

RAMAN SPECTRA OF DIMETHYLGERMANIUM DIHYDROXIDE IN AQUEOUS SOLUTION: ACIDITY TRENDS IN THE SEQUENCE $(\text{CH}_3)_2\text{Ge(IV)}$, $(\text{CH}_3)_2\text{Sn(IV)}$, AND $(\text{CH}_3)_2\text{Pb(IV)}$

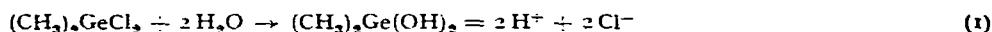
R. STUART TOBIAS AND SISTER SIGRID HUTCHESON, O.S.B.

Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455 (U.S.A.)

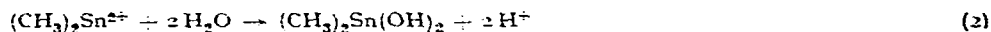
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INTRODUCTION

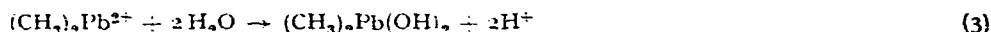
It has been known for some time that the equilibrium constants for the hydrolysis of the di- and trialkylgermanium chlorides are very much larger than for the hydrolysis of the corresponding alkyltin chlorides. Rochow and Allred observed that reaction (1) went essentially to completion in dilute solution¹. It was also observed that displacement of the chloride required a solvent which is a good electron donor^{2,3}.



The extensive hydrolysis of the di- and trialkylgermanium compounds is in marked contrast to the relatively slight hydrolysis of the corresponding organotin compounds. For example, the equilibrium constant, $^*\beta_{21}$, for reaction (2) is very small



and has the value $\log ^*\beta_{21} = -9.00$ in a 3 M NaClO_4 medium^{4,5}. The pronounced hydrolysis of the germanium compounds was originally used in support of the Allred-Rochow Group IV electronegativities for sp^3 hybridization where the values are 2.00 for germanium and 1.93 for tin⁶. It is interesting to note that the corresponding hydrolysis reaction for dimethyllead(IV), reaction (3) is still considerably less than that



of tin, and the equilibrium constant has the value $\log ^*\beta_{21} = -15.59^7$. On the Allred-Rochow scale, an electronegativity of 2.45 was assigned to lead. Drago has suggested that the usual Pauling values of $\text{Ge} = 1.8$, $\text{Sn} = 1.8$, and $\text{Pb} = 1.8$ are more appropriate⁸.

Hydrolysis of $(\text{CH}_3)_2\text{GeCl}_2$ with aqueous sodium hydroxide followed by extraction with petroleum ether yields dimethylgermanium oxide which has been shown by cryoscopy to exist as the tetramer $[(\text{CH}_3)_2\text{GeO}]_4$ in benzene solution⁹. The oxide is readily soluble both in organic solvents and in water where it apparently is present as the monomeric hydroxide¹. Hydrolysis of $(\text{CH}_3)_2\text{SnCl}_2$ under comparable conditions yields $(\text{CH}_3)_2\text{SnO}$ which is virtually insoluble in both organic solvents and

water¹⁰. Treatment of $(\text{CH}_3)_2\text{PbCl}_2$, which is only slightly soluble in water, with Ag_2O in an aqueous system yields rather concentrated solutions of $(\text{CH}_3)_2\text{Pb}(\text{OH})_2$ ¹¹.

It is apparent that there are vast differences in the acidity of the dimethyl-germanium(IV), -tin(IV), and -lead(IV) moieties and in the properties of their oxygen containing compounds which probably are reflected in structural differences. Neither the Allred-Rochow nor the Pauling electronegativities correlate well with the known acidities. In order to characterize better the dimethylgermanium species in aqueous solutions and to obtain information on the nature of the germanium-oxygen bond, the Raman spectra of aqueous solutions of dimethylgermanium oxide were determined.

EXPERIMENTAL

Dimethylgermanium oxide

The direct synthesis method of Rochow¹² was used to prepare $(\text{CH}_3)_2\text{GeBr}_2$. Germanium powder supplied by the Germanium Information Center of the Midwest Research Institute was mixed with copper powder in a 4:1 w/w ratio, and CH_3Br was passed over the mixture slowly at 350°. The product was collected and distilled and a cut from 145–55° was taken as $(\text{CH}_3)_2\text{GeBr}_2$: b.p. *lit.* 153° at 746 mm¹³. The $(\text{CH}_3)_2\text{GeBr}_2$ was hydrolyzed with 50% aqueous NaOH, allowed to stand overnight, and refluxed with petroleum ether for 5 h. The ether layer was separated, the aqueous solution was extracted again, and the solutions combined and evaporated. The crude $[(\text{CH}_3)_2\text{GeO}]_4$ was recrystallized from petroleum ether: m.p., uncorrected 89–91, *lit.*⁹ 91–2°. Solutions were prepared by dissolving the oxide in water and nitric acid solution.

