reactions were carried out in glass-stoppered 250 ml. Erlenmeyer flasks which had been dried at 140° and cooled in a desiccator. 10.00 ml. of ethyl ether saturated with water, and 10.00 ml. of ethyl ether containing 4.2 mg. per ml. of glacial acetic acid were placed in each flask. 3.00 ml. of the xylene solution of polymer were added, and zero time taken when the last drop of solution left the pipet. A blank with no polymer was titrated to determine original $H_2O$ content. The hydrolysis reaction was stopped by adding a large excess of methanol and glacial acetic acid (25 and 5 ml.) which had been pretitrated to a red end-point with Karl Fischer reagent. During the titration a yellow solid formed in the flask, but this did not obscure the end-point. The end-point was taken when a definite red color persisted for 1 minute. Successive titrations of samples "killed" at the same time agreed within 1–1.5 mg. of $H_2O$.

In a typical experiment, a volume of solution equivalent to 452 mg. of polymer I was added to each of ten flasks and left at 26°. At successive intervals of 20 minutes a flask was removed and titrated as described. Theoretical consumption of water was calculated to be 70 mg., which, at the observed rate, would give a half-reaction time of 138 minutes. Similar calculation of half-reaction time for the ladder-type polymer II was 420 minutes, or 3.04 times as long.

**Reaction of the Ladder-type Polymer II with Excess Copper(II) Chloride.**—A sample of the xylene-soluble ladder-type polymer II was hydrolyzed with 1 *N* nitric acid. The hydrolyzed material gave a negative test for copper with cuproin.[9] To determine whether the polymer II could coordinate with copper, a 1.86 g. sample of the polymer was dissolved in xylene. 0.55 g. of copper (II) chloride was added and the suspension refluxed for 6 hr. After cooling, the supernatant liquid was green in color. The suspension was filtered through a medium glass frit to give a clear, green filtrate. This was freed of xylene under reduced pressure, and a sample of the residue was hydrolyzed in nitric acid and analyzed for copper using EDTA. Found: 1.7% copper.

**Reaction of Cross-linked Copper-containing Polymer III with Ethylenediamine in Xylene.**—A 48 mg. sample of the polymer was placed in 25 ml. of xylene, and the xylene brought to reflux temperature. The sample did not dissolve but swelled to give a blue gelatinous material. After cooling, 1.00 ml. (900 mg.) of ethylenediamine was added, and the temperature brought up to 100°. After 2.5 hr. the cooled solution was filtered to give a very small amount of purple solid and a yellow filtrate. The filtrate was freed of xylene, and a hydrolyzed sample gave a faint positive test for copper with cuproïn, but there was not enough copper present to obtain a significant analysis with 0.002 *N* EDTA. The original sample contained 3.5% copper.

## Conclusion

The nitrogen atoms of the dimethylsilylamine polymer I are capable of coördination with $Cu^{++}$ ions, but the polymer is stretched thereby into a new configuration, the ladder-type silazane polymer II. Nitrogen atoms of the latter are poorer donors than those of I, probably because of $d\pi$–$p\pi$ bonding to two silicon atoms instead of one. The silazane polymer II coördinates reversibly to copper ion ( if in excess) but loses the copper to free ethylenediamine, which is a stronger donor. Copper-containing silazane polymer III is swelled by xylene but is insoluble in it and in mixtures of xylene with ketones and ethers. It very probably is further cross-linked by the coördination of its chains to copper. Other ions with different coördination requirements might be expected to react differently with I and with related polymeric organosilylamines; results on several such reactions will be reported separately.

**Acknowledgment.**—The authors are grateful to the Office of Naval Research for funds to defray the cost of reagents and combustion analyses.

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[9] F. Feigl, "Spot Tests in Inorganic Analysis," Elsevier Publishing Co., Houston, Texas, 1958, p. 92.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

# Coördination of Polymeric Organosilyl Amines. II. Reactions with Anhydrous Beryllium Chloride[1]

BY RONN MINNÉ AND EUGENE G. ROCHOW

RECEIVED APRIL 1, 1960

Anhydrous $BeCl_2$ reacts with a polymeric silylamine, $[Me_2SiNHCH_2CH_2NH]_n$, in xylene solution to form a coördination polymer in which about one-third of the nitrogen is coördinated to beryllium. The coördinated polymer is more stable towards hydrolysis than the original polymeric silylamine and has very different physical properties. It also differs markedly from the corresponding reaction product of $CuCl_2$ with the same silylamine.

