Dielectric dispersion measurements of Jungner and Jungner[17] on thymonucleic acid show that the component of the dipole moment along the long axis is zero and that the transverse component is directly proportional to the molecular weight. For a sample with a molecular weight equal to that of Benoit's, they give a value of the transverse dipole moment, calculated according to Kirkwood,[18] of 20,800 *D*. This is in very satisfactory agreement.

Acknowledgment.—The author wishes to express his appreciation to Professor J. G. Kirkwood for his valuable suggestions and his helpful discussions throughout this work.

---

[17] A. Jungner and I. Jungner, *Acta Chem. Scand.*, **6**, 1391 (1952).

[18] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Dissociation and Ionic Reactions of Dimethylgermanium Dichloride

BY EUGENE G. ROCHOW AND A. LOUIS ALLRED[1]

RECEIVED MARCH 23, 1955

In order to contribute information concerning the relative electronegativities of the Group IVB elements, the ionic dissociation and degree of hydrolysis of dimethylgermanium dichloride in water have been investigated. Comparison of the results with those for dimethyltin dichloride shows that germanium has a surprisingly high electronegativity, in keeping with recent predictions and with other experimental evidence. Some metathetic reactions of dimethylgermanium dichloride in aqueous solution also are described.

There is some controversy concerning the relative electronegativities of the Group IV elements silicon, germanium, tin and lead. In particular, Sanderson[2] shows a regression of metallic character for the first period of eighteen elements, leading to the values Si 2.6, Ge 3.6, Sn 3.1, and Pb 3.7. Older sources indicate[3] the more uniform values Si 1.8, Ge 1.7, and Sn 1.7. Chemical evidence obtained in the course of experiments on these elements in this Laboratory has indicated that germanium does indeed exhibit an electronegativity considerably higher than that of silicon or of tin.[4] Further conclusions are possible through study of the behavior of the R_2M^{++} ions, such as the dimethyltin ion $(CH_3)_2Sn^{++}$.[5-7] We are concerned here with the electrolytic dissociation, degree of hydrolysis, and metathetic ionic reactions of dimethylgermanium dichloride, particularly as they relate to the corresponding properties of dimethyltin dichloride.

Experimental

Dissociation and Hydrolysis.—Dimethylgermanium dichloride was prepared from germanium as previously described[8] and was purified by distillation. Chlorine was determined by titration with alcoholic KOH.[9] Dilute solutions were prepared and used for the cryoscopic determination of the van't Hoff *i* factor and the *p*H. The results are summarized in Table I.

TABLE I

AQUEOUS SOLUTIONS OF $(CH_3)_2GeCl_2$

Molality	0.0760	0.0350	0.0216	0.0145	0.00478	0.0019
i factor	5.01	5.03	5.21	5.19	^{a}	^{a}
Obsd. *p*H	1.02	1.20	1.32	1.50	2.11	2.37
Calcd. *p*H	0.82	1.16	1.37	1.54	2.03	2.42

(see Discussion)

^{a} Large variations were encountered with these dilute solutions, but the average *i* was 5.0.

A solution of 1.2479 g. of $(CH_3)_2GeCl_2$ in 125.0 ml. of water was titrated with 0.0976 *N* NaOH, measuring the *p*H with a Beckman meter. The result of 125 observations during the titration is given on curve A of Fig. 1, in which the equivalents of base per equivalent of $(CH_3)_2GeCl_2$ are plotted against *p*H. The results of titrating a 0.1016 *N* solution of $(CH_3)_2SnCl_2$ with base by the same technique (from ref. 5) are plotted on the same scale (curve B) for comparison. While precipitation of dimethyltin oxide occurred at approximately one equivalent of base per equivalent of $(CH_3)_2SnCl_2$, in the present work no dimethylgermanium oxide precipitated at any point.

