[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# The Partial Hydrolysis of Germanium Tetrachloride[1]

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The partial hydrolysis of germanium tetrachloride at −78° in various organic solvents has led to the isolation of only solid, polymerized products with compositions close to $Ge_2O_3Cl_2$. The hydrolysis reaction was found to cease when the aqueous phase had absorbed a sufficient quantity of the liberated HCl to bring its concentration to about 6.5 molar. Calculations based on an analytical examination of the reaction mixtures indicate that small amounts of one or more members of what would be a homologous series of oxychlorides, $Ge_nO_{n-1}Cl_{2n+2}$, are also possible products of the hydrolysis.

Recent work in this Laboratory has served to arouse considerable interest in the oxyhalides of silicon, which are compounds taking the form of a homologous, linear series, $Si_nO_{n-1}X_{2n+2}$, and a cyclic tetramer, $(SiOX_2)_4$, where X represents chlorine or bromine and $n$ is an integer greater than one.[2–5] Of particular interest is the method of preparation conceived by Schumb and Stevens,[5] which involves the controlled, low temperature hydrolysis of silicon tetrachloride in ethereal solution.[5] This technique has been further extended by Schumb and Lefever in their partial hydrolysis of hexachlorodisilane, whereby a new series of silicon oxychlorides with the general formula $Si_{2n+2}O_nCl_{4n+6}$ has been shown to exist.[6] It is interesting to note that cyclic oxychlorides have not been isolated from either of these reactions.[5–7]

In a recent publication Schwarz and Knauff have described the partial hydrolysis of tetramethoxygermane and tetraisopropoxygermane.[8] Hexaisopropoxydigermoxane, $Ge_2O(OC_3H_7)_6$, was isolated from the latter reaction by very careful vacuum fractionation. Polymerized solid products with compositions approaching $Ge_2O_3(OC_3H_7)_2$ were also reported.

Two oxychlorides of germanium have been reported in the literature. Hexachlorodigermoxane, $Ge_2OCl_6$, has been prepared by the lengthy reaction of $GeCl_4$ with oxygen at 950°.[9] This preparation has been repeated and confirmed in the course of the present work. Another oxychloride, $GeOCl_2$, has been reported as the product of the reaction of trichlorogermane with silver oxide.[10] This reaction was also repeated and the authors have submitted a note for publication which indicates that the earlier work was in error.

The reported existence of $Ge_2OCl_6$, which would be the first member of a homologous series of germanium oxychlorides, $Ge_nO_{n-1}Cl_{2n+2}$, suggested that the partial hydrolysis of $GeCl_4$ might yield this compound as well as higher members of this series. On the contrary, it was found that no volatile oxychlorides of germanium could be isolated from this reaction, although small quantities seem to have been formed. The principal product was found to be a polymerized solid with the composition $Ge_2O_3Cl_2$.

## Experimental

The partial hydrolysis technique has been thoroughly described in earlier publications.[5,7] As applied here it was carried out at −78° in one of the three solvents: ethyl ether, chloroform or $n$-pentane. The amount of water employed was varied between $GeCl_4$:$H_2O$ molar ratios of 5:1 and 1:1 with values near 2:1 being more commonly used. The variation of solvent:$GeCl_4$ ratio was found to have no observable effect down to volume ratios of 2:1 which was the minimum used.

The $GeCl_4$ was prepared both by the reaction of $GeO_2$ with hydrochloric acid as described in "Inorganic Syntheses,"[11] and by the direct chlorination of the metal. The latter is the more efficient method if the metal is available. The product was carefully fractionated from anhydrous $Na_2CO_3$ to remove HCl when the first method was employed, and from $Hg_2Cl_2$ to remove $Cl_2$ when the direct chlorination was used.

The samples were analyzed by the following method. Samples were weighed in small, thin-walled glass bulbs which were then broken in an excess of water in a stoppered flask. Chloride was determined by titration with standard base, after which the solution was boiled to dissolve $GeO_2$ and 10 g. of $d$-mannitol was added. When cool, the germanium dioxide-mannitol complex acid was also titrated with standard base. A Beckman Model G $p$H meter was used to determine both end-points. The oxygen contents of the products were calculated from the valence requirements. No evidence was ever noted of degradation to lower valent germanium or to the metal. Molecular weights were determined cryoscopically in benzene.

