2$, 72·3% ; Cl : $C_6H_5{\cdot}NH_2$ = 1 : 1·04) ; it was therefore aniline hydrochloride of 99·7% purity. It is thus clear that in this reaction one-half of the aniline is converted into aniline hydrochloride.

FIG. 1.



The examination of the portion soluble in ether was complicated by the fact that in every case a further small quantity of aniline hydrochloride slowly settled from the filtrate. A second filtration was therefore necessary, and the apparatus was constructed to provide for this (see Fig. 1). The clear filtrate finally obtained contained, in addition to the soluble product of the reaction, the excess of germanium tetrachloride and the solvent used. These were removed by heating the flask for about 6 hours at 85°, a current of dry air being meanwhile passed through it. In this way

1·64 g. of a glassy, non-crystalline substance were obtained (Found : Ge, 21·6; Cl, 22·1; $C_6H_5{\cdot}NH_2$, 54·0%; Ge : Cl : $C_6H_5{\cdot}NH_2$ = 1 : 2·15 : 1·95). When treated with water, this decomposed, forming a white solid, insoluble in water but slowly soluble in dilute sulphuric acid. It contained half the total aniline that had taken part in the reaction, and appeared to be the *dihydrochloride* of *germanium diphenyldi-imide*, formed according to the equation $GeCl_4 + 4NH_2Ph = 2NH_2Ph,HCl + Ge(NPh,HCl)_2$.

On hydrolysis of this substance, aniline was formed, but no ammonia or secondary base could be detected. The aniline formed was estimated and the amount liberated from this soluble fraction was found to be almost exactly one-half of the total quantity of aniline that had taken part in the reaction.

The Action of Ethylamine on Germanium Tetrachloride.

Preliminary experiments showed that the composition of the final product in this case depends on the proportions of the reacting materials, but as it was more convenient to use an excess of base, this course was generally followed. To investigate the reaction in the vapour phase, 0·62 g. of germanium chloride was introduced through a vertical tube into a bulb of about 75 c.c. capacity blown in the middle of a horizontal glass tube 25 cm. long. This tube was then immediately sealed. The bulb was next connected with a small apparatus for generating ethylamine from the hydrochloride of the base by heating it with freshly burnt lime. The other end of the bulb tube was connected with absorption vessels containing quick-lime and concentrated sulphuric acid respectively. As soon as the amine reached the bulb, a vigorous reaction took place in the vapour phase, and, to prevent loss of the extremely light product, a tap on the exit tube was closed except for brief intervals when it was opened to release any excess pressure. During the reaction the bulb was cooled in ice. When all the amine had distilled over, the bulb contained a white, moist, vitreous solid. Excess of amine was removed by passing a slow stream of dry air through the apparatus for several hours. The bulb was then disconnected, quickly stoppered, and weighed. The contents were dissolved in dilute sulphuric acid and the weight of the empty bulb found. The *product* (1·246 g.) was analysed (Found : Ge, 15·15; Cl, 30·5; $C_2H_5{\cdot}NH_2$, 55·6%; Ge : Cl : $C_2H_5{\cdot}NH_2$ = 1 : 4·11 : 6·17. $GeCl_4,6C_2H_5{\cdot}NH_2$ requires Ge, 15·0; Cl, 29·3; $C_2H_5{\cdot}NH_2$, 55·7%); its composition is thus analogous to that of the substance formed by the interaction of germanium tetrachloride and ammonia.

It was observed, however, that the Cl : $C_2H_5{\cdot}NH_2$ ratio was almost invariably between 4 : 5 and 4 : 6, not only when the reaction took place in the vapour phase, but also when excess of amine was passed into a solution of the chloride in ether; and, further, that the ratio depended on the length of time during which air was passed over the product. In another experiment, carried out as above except that the stream of air was continued for several hours longer, 0·89 g. of germanium chloride yielded 1·56 g. of a *product* closely resembling that previously described, but giving an entirely different analysis (Found : Ge, 18·8; Cl, 35·8; $C_2H_5{\cdot}NH_2$, 46·3%; Ge : Cl : $C_2H_5{\cdot}NH_2$ = 1 : 3·9 : 4·14. $GeCl_4,4C_2H_5{\cdot}NH_2$ requires Ge, 18·4; Cl, 36·0; $C_2H_5{\cdot}NH_2$, 45·6%). In this instance, therefore, 1 mol. of germanium tetrachloride appears to have reacted with 4 mols. of ethylamine.