Raman spectra

The Raman displacements from the 4358 Å mercury line were recorded photoelectrically with a Cary model 81 spectrophotometer. The scan rate was 0.5 or 2.5 $\text{cm}^{-1}/\text{sec}$ except for the accurate determination of line frequencies which were made at a rate of 0.05 $\text{cm}^{-1}/\text{sec}$. The frequency scale of the instrument was calibrated with spectra of carbon tetrachloride and benzene, and the frequencies of sharp lines are believed to be correct to $\pm 2 \text{ cm}^{-1}$. Since only relatively small samples of the oxide were available, the solutions were sealed in specially made 6 mm tubes having an illuminated length of *ca.* 8 in. Because of the small sample tubes, some scattering from the glass was observed, and this gave broad, weak lines at *ca.* 450 and 825 cm^{-1} . The solution of $[(\text{CH}_3)_2\text{GeO}]_4$ in water was very stable. A Raman spectrum was obtained 18 months after the initial spectrum, and there were no appreciable changes in line intensities. The Raman signals were integrated with a Gelman planimeter. The line assigned to the germanium solute at *ca.* 180 cm^{-1} is definitely due to the solute, since it is some 10 cm^{-1} higher in frequency and several orders of magnitude more intense than the grating ghost observed in this region with Cary 81 instruments.

DISCUSSION

The Raman spectrum of a 4.5 M solution of $(\text{CH}_3)_2\text{GeO}$ in water is shown in Fig. 1. There was an appreciable background apparently because of some fluorescence. Values of the Raman shifts, the integrated intensities, and the state of polarization of the lines are given in Table 1.

Two intense lines, one polarized and one depolarized are observed in the region where Ge-C bond stretching vibrations are expected to appear. This indicates that the C-Ge-C skeleton in the $(\text{CH}_3)_2\text{Ge}$ moiety is appreciably bent and that the solute has effective C_{2v} symmetry.

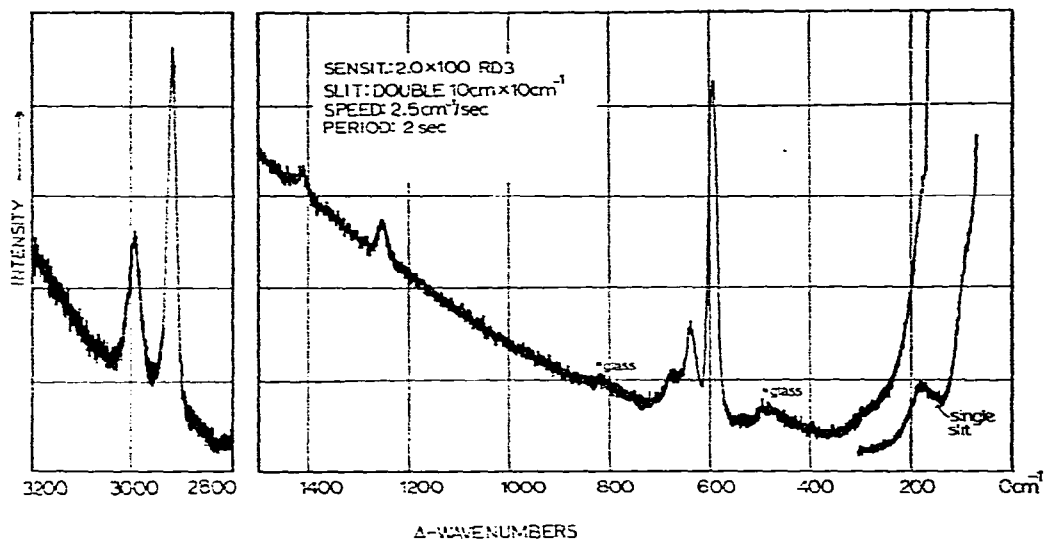


Fig. 1. Survey spectrum of aqueous 4.5 M $(\text{CH}_3)_2\text{GeO}$.