The solvents were Mallinckrodt analytical reagent grade ethyl ether, chloroform and benzene, and Phillips pure pentane. All of these were found to be satisfactory without further treatment.

Lengthy manipulations of the hydrolyzable materials were carried out in a carefully maintained dry-box. It was found, however, that many steps could be carried out in the open air without introducing detectable errors if the exposure was kept at a minimum.

The fractional distillations were carried out in a 50 × 10 cm. column packed with $^3/_{32}$-inch Fenske helices.

## Results and Discussion

Repeated attempts to isolate volatile germanium oxychlorides from the partial hydrolysis products by low pressure fractional distillation were unsuccessful. In every low pressure fractionation of the hydrolysis products only unreacted $GeCl_4$ and the solvent were distillable, and a large non-volatile residue remained which consisted of an extremely viscous oil or glassy solid. Removal of the volatile materials by suction at room temperature gave the same results. When the volatile materials from

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[1] Based on part of a thesis presented by D. M. Smyth to the Department of Chemistry, Massachusetts Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] W. C. Schumb and D. F. Holloway, *ibid.*, **63**, 2753 (1941).

[4] W. C. Schumb, *Chem. Revs.*, **31**, 587 (1942).

[5] W. C. Schumb and A. J. Stevens, THIS JOURNAL, **72**, 3178 (1950).

[6] W. C. Schumb and R. A. Lefever, *ibid.*, **75**, 1513 (1953).

[7] J. Goubeau and R. Warncke, *Z. anorg. Chem.*, **259**, 109 (1949).

[8] R. Schwarz and K. G. Knauff, *Z. anorg. allgem. Chem.*, **275**, 193 (1954).

[9] R. Schwarz, P. W. Schenk and H. Giese, *Ber.*, **64B**, 362 (1931).

[10] R. Schwarz and F. Heinrich, *Z. anorg. allgem. Chem.*, **209**, 273 (1930).

[11] W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 109.

four successive hydrolysis reactions were combined and fractionated, a small quantity of non-volatile solid was obtained, indicating that some volatile species was formed which was decomposed by the heat of the subsequent distillation. This volatile material could have been $Ge_2OCl_6$ which has been found to be thermally unstable to a considerable extent. When prepared by Schwarz's method,[9] this compound was isolated in only small quantities by distillation from ten to twenty times as much crude product. Decomposition was also indicated by the difficulty in obtaining a consistent boiling point for the $Ge_2OCl_6$. The best value seemed to be 56° at 13.5 mm., which is considerably higher than the previously reported value. On redistillation at 13.5 mm. a ten-gram sample of $Ge_2OCl_6$ decomposed completely to a glassy white solid. This behavior was strikingly similar to that of the hydrolysis products and is in accord with the concept that $Ge_2OCl_6$ may have been a minor hydrolysis product.

The non-volatile residues varied considerably in consistency, and analyses showed a parallel trend whereby the more viscous materials were relatively poorer in chlorine content. It was found that extraction with anhydrous benzene left a white, insoluble solid, and the analyses of these residues showed compositions very close to $Ge_2O_3Cl_2$, depending on the efficiency of the extraction. As examples, one product which was extracted for one day at room temperature gave a residue with a Cl:Ge atomic ratio of 1.10:1.00; another which was extracted for a day with hot benzene in a Soxhlet extractor gave a ratio of 0.97:1.00. These correspond to approximate formulas of $Ge_{2.00}O_{2.90}Cl_{2.20}$ and $Ge_{2.00}O_{3.03}Cl_{1.94}$, respectively. The change of composition due to the extraction indicated that relatively chlorine-rich material was being removed (presumably $GeCl_4$ and possibly $Ge_2OCl_6$ or higher members of this series). A number of these experiments gave similar results regardless of whether ethyl ether, chloroform or *n*-pentane was employed as the solvent during the hydrolysis. The solid distillation residue from a preparation of $Ge_2OCl_6$ by the thermal oxidation of $GeCl_4$ was also subjected to this extraction treatment and yielded a similar residue with the composition $Ge_{2.00}O_{3.08}Cl_{1.84}$. This is in agreement with the earlier experiments which indicate that $Ge_2OCl_6$ is transformed into the solid polymer by the action of heat.

These solids were found to retain the benzene very tenaciously, and even several hours of pumping would not remove the last few percentage of solvent. For this reason the compositions were derived from the Cl:Ge ratios rather than the absolute percentages. This was justified by the reliability of the analytical method as indicated by its accuracy when used on samples not containing benzene.