When the reaction was carried out in ethereal solution, the product could be separated into two portions, as in the case of aniline: one soluble and the other insoluble in ether. A slightly modified form of the apparatus shown in Fig. 1 was used. 0·65 G. of germanium chloride was introduced into the reaction vessel through the inlet tube K. After withdrawal of the capillary, the clearing rod was quickly replaced, and 5 g. of ethylamine, stored over quick-lime in the vessel A, were slowly carried into the reaction vessel by means of a current of dry air. The thick white precipitate formed was transferred to the filter and washed with fresh ether in the usual way. The residue on the filter (1·016 g.) was analysed (Found : Cl, 42·8; $C_2H_5{\cdot}NH_2$, 54·4%. Cl : $C_2H_5{\cdot}NH_2$ = 1 : 0·96). Ammonia and secondary and tertiary bases were absent, and the insoluble product is clearly ethylamine hydrochloride.

The clear filtrate was evaporated at 60°, and excess of base and the last traces of solvent were removed by drawing a current of air through the apparatus. A white solid (0·51 g.) was thus obtained [Found : Ge, 45·4; $C_2H_5{\cdot}NH_2$, 54·8; Ge : $C_2H_5{\cdot}NH_2$ = 1 : 2·03. $Ge(NEt)_2$ requires Ge, 45·77; $C_2H_5{\cdot}NH_2$, 56·75%]. This *substance* reacted very vigorously with dilute sulphuric acid, much heat being evolved. A quantity of white solid, presumably germanium hydroxide, first separated, but this slowly dissolved. If the reaction were correctly represented by the equation

$$GeCl_4 + 6NH_2Et = Ge(NEt)_2 + 4EtNH_2,HCl,$$

0·65 g. of the tetrachloride should have yielded 0·99 g. of ethylamine hydrochloride and 0·48 g. of germanium diethyldi-imide instead of the 1·016 g. and 0·51 g. respectively actually obtained.

The constitution of the supposed substituted imide was investigated in the following way. The ethereal solution, containing about 0·5 g. of the soluble product, was evaporated to small bulk and then hydrolysed by boiling with a concentrated solution of sodium hydroxide. The volatile bases were converted into hydrochlorides by absorbing them in hydrochloric acid and evaporating the solution to dryness. The white crystals thus obtained were extracted three times with dry chloroform, twice with dry ether, and finally with a saturated solution of ammonium chloride in absolute alcohol. No residue remained, and consequently the crystals did not contain ammonium chloride. This was confirmed by adding Nessler's reagent to their solution; a white precipitate was formed, in no way resembling the precipitate obtained when traces of ammonium chloride were similarly treated. Since no ammonia is formed on hydrolysis, the formation of secondary amine is also excluded. This was confirmed by dissolving some of the crystals in hydrochloric acid and treating the solution with sodium nitrite in the cold. No nitrosoamine separated. On extraction with ether and addition of dilute sodium hydroxide, no colour developed in the ethereal extract. Finally, the ether was removed by evaporation, and the remaining liquid poured into a solution of phenol in concentrated sulphuric acid. No coloration appeared. On the other hand, the crystals, when treated with potassium hydroxide and chloroform, gave the characteristic carbylamine reaction. Primary amine is thus the only base produced by hydrolysis, and the substance must, therefore, have a symmetrical structure.

The Action of Diethylamine on Germanium Tetrachloride.

For the reaction in the vapour phase, the apparatus previously described was used, except that the diethylamine was introduced by passing a slow stream of dry air through a small wash-bottle in which the liquid was standing over freshly burnt lime. A vigorous reaction took place in the vapour phase, and a fine white solid formed which dissolved almost completely in the excess of base used. During the reaction the bulb was kept cold, and subsequently the excess of base was removed by passing a stream of dry air through the cooled bulb. 1·12 G. of germanium chloride yielded 3·17 g. of a crystalline white solid, which was dissolved in dilute sulphuric acid and then analysed [Found: Ge, 10·7; Cl, 22·6; basic N, 12·46; Ge : Cl : N = 1 : 4·2 : 6·04. The solid product of the reaction

$$GeCl_4 + 6NHEt_2 = (NEt_2)_2 Ge{:}NEt,HCl + 2NHEt_2,HCl + NEt_3,HCl$$

requires Ge, 11·12; Cl, 21·75; H, 12·83%].

In a second experiment, the reaction vessel was kept at 30° for 3 hours after the reaction was over, dry air being meanwhile passed through the apparatus. The vessel was then exhausted, and the temperature raised to 95°, at which it was maintained for 8 hours.