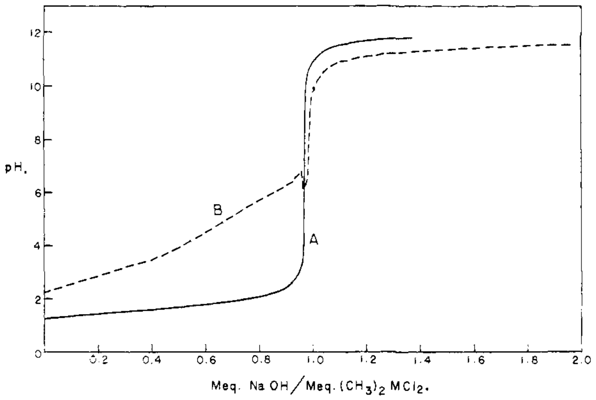

Fig. 1.

Compounds of the Dimethylgermanium Cation.—When an acidified aqueous solution of $(CH_3)_2GeCl_2$ is treated with hydrogen sulfide, a precipitate of white waxy dimethylgermanium sulfide forms at once.[10] The possibility of similar reactions was studied as a rapid means of preparing new organogermanium compounds. Two methods were used: (1) $(CH_3)_2GeCl_2$ was added to an aqueous solution of the desired anion and the product isolated by filtration or evaporation, or (2) an anion-exchange resin was treated with a solution containing the desired anion, washed with water, and then treated with a solution of $(CH_3)_2GeCl_2$.

---

[1] Natvar Fellow at Harvard University, 1954–1955.

[2] R. T. Sanderson, *J. Chem. Ed.*, **31**, 238 (1954); **32**, 140 (1955).

[3] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd Ed., 1948, p. 64.

[4] See, for example, the reduction of Ge–Br to Ge–H by zinc dust and hydrochloric acid, impossible with Si or Sn and reminiscent of As: R. West, THIS JOURNAL, **75**, 6080 (1953).

[5] E. G. Rochow and D. Seyferth, *ibid.*, **75**, 2877 (1953).

[6] E. G. Rochow, D. Seyferth and A. C. Smith *ibid.*, **75**, 3099 (1953).

[7] K. Gingold, E. G. Rochow, D. Seyferth, A. C. Smith and R. West, *ibid.*, **74**, 6306 (1952).

[8] E. G. Rochow, *ibid.*, **69**, 1729 (1947).

[9] E. G. Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 165.

[10] E. G. Rochow, THIS JOURNAL, **70**, 1801 (1948).

The latter method gave chloride-free solutions which were evaporated (usually at room temperature in a vacuum desiccator) to obtain the product.

Dimethylgermanium chromate was prepared by method (1) from 0.5 g. of K_2CrO_4 and 0.2 g. of $(CH_3)_2GeCl_2$ in 5 ml. of water. It precipitates as orange crystals which decompose in light or when heated to 158° and are insoluble in acetone, chloroform, benzene and ethanol. Mr. Hans Schlochauer had previously prepared the same substance in this Laboratory and had recrystallized it from water; his product decomposed at 151–158° and had the following analysis.

Anal. Calcd. for $(C_2H_6)GeCrO_4$: C, 11.0; H, 2.78; Cr, 23.8. Found: C, 10.62; H, 2.88; Cr (by iodimetry), 23.5.

Dimethylgermanium thiocyanate also was prepared by Mr. Schlochauer by method (1), yielding a yellow oil extractable by ether. Distillation yielded a colorless, odorless liquid which crystallized to white needles soluble in alcohol and benzene, m.p. 45.5–47°, b.p. 266–268°.

Anal. Calcd for $C_4H_6GeN_2S_2$: C, 22.0; H, 2.8; CNS^-, 53.0. Found: C, 21.6; H, 2.66; CNS^-, 52.0.

Method (2) was applied to the attempted preparation of dimethylgermanium formate, acetate and succinate by treating Dowex-2 anion-exchange resin with solutions of the sodium salts of these acids and then with an aqueous solution of $(CH_3)_2GeCl_2$. The eluents from these experiments were evaporated at room temperature in a vacuum desiccator. In all three experiments there was obtained a fibrous white solid soluble in absolute ethanol and in benzene but insoluble in acetone, carbon disulfide or diethyl ether. The three products melted at 119, 124 and 127°; an equal mixture of the first two melted at 116° and a mixture of the latter two melted at 120°. Such similarity of properties made it evident that we were dealing with three somewhat impure samples of the same substance, probably dimethylgermanium oxide, $[(CH_3)_2GeO]_4$, which melts at 133.4°.[8] The third product was analyzed by combustion and was indeed dimethylgermanium oxide.