In the previous paper in this series, the preparation of a linear polymeric silylamine by the reaction of anhydrous ethylene diamine with dimethyldichlorosilane was reported, together with a discussion of the rearrangement of this polymer under the influence of copper(II) ions to form a cross-linked silazane. It was postulated that the role of the copper ion was to form a square-planar intermediate in which two polymer chains were coördinated to the copper ion and that the resulting distortion of structure led to the splitting out of ethylene diamine, resulting in a polymeric silazane.

This paper deals with the reaction of anhydrous beryllium chloride with the same polymeric silylamine. Beryllium ion was chosen for the second study of organosilicon coördination polymers because it is known to have very strong coördinating properties and because its tetrahedral coördination would provide a means of testing the theory that a square-planar complex brings about rearrangement of the polymeric silylamine.[2] Also, if an appreciable amount of beryllium were to be taken up by the polymer and remain coördinated to the amine or silazane nitrogen atoms, the rate of hydrolysis of the polymer should be affected. Normally, beryllium–amine links would be expected to hydrolyze, but the complex $Been_2Cl_2$ is reported to be fairly stable to hydrolysis.[2] If the beryllium ions were strongly held in the polymer, there should

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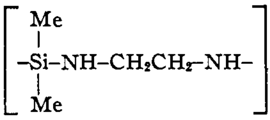
[1] For Part I in this series see THIS JOURNAL, **82**, 5625 (1960).

[2] R. Fricke and L. Havestadt, *Z. Anorg. Chem.*, **152**, 357 (1926).

be correspondingly less tendency to hydrolyze.

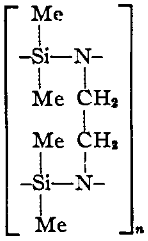
These matters were tested by adding the polymeric $[-(CH_3)_2SiNHC_2H_4NH-]_x$ in xylene solution to finely-ground anhydrous beryllium chloride and refluxing in an atmosphere of dry nitrogen for 3 to 4 hr. As the boiling point of xylene, *ca.* 140°, was approached, the colorless solution became tan in color. Some residual solid was removed by filtration, and an aliquot was freed of xylene. This left a hard, brittle, transparent, resinous substance, in contrast to the original liquid linear polymer. (The product also differed markedly from the rearranged polymer described in the preceding paper, which was a firm waxy material.) The weight of solid residue recovered was only two-thirds of the weight of the original beryllium chloride, indicating that a considerable amount of beryllium had gone into solution. To determine whether the beryllium was actually coordinated or was merely going into solution as $BeCl_2$ or $Been_2Cl_2$, a separate sample of beryllium chloride was refluxed in a mixture of xylene and ethylene diamine. A quantitative yield of insoluble $Been_2Cl_2$ was obtained, and evaporation of the filtrate left no weighable residue.

Upon analysis, a sample of the beryllium-containing polymer was found to contain 1.11% Be. Allowing for the equivalent proportion of chloride ion, the remaining theoretical content of carbon, hydrogen, nitrogen and silicon was calculated by proportion, based on theoretical values for the original linear polymer (I) and the cross-linked silazane polymer (II) obtained by reaction with copper chloride.[1] The calculated values for I and II, together with the analytical results, are summarized in Table I. These analytical results show that there is very little rearrangement of the linear polymer upon refluxing with beryllium chloride, whereas under the same conditions refluxing with copper (II) chloride brings about complete rearrangement. This supports the view that a copper-coördinated square-planar intermediate brings about rearrangement,[1] while tetrahedral coördination does not.



$$\left[-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}-NH-CH_2CH_2-NH-\right]_n$$

I



II

TABLE I

ANALYTICAL RESULTS FOR BERYLLIUM-CONTAINING POLYMER

| | Theory | | |
|---|---|---|---|
| | I | II | Found |
| Be | 1.11 | 1.11 | 1.11 |
| Cl | 8.7 | 8.7 | 9.2 |
| C | 37.2 | 37.7 | 36.91 |
| H | 9.4 | 8.45 | 9.46 |
| N | 21.7 | 14.7 | 21.25 |
| Si | 21.8 | 29.4 | 23.4 |
| S:N | 1:2 | 1:1 | 1:1.83 |
| | | | Be:N = 1:12.3 |

From the analytical data the Be:N ratio was calculated as 1:12.3. Assuming that beryllium is four-coördinate, this means that 32.5% of the nitrogen atoms in the polymer are coördinated. To test the effect this coördination would have on the tendency to hydrolyze, homogeneous hydrolyses in ethyl ether containing known amounts of water and acetic acid were carried out as described in the previous paper.[1] From two plots of nine determinations each, the time of half-reaction for the beryllium coördination polymer was 205 minutes, compared with 135 minutes for the linear polymer. If it be assumed that all uncoördinated nitrogen atoms have equal opportunity to hydrolyze by taking up protons, whereas all coördinated nitrogen atoms are blocked, then the beryllium-containing polymer should reach half hydrolysis in $\frac{100}{67.5} \times 135$ minutes, or 200 minutes. It would seem, then, that tight coördination to beryllium ions almost eliminates the tendency to hydrolyze at room temperature.