Oily drops of a colourless liquid were seen on the sides of the tube above the level of the liquid in the heating bath, but these gradually disappeared and a white crystalline solid remained [Found : Ge, 12·6; Cl, 24·3; N, 12·23. Ge : Cl : N = 1 : 3·97 : 5·03. The product of the reaction

$$GeCl_4 + 5NHEt_2 = Ge(NEt)_2,HCl + 2NEt_3,HCl + NHEt_2,HCl$$

requires Ge, 12·53; Cl, 24·5; N, 12·08%; Ge : Cl : N = 1 : 4 : 5].

Similar results were obtained when the reaction was carried out in ether. 0·96 G. of germanium chloride was dissolved in 75 c.c. of dry ether, and an excess of diethylamine was passed into the solution. On evaporation to dryness and removal of the last traces of free base and of solvent at a low temperature by means of a current of air, 2·47 g. of a white powder readily soluble in dilute sulphuric acid were obtained (Found : Ge, 11·1; Cl, 22·4; N, 12·4%. Ge : Cl : N = 1 : 4·12 : 5·8).

Another specimen of this material, prepared in a similar way, was heated in a vacuum to 85° for 5 hours. The product was faintly yellow and readily soluble in sulphuric acid (Found : Ge, 11·7; Cl, 22·6; N, 11·4%; Ge : Cl : N = 1 : 3·95 : 5·05). From these experiments it is clear that the reaction follows the same course whether carried out in the vapour phase or in ethereal solution.

To determine the nature of the 1 : 4 : 5 substance, 0·9 g. of germanium tetrachloride was dissolved in ether and treated with an excess of diethylamine. The apparatus shown in Fig. 1 was again used. The precipitated material was filtered, and washed eight times with fresh solvent. The residue was thoroughly dried by means of a current of air, and weighed 1·4 g. (Found : Cl, 30·4; N, 12·3. Cl : N = 1 : 1·03. Calc. for $NEt_3,HCl + 2NHEt_2,HCl$: Cl, 30·73; N, 11·8%). The substance when treated with alcoholic potassium hydroxide and chloroform gave no smell of carbylamine, but when a cold solution of sodium nitrite was added to its acid solution, oily drops of nitrosoamine were obtained.

The ethereal extract was evaporated to dryness, and the residue heated at 80° in a current of air for 3 hours. A white crystalline solid weighing 0·97 g. remained, and was dissolved in dilute sulphuric acid and analysed [Found : Ge, 30·74; Cl, 14·91; N, 14·4; Ge : Cl : N = 1 : 0·99 : 2·45. $Ge(:NEt,HCl)(:NEt)$ requires Ge, 37·2; Cl, 18·2; N, 14·5%]; if this monohydrochloride is the final product of the action it must still have been mixed with triethylamine.

In another experiment carried out in the same way except that the final product was heated in a vacuum for 5 hours at 90°, the following results were obtained : 1·02 g. of germanium chloride yielded 1·46 g. of material insoluble in ether (Found : Cl, 30·1;

N, 11·7%; Cl : N = 1 : 0·99). This confirms the result previously obtained. The final residue from the ethereal extract contained some substance insoluble in sulphuric acid, probably produced by the action of the base on the rubber holding the clearing tube in position. Corrected for this impurity, the product weighed 0·89 g. (Found: Ge, 32·06; Cl, 16·6; N, 13·0%; Ge : Cl : N = 1 : 1·06 : 2·1). The substance thus appears to be the *monohydrochloride* of germanium diethyldi-imide; this view was confirmed by boiling it with sodium hydroxide and examining the volatile products of the hydrolysis: neither ammonia nor secondary amine could be detected, but the carbylamine test showed that much primary amine had been produced.

Action of Diethylaniline on Germanium Tetrachloride.

It was considered advisable to investigate whether or not tertiary bases will react with germanium tetrachloride. Accordingly, diethylaniline (excess over 4 mols.) was added to germanium chloride; in the cold no obvious reaction occurred and the liquids separated into two layers, the lower being germanium tetrachloride. After about an hour, a few tiny crystals appeared at the boundary between the two liquids, but as the quantity did not increase either on long standing or on warming, they were deemed to be crystals of the hydrochloride of the base, their formation being ascribed to traces of water which had eluded the traps.

The mixture was then warmed under reflux to 90° in a glycerol-bath, but no change could be detected after several hours. The apparatus was then rearranged so that distillation under reduced pressure could take place, an absorption tube containing pellets of solid sodium hydroxide being placed between the U-tube in which the distillate was collected and the pump to absorb escaping germanium chloride. The temperature was then gradually raised to 160°, and after an hour only a small quantity of liquid (containing no germanium) remained in the distillation vessel. In the receiver a quantity of yellow liquid, approximately equal in volume to the diethylaniline originally used, had collected (Found: Ge, 2·3; Cl, 4·8; $NPhEt_2$, 91·6%; Ge : Cl : $NPhEt_2$ = 1 : 4·2 : 19·6), and was probably a solution of germanium chloride in diethylaniline. Practically the whole of the germanium chloride had been absorbed in the vessel containing sodium hydroxide.