Anal. Calcd. for C_2H_6GeO: C, 20.25; H, 5.07. Found: C, 20.19; H, 5.12.

In view of the solubility of dimethyltin benzoate in benzene,[6] an attempt was made to extract dimethylgermanium benzoate into benzene from an aqueous solution of C_6H_5-COONa and $(CH_3)_2GeCl_2$. but no extract was obtained. In one experiment a white precipitate which did not melt at 360° was obtained from a concentrated solution of the reactants, but it hydrolyzed to benzoic acid upon recrystallization. Similarly, only phthalic acid was precipitated from a solution of potassium hydrogen phthalate by $(CH_3)_2GeCl_2$, even in 0.5 *N* KOH. Sodium tungstate and $(CH_3)_2GeCl_2$ yielded some tungstate blue and a condensed polyacid which could not be separated or purified. No precipitation occurred after the addition of a solution of $(CH_3)_2$-$GeCl_2$ to solutions of NaH_2PO_2, Na_2HAsO_4, NaOAc or $Na_2C_2O_4$. Other attempts to prepare salts analogous to those of the $(CH_3)_2Sn^{++}$ ion (6) were unsuccessful.

Discussion

The data of Table I indicate that dimethylgermanium dichloride dissociates and hydrolyses completely, according to the equations

$$(CH_3)_2GeCl_2 \rightleftarrows (CH_3)_2Ge^{++} + 2Cl^- \qquad (1)$$

$$(CH_3)_2Ge^{++} + H_2O \rightleftarrows (CH_3)_2Ge(OH)^+ + H^+ \qquad (2)$$

$$(CH_3)_2Ge(OH)^+ + H_2O \rightleftarrows (CH_3)_2Ge(OH)_2 + H^+ \qquad (3)$$

One mole of the dichloride therefore supplies two equivalents of acid quite apart from any possible amphoteric behavior of the dimethylgermanium hydroxide, and the *i* factor is five. If this remains true over the 40-fold range of concentrations in our experiments, the hydrogen ion concentration at any point should be twice the molarity (and nearly twice the molality) of the dimethylgermanium dichloride. The *p*H values on the last line of Table I were calculated on this basis, and they agree closely with the observed values. This behavior stands in interesting contrast to that of dimethyltin dichloride, which is only 10 to 45% hydrolysed over the same range of concentrations.[5]

It is apparent from curve A of Fig. 1 that dimethylgermanium dichloride behaves in solution like a strong acid. It shows no amphoteric behavior like that of dimethyltin dichloride (curve B of Fig. 1), and since the hydroxide formed in accordance with equation 3 maintains no *p*H level of its own below 12, it is considered to be a weak base. As discussed elsewhere,[5] the addition of 0.1 *N* NaOH to the $(CH_3)_2SnCl_2$ solution caused precipitation of oxide in the *p*H range 6.06 to 11.52, and the further addition of 0.1 *N* NaOH dissolved the precipitate as the disodium salt. In the *p*H range in which dimethyltin oxide is removed by precipitation, the dimethyltin dichloride solution is less basic than the dimethylgermanium dichloride solution as indicated by Fig. 1. Above *p*H 11.52, the solution of Na_2-$(CH_3)_2Sn(OH)_4$ would probably be at least as basic as the $(CH_3)_2Ge(OH)_2$ solution, as the ascending curve B indicates. However, insoluble material is present from the upper inflection of B out to the end of the curve, and hence comparison of the basic solutions at equal concentration of tin and germanium remains impossible. Ample opportunity for comparison still is provided by the lower sections of both curves, and there seems no doubt that $(CH_3)_2GeCl_2$ is the stronger acid. This supports the previous evidence for a relatively high electronegativity for germanium. The alternation in solubilities of dimethylsilicon oxide (methyl silicone, highly insoluble and water-repellent), dimethylgermanium oxide (completely soluble at 0.1 *M*), and dimethyltin oxide (insoluble only in the *p*H range 6–11.6) eventually may prove informative in some other way, but at present these variations serve only to introduce serious experimental difficulties when a direct comparison of their solvolytic behavior is attempted.

CAMBRIDGE, MASSACHUSETTS