## Experimental

**A. Reaction of Anhydrous $BeCl_2$ with the Polymeric Silylamine.**—Anhydrous $BeCl_2$ (Clifton Products Co.) was ground to a fine powder, and 2.15 g. was placed in a 125 ml. round-bottom flask. Seventy-five ml. of polymer solution in xylene (containing 12.58 g. of polymer) were pipetted in, and the flask fitted with a reflux condenser. The system was purged with dry nitrogen for 15 minutes and then refluxed under nitrogen for 3.5 hr. After the contents of the flask had cooled, the unreacted solid was removed by filtration through a medium glass frit. An aliquot of the filtrate was freed of xylene at 30 mm. pressure, yielding 13.20 g. of polymer.

The solid residue from refluxing weighed 1.54 g. Since it was possible that the residue contained ethylenediamine as the metal complex,[1] it was analyzed for Be, Cl, C, H and N.

*Anal.* Calcd. for $BeCl_2$: Be, 11.28; Cl, 88.72. Found: Be, 6.78; Cl, 42.1. Assuming balance to be $C_2H_8N_2$, Calcd. C, 20.4; H, 6.8; N, 23.6. Found: C, 19.67; H, 6.92; N, 24.46.

**B. Determination of Solubility of $Been_2Cl_2$ in Xylene.**—A sample of anhydrous $BeCl_2$ (1.02 g.) was placed in a flask with 25 ml. of dried xylene, and 2.00 ml. (1.798 g.) of anhydrous ethylenediamine was added (a slight excess over the amount calculated for $Been_2Cl_2$). The suspension was refluxed under $N_2$ for 4 hr., cooled, and the solid recovered by suction filtration. The yield of $Been_2Cl_2$ was 2.47 g., 97% based on $BeCl_2$.

*Anal.* Calcd. for $Been_2Cl_2$: Be, 4.67; Cl, 36.92. Found: Be, 4.54; Cl, 36.1.

The xylene filtrate was evaporated to dryness in a tared flask. There was no weighable residue.

**Analytical.**—Carbon, hydrogen and nitrogen were determined commercially by combustion analysis. Chlorine was determined by titration with mercury (II) nitrate using diphenyl carbazide as indicator. The method given by Kolthoff and Stenger[3] was used, except it was found that preparing the sample in a 50% aqueous methanol solution gave sharper end points.

The beryllium in $BeCl_2$ and $Been_2Cl_2$ was determined by precipitation as the hydroxide and ignition to the oxide.[4] To determine beryllium and silicon in the coördinated polymer, a weighed sample was oxidized with fuming nitric and sulfuric acids in a platinum crucible and the residue ignited and weighed. The white ash was then treated with sulfuric and hydrofluoric acids and the silicon fumed off as

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(3) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishing Co., New York, N. Y., 1947, p. 335.

(4) Hillebrand and Lundell, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 522.

silicon tetrafluoride. The remaining beryllium sulfate was ignited to the oxide and the crucible weighed. The loss in weight gave the amount of $SiO_2$. The amounts of acids used gave no weighable residue. To check the procedure, an ignited, weighed sample of beryllium oxide was dissolved in hydrofluoric and sulfuric acids; the acids were fumed off and the residue reignited. The recovery of the beryllium oxide was quantitative.

The authors wish to thank the Office of Naval Research for funds to defray the cost of analysis and reagents.

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# Reactions of Alkaline Earth Oxides. III. A Re-examination of the Hedvall Effect[1,2]

BY HANS J. BORCHARDT[3] AND BARBARA A. THOMPSON

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The original experiments which are the basis of the postulate known as the Hedvall effect have been re-examined. It was found that the observed phenomena are not related to a phase transition as is generally supposed but appear to be the consequence of the formation of a liquid phase. The credibility of the Hedvall effect is discussed in the light of these and other data.