A similar result was obtained when the reactants were mixed in ether. The composition of the liquid remaining after removal of ether was variable, and, when it was kept for some time under low pressures, all the germanium tetrachloride was removed. Diethylaniline is thus without action on germanium tetrachloride.

The Action of Piperidine on Germanium Tetrachloride.

In experiments with this base special precautions were taken to exclude carbon dioxide as well as moisture from the reaction vessel. Guard tubes containing soda–lime were used for this purpose. Germanium tetrachloride (1·11 g.) was placed in a reaction vessel similar to that previously described, except that the inlet tube did not pass to the bottom of the vessel, and the clearing apparatus was dispensed with. This vessel was sealed to a small wash-bottle in which the piperidine was kept in contact with freshly burnt lime. The base was introduced into the reaction vessel by heating the wash-bottle in a glycerol-bath and passing a slow current of dry air through the apparatus. The considerable excess of base used was removed from the reaction vessel, when the reaction was finished, in a similar way. A white crystalline solid (4·47 g.), partly soluble in piperidine, but sparingly soluble in water and slowly in dilute sulphuric acid, was thus obtained (Found: Ge, 7·6; Cl, 15·4; $C_5H_{11}N$, 71·9%; Ge : Cl : $C_5H_{11}N$ = 1 : 4·1 : 8·05).

The substance was then prepared in dry ether, and the precipitate filtered, washed with fresh quantities of ether in the usual way, dried, weighed (1·57 g.), and analysed (Found: Ge, 2·4; Cl, 27·8; HCl, 28·6; $C_5H_{11}N$, 67·6%; Cl : $C_5H_{11}N$ = 1 : 1·02); it was therefore piperidine hydrochloride.

The ethereal extract was evaporated to dryness and then heated for several hours in a vacuum at 60°. The residue was a viscous liquid which, however, on cooling and standing over-night, crystallised. These white crystals were further heated under reduced pressure at 95° for 2 hours, then cooled, and weighed (1·49 g.) [Found: Ge, 17·4; Cl, 0·6; $C_5H_{11}N$, 81·8; Ge : $C_5H_{11}N$ = 1 : 4·01. $Ge(C_5H_{10}N)_4$ requires Ge, 17·8; $C_5H_{11}N$, 83·2%]; they were readily soluble in dilute sulphuric acid.

From these experiments it is seen that germanium chloride and piperidine react in the molecular proportion 1 : 8, and that the product consists of a mixture of four molecules of piperidine hydrochloride with one of a fully saturated *compound* $Ge(C_5H_{10}N)_4$.

Summary.

(1) In its action on organic bases germanium tetrachloride resembles silicon tetrachloride much more closely than it does the other elements of the fourth group. They differ, however, in important respects.

(2) Germanium tetrachloride reacts with 4 mols. of aniline to give aniline hydrochloride and the dihydrochloride of germanium diphenyldi-imide. No other compound could be detected.

(3) With ethylamine, germanium chloride reacts in two pro-

portions, forming $GeCl_4,4C_2H_5\cdot NH_2$ and $GeCl_4,6C_2H_5\cdot NH_2$. The latter is analogous to the ammonia compound. It was separated by treatment with ether into ethylamine hydrochloride and germanium diethyldi-imide.

(4) On treatment with diethylamine, germanium tetrachloride gives, in the first place, a product in which the ratio $GeCl_4 : NHEt_2 = 1 : 6$. This, however, readily loses base, giving a substance in which the ratio $Ge : Cl : N = 1 : 4 : 5$. This product also was separated into a mixture of diethylamine and triethylamine hydrochlorides, on the one hand, and the monohydrochloride of germanium diethyldi-imide on the other. A mechanism for the reaction is suggested.

(5) Germanium tetrachloride is without action on tertiary bases.

(6) Germanium tetrachloride reacts readily with 8 mols. of piperidine, giving piperidine hydrochloride and a fully saturated compound $Ge(C_5H_{10}N)_4$. Hence, it is concluded that an unstable fully saturated compound is the first product of the interaction of germanium tetrachloride with ammonia and organic bases.

(7) The unsaturated, ether-soluble products of the interaction of germanium chloride with organic bases yield, on hydrolysis, primary amines only. These substituted imides are, therefore, symmetrical in structure, and it is considered that germanium di-imide itself is also symmetrical.

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