The general composition of $Ge_2O_3Cl_2$ finds some interesting parallels in other work. Schwarz has reported that the partial hydrolysis of tetraisopropoxygermane leads to considerable quantities of a solid polymer with the composition $Ge_2O_3(OC_3H_7)_2$.[8] Schwarz describes this product as having a fibrous structure and postulates a linear type of polymerization. No such appearance was noted in $Ge_2O_3Cl_2$ and this may be due to a more random type of polymerized structure. Work in this Laboratory on the thiohydrolysis of $SiCl_4$ has led to the isolation of solid products having compositions very close to $Si_2S_3Cl_2$.[12] The so-called silicoformic anhydride, $Si_2O_3H_2$, is also of similar composition. These examples indicate that this composition has a much greater generality than has been previously realized.

It was found in the hydrolyses in which the solvent was pentane or chloroform, that much of the water was not consumed by the hydrolysis reaction. In ether solution a much greater quantity of water was consumed by the reaction. This phenomenon was attributed to the fact that $GeCl_4$ is not hydrolyzed by relatively concentrated solutions of hydrochloric acid.[13,14] This is a marked difference from the case of $SiCl_4$. Apparently the HCl liberated by the hydrolysis was rapidly dissolved into the aqueous phase until its concentration reached the limiting value, at which point the hydrolysis ceased. An examination of these unreacted aqueous phases showed this equilibrium concentration of hydrochloric acid with $GeCl_4$ to be 6.5 ± 0.5 molar in the reactions in which ethyl ether or chloroform were the solvents. Determinations in pentane solution were handicapped by the fact that emulsions were formed of the pentane phase in the aqueous phase. Presumably the extent of hydrolysis could be increased by the use of larger amounts of water or by the addition of an acceptor for the HCl. The limiting concentration of HCl at which hydrolysis of $GeCl_4$ ceases is in reasonable agreement with other published work in which the limiting value was found by less direct means.[13,14]

Ethyl ether is a much better solvent for HCl than chloroform and *n*-pentane, and for this reason the hydrolysis proceeded to a much greater extent in this solvent, since more HCl was required to make the aqueous phase 6.5 molar in HCl in equilibrium with the ether phase. The water was completely consumed by the reaction in ether solution when the initial $GeCl_4:H_2O$ molar ratio was greater than about 2.2:1.0. On the other hand, the reaction was not complete in the other two solvents even at $GeCl_4:H_2O$ ratios as high as 5.0:1.0.

It is interesting to note that in the case of all three solvents used in this study, ethyl ether, *n*-pentane and chloroform, only minute traces of $GeO_2$ were observed as a hydrolysis product. In the partial hydrolysis of $SiCl_4$ it has been shown that ethers are the only suitable solvents, since a wide variety of other solvents led to the formation of only silica.[5]

An analytical study of this reaction has further clarified the nature of the hydrolysis products. For this purpose several hydrolyses were carried out, and after the solvent was removed by distillation, occasional samples were withdrawn from the distilling pot while the unreacted $GeCl_4$ was being removed. These samples were analyzed for chlorine and germanium and the molecular weights were determined by the freezing point depression of ben-

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TABLE I

| | | | | | $n$ | | | Concn. of products, moles/100 g. ($a$ = 1) | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Cl | Ge | Total % accounted for | $M$ | $a = 1$ | $a = 4$ | $a = \infty$ | $(Ge_2O_3Cl_2)_a$ | $Ge_nO_{n-1}Cl_{2n+2}$ |
| A1 | 1.797 | 0.482 | 99.74 | 239 | 1.15 | 1.15 | 1.15 | 0.0008 | 0.418 |
| A2 | 1.762 | .490 | 99.63 | 250 | 1.21 | 1.19 | 1.18 | .0054 | .396 |
| B1 | 1.823 | .484 | 100.71 | 230 | 1.11 | 1.09 | 1.08 | .0028 | .430 |
| B2 | 1.714 | .505 | 99.91 | 265 | 1.31 | 1.24 | 1.20 | .0132 | .365 |
| C1 | 1.627 | .530 | 100.08 | 313 | 1.64 | 1.51 | 1.43 | .0179 | .302 |
| C2 | 1.600 | .534 | 99.98 | 339 | 1.80 | 1.69 | 1.62 | .0141 | .281 |
| C3 | 1.577 | .541 | 99.99 | 364 | 1.97 | 1.85 | 1.77 | .0142 | .261 |
| D1 | 1.642 | .523 | 99.87 | 295 | 1.51 | 1.38 | 1.30 | .0214 | .319 |
| D2 | 1.613 | .532 | 100.00 | 314 | 1.65 | 1.49 | 1.40 | .0219 | .296 |
| D3 | 1.571 | .544 | 100.20 | 336 | 1.81 | 1.58 | 1.45 | .0282 | .270 |
| D4 | 1.500 | .569 | 100.76 | 383 | 2.21 | 1.80 | 1.57 | .0395 | .221 |