The increased reactivity of a solid during, and as a consequence of a crystallographic transformation, is known as the Hedvall effect.[4-9] This apparent behavior was first reported by Hedvall and Heuberger[10] who observed it in the course of the work with alkaline earth oxides which was previously discussed.[1,11] The original observations which were made on the reactions of BaO, SrO and CaO with $AgNO_3$ and $Ag_2SO_4$ are summarized in Table I. Today these data are still among the most widely quoted ones in support of the Hedvall rule.[4,6,9]

Table I lists the "reaction temperatures" of BaO, SrO and CaO with $AgNO_3$ and $Ag_2SO_4$. Phase transitions occur at 160 and 430° in $AgNO_3$ and $Ag_2SO_4$, respectively. Since it was thought that BaO, SrO and CaO have characteristic "reaction temperatures" of 345, 455 and 530°, respectively, the lowering of these values to those given in Table I was interpreted to be a consequence of the increased reactivity brought about by the transition in the silver salts.

TABLE I

| Oxide | Reaction temp. with $AgNO_3$,[a] °C. | Reaction temp. with $Ag_2SO_4$,[b] °C. |
|---|---|---|
| BaO | 170 | 342 |
| SrO | 172 | 422 |
| CaO | 164 | 422 |

[a] Transition temp., 160°. [b] Transition temp., 430°.

In previous work,[1] it was shown that the concept of a characteristic "reaction temperature" as applied to the alkaline earth oxides is ill-founded. The cited interpretation of the data in Table I, is, consequently, also questionable. The reactions of BaO, SrO and CaO with $AgNO_3$ and $Ag_2SO_4$ have, therefore, been re-examined.

## Experimental

Two sets of experiments were performed: (1) differential thermal analysis of each reaction mixture and (2) direct microscopic examination of several reaction mixtures at temperatures in the neighborhood of the transition point. The purpose of the first is to reproduce the original experiments. Visual observation was expected to reveal what actually occurs at the transition point.

Differential thermal analyses were made with 50–50 mole per cent. mixtures of the reactants as well as with the pure materials under conditions previously described.[11] Microscopic examinations at elevated temperatures were performed at 60X with incident illumination on a Leitz microscope heating stage at atmospheric pressure in laboratory air. BaO, SrO and CaO were prepared as before.[1,11] Mallinckrodt analytical reagent grade $AgNO_3$ and $Ag_2SO_4$ were utilized without further treatment.

## Results

The several DTA patterns are seen in Fig. 1. The sharp exotherm is in each case due to reaction to form the alkaline earth salt and $Ag_2O$ or $Ag^0$. In the case of the reactions with $AgNO_3$, $Ag_2O$ is formed first. With $Ag_2SO_4$, elemental silver is present after reaction. This was established by X-ray analysis of the samples immediately after occurrence of the exotherm.

The time between observed initiation and termination of reaction is of the order of one minute. This is in agreement with the comments of Hedvall who describe these as very rapid reactions. However, the "reaction temperatures" observed here are all above those listed in Table I. BaO and SrO are seen to react with $AgNO_3$ at a temperature close to the melting point of the latter. (Compare curves in Fig. 1.) Only the exotherm due to the reaction of CaO with $AgNO_3$ is observed to initiate below this temperature.

The reaction of $Ag_2SO_4$ with BaO as well as SrO is seen to "trigger-off" in the same manner and at the same temperature as the reactions of carbonates and other sulfates with these oxides.[11] The "reaction temperature" of $Ag_2SO_4$ + CaO is seen to correspond to the melting point of $Ag_2SO_4$.

$AgNO_3$ alone as well as the mixtures BaO-$AgNO_3$, SrO-$AgNO_3$ and CaO-$AgNO_3$ were observed on the

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(1) Part II, THIS JOURNAL, **82**, 355 (1960).

(2) Presented in part at the 136th National Meeting of the American Chemical Society, September, 1959, Atlantic City, N. J.

(3) Explosives Department, Experimental Station Laboratory, E. I. du Pont de Nemours & Co., Wilmington 98, Delaware.

(4) J. A. Hedvall, "Einführung in die Festkörperchemie," Fr. Vieweg and Son, Publishers, Braunschweig, 1952, p. 180ff.

(5) K. Hauffe, "Reaktionen in und an Festen Stoffen," Springer Publishing Co., Berlin, 1955, p. 628–629.

(6) G. Cohen, *Chem. Revs.*, **42**, 566 (1948).

(7) W. E. Garner, "Chemistry of the Solid State," Butterworth's Scientific Publications, London, 1955, p. 309.

(8) A. L. G. Rees, "Chemistry of the Defect Solid State," Methuen and Co., London, 1954, p. 91.

(9) T. J. Gray, Ed., "The Defect Solid State," Interscience Publishers, Inc., New York, N. Y., 1957, pp. 127–132.

(10) J. A. Hedvall and J. Heuberger, *Z. anorg. Chem.*, **128**, 1 (1923); **135**, 49 (1924).

(11) H. J. Borchardt and B. A. Thompson, THIS JOURNAL, **81**, 4182 (1959).