zene. The oxygen content could be calculated by the valence requirements and the percentage totals thus accounted for are shown in Table I.

If the products are assumed to be composed of only $(Ge_2O_3Cl_2)_a$ and unreacted $GeCl_4$, the concentration of the oxychloride and its degree of polymerization $a$ can be calculated from the data. In each case negative quantities of $(Ge_2O_5Cl_2)_a$ and negative values of $a$ are required to satisfy the data. The postulate is obviously incorrect. If, on the other hand, the products are assumed to be $(Ge_2O_3Cl_2)_a$ and members of the linear homologous series, $Ge_nO_{n-1}Cl_{2n+2}$ (which includes $GeCl_4$ as the case $n = 1$), the relative amounts of each can be calculated along with corresponding values of $n$ for various values of $a$, the degree of polymerization of the $(Ge_2O_3Cl_2)_a$. The results of these calculations are shown in Table I. A and B represent two hydrolyses in which $n$-pentane was the solvent, and C and D were two reactions in which ethyl ether was the solvent. Only two samples were withdrawn from each of the pentane solutions because of the relatively smaller extent of hydrolysis in this solvent as explained earlier. The calculations were based on the following formulas, which can be easily derived.

$$n = \frac{2a[200 + M(\text{Ge} - \text{Cl})] - 2M\text{Ge}}{M(2\text{Ge} - \text{Cl}) - 200} \tag{1}$$

$$y = \frac{\text{Cl} - \text{Ge}}{n + 2} \tag{2}$$

$$x = \frac{\text{Ge}(n + 2) - n(\text{Cl} - \text{Ge})}{2a(n + 2)} \tag{3}$$

In these equations $y$ represents the concentration of $Ge_nO_{n-1}Cl_{2n+2}$ in moles per 100 g., and $x$ denotes the concentration of $(Ge_2O_3Cl_2)_a$. Cl and Ge represent the gram atoms per 100 g. of the two elements and $M$ is the experimental molecular weight. $a$ and $n$ have the same significance as in the preceding discussion. $a$ has been left as an adjustable parameter in the equations.

It is easily seen that the value of $a$ has very little effect on the calculated quantities, except, of course, the concentration of $(Ge_2O_3Cl_2)_a$, which is inversely proportional to $a$. This means that the calculations offer no useful information as to the degree of polymerization of the $Ge_2O_3Cl_2$. All of the derived values and the trends shown in each experiment (with the single exception of the value of $x$ for sample C-1) are consistent with expectations. Thus $n$ is always slightly greater than one and increases as $GeCl_4$ is removed, and the concentration of $Ge_nO_{n-1}Cl_{2n+2}$ decreases and that of $(Ge_2O_3Cl_2)_a$ increases as $GeCl_4$ is removed. Thus the postulated product mixture is compatible with the data. The indication is that small quantities of the linear oxychlorides are formed, and this is in agreement with the experimental fact that some volatile products were detected which polymerized during distillation attempts. The bulk product appears to be the material $(Ge_2O_3Cl_2)_a$ with $a$ having possible values from one to infinity (presumably as $a$ approaches infinity the material would become colloidal in nature). The observation that the viscous, non-volatile products had a pronounced tendency to form gel-like structures with benzene lends some support to the idea that the product is present as a colloidally dispersed phase.

Differential error functions have been derived for equations 1, 2 and 3, and their evaluations at the experimental points with assumptions of reasonable error limits have indicated that the calculated values are significant.

The authors wish to point out very clearly that the assumptions made above are not unique in fitting the data. Several hypothetical mixtures can be proposed which are equally compatible, but the products discussed above are much more obvious choices in view of the experimental facts and the chemistry of analogous silicon compounds which can often profitably be compared with that of germanium. It should also be stated that the indicated amounts of the linear compounds, $Ge_nO_{n-1}Cl_{2n+2}$, could very well be expressed entirely in terms of the known member of this series, $Ge_2OCl_6$, but the more general case has been used here.

The germanium analog of trichlorosilanol, $SiCl_3OH$, has not been observed during this investigation. The silicon compound was reported by Goubeau and Warncke[7] who isolated it from the partial hydrolysis of $SiCl_4$ by fractional distillation at atmospheric pressure, and by Emeléus and Welch[15] from the photoöxidation of trichlorosilane. Actually, serious discrepancies exist between the descriptions of this compound provided by the two separate investigations. The presence of the germanium analog, once the hydrolysis solvent has been removed and the product has reached the boiling point of $GeCl_4$, was eliminated by the analytical data which indicate that the product consists only of germanium, chlorine and oxygen at this point. An additional study has shown that the water which is consumed is essentially quantitatively con-

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verted to HCl by this point in the experiment. A weighed amount of water was used for a hydrolysis and 98.6% of its theoretical equivalent as HCl was captured and determined during the distillation. Both of these facts show that there is little hope of isolating $GeCl_3OH$ from this reaction by distillation, but they do not eliminate its existence during the earlier stages of the reaction where it may be formed and then consumed by rapid condensation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

# Some Heteropoly 6-Molybdate Anions: Their Formulas, Strengths of their Free Acids, and Structural Considerations[1]

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A study of 6-molybdo heteropoly anions, in which tervalent aluminum, chromium, iron or cobalt functions as central atom, indicates that $[(XO_6Mo_6O_{15})_n]^{-3n}$ is a reasonable formula for these anions, rather than $[X^{+3}(MoO_4)_6]^{-9}$, as given in an older notation. $XO_6$ is an octahedral group containing the central atom and $n$ is an undetermined integer which is probably small but probably not unity. Structural considerations, which are included, suggest that the compounds may be bimolecular. A method is given for the preparation of ammonium 6-molybdoferrate(III) in a pure state. The free acid of the aluminum complex is described. It is made evident that there is neither a general formula nor a single structural model which can represent 6-heteropoly anions as a class.

Recent work[3] on the determination of the valence of a heteropoly anion of the 12-molybdo class suggested a restudy of 6-molybdo heteropoly anions containing tervalent aluminum, chromium, iron and cobalt as central atoms.

These 6-molybdo compounds, discovered a century ago,[4] were the subject of several early investigations,[5-7] in whch dualistic "oxide" formulas were used. Miolati-Rosenheim[8-11] formulas, modifications thereof, and formulas implying the same anionic composition have been widely used by recent workers[12-17] to represent these and other 6-heteropoly compounds. Examples of such formulas are: $(NH_4)_3H_6[X(MoO_4)_6]\cdot 10H_2O$ or $(NH_4)_3H_6[XMo_6O_{24}]\cdot 10H_2O$, where X represents one of the tervalent elements listed above.

In 1929, Pauling[18] accepted Rosenheim's formulas and structure for the 6-heteropoly anions considered herein. In the same paper he rejected the Miolati–Rosenheim formulas for 12-heteropoly compounds and made the fundamental suggestions concerning the considerations governing their structures which, after certain important modifications, led to the "Keggin Type" formula for 12-heteropoly anions.[3,19-23]

In 1937, Anderson[13,24] proposed a structure for 6-heteropoly anions based on the principles made evident by the above-mentioned studies of 12-heteropoly compounds. The central atom in the Anderson model is in octahedral coördination with oxygen, and the central octahedron is surrounded by a hexagon of $MoO_6$ octahedra. All of the octahedra lie in one plane. The anion, as in the Rosenheim formula, contains twenty-four oxygen atoms. This hypothetical configuration received experimental support when Evans[25] showed by X-ray analysis that it is an extremely probable structure for the 6-molybdotellurate(VI) anion in $(NH_4)_6[TeO_6Mo_6O_{18}]\cdot 7H_2O$ and $K_6[TeO_6Mo_6O_{18}]\cdot 7H_2O$. Evans has recently reported further X-ray evidence which conclusively establishes his former view.[26]

The work described in this paper, on 6-molybdo complexes of tervalent metals, is not in agreement with the views of Rosenheim and Schwer.[9] Their conclusions were based on conductivity measurements (which Rosenheim observed might also be interpreted as consistent with normal salt formulas) and, especially, on dehydration data. Their results

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