Aside from the absence of lines arising from vibrations associated with the GeCl_2 moiety, the Raman spectrum of $(\text{CH}_3)_2\text{GeO} \cdot x\text{H}_2\text{O}$ is very similar to that of the dichloride measured as the neat liquid¹⁴. This tends to indicate that, indeed, a simple

TABLE I

RAMAN SPECTRUM OF 4.5 M AQUEOUS $(\text{CH}_3)_2\text{GeO}$

λ_r (cm^{-1})	A^a	State of polarization
180	1000	dp
596	1540	p
937	530	dp
673	370	$dp(?)$
1253	200	p
1413	140	dp
2922	2030	p
2998	1140	dp

^a A is the integrated intensity ($\text{cm}^{-1} \times \% \text{ deflection}$).

I to I substitution of the chloride by hydroxide occurs upon hydrolysis, and two hydroxo oxygens and the methyl carbons are presumably arranged at tetrahedral vertices about the germanium atom. It would be anticipated that Ge-O₂ bond stretching vibrations should be observed in the same region where the Ge-C₂ stretching

vibrations occur, and there is an additional broad line in the spectrum at *ca.* 673 cm^{-1} . A band at 676 cm^{-1} has been assigned to symmetrical Ge-OH bond stretching in infrared spectra of crystalline SrH_2GeO_4 ¹⁵. The structure of this compound is similar to that of KHPO_4 , and it contains discrete $[\text{GeO}_2(\text{OH})_2]^{2-}$ anions¹⁶. Recently, Raman spectra have been obtained for solutions prepared by dissolving GeO_2 in nearly saturated aqueous KOH ¹⁷. The solutions appear to contain primarily $[\text{H}_2\text{GeO}_4]^{2-}$ and $[\text{Ge}_2\text{O}_7]^{2-}$. A broad, weakly polarized Raman line at 667 cm^{-1} was assigned to both the symmetrical and antisymmetrical vibrations involving primarily the Ge-(OH)₂ portion of $[\text{H}_2\text{GeO}_4]^{2-}$.

In the following discussion of the vibrational assignments, only the $(\text{CH}_3)_2\text{GeO}_2$ unit will be considered, since vibrations involving the hydroxyl hydrogen atoms are

TABLE 2

VIBRATIONAL ASSIGNMENTS FOR THE $(\text{CH}_3)_2\text{GeO}_2$ PART OF $(\text{CH}_3)_2\text{Ge}(\text{OH})_2$
Effective point group C_{2v} ; ν in cm^{-1} .

Approximate description of mode	$\nu[(\text{CH}_3)_2\text{Ge}(\text{OH})_2]$	$\nu[(\text{CH}_3)_2\text{GeCl}_2]$ ¹⁴	$\nu[\text{O}_2\text{Ge}(\text{OH})_2]^{2-}$ ¹⁷
CH_3 stretch (antisym.) $\nu_1 (A_1), \nu_{10} (A_2),$ $\nu_{15} (B_1), \nu_{21} (B_2)$	2998	3002	
CH_3 stretch (sym.) $\nu_2 (A_1), \nu_{22} (B_2)$	2922	2924	
CH_3 deform. (antisym.) $\nu_3 (A_1), \nu_{11} (A_2),$ $\nu_{16} (B_1), \nu_{23} (B_2)$	1413	1410	
CH_3 deform. (sym.) $\nu_4 (A_1), \nu_{24} (B_2)$	1253	1243	
Ge-O ₂ stretch (antisym.) $\nu_{13} (B_1)$	673		667
Ge-O ₂ stretch (sym.) $\nu_6 (A_1)$	673		667
Ge-C ₂ stretch (antisym.) $\nu_{25} (B_2)$	637	634	
Ge-C ₂ stretch (sym.) $\nu_7 (A_1)$	596	592	
Ge-O ₂ deform. $\nu_8 (A_1), \nu_{13} (A_2), \nu_{19} (B_1),$ $\nu_{27} (B_2)$	180		
Ge-C ₂ deform. $\nu_9 (A_1)$	180	188	

not distinguishable from those of the solvent water. This $(\text{CH}_3)_2\text{GeO}_2$ unit has 27 normal modes; however, by analogy with $(\text{CH}_3)_2\text{GeCl}_2$ ¹⁴ many of these would be expected to be accidentally degenerate. Table 2 gives approximate descriptions for the normal modes associated with the observed vibrations of the $(\text{CH}_3)_2\text{GeO}_2$ unit, the assignments, the frequencies reported for neat $(\text{CH}_3)_2\text{GeCl}_2$ ¹⁴, and the frequencies for the Ge-(OH)₂ portion of $[\text{O}_2\text{Ge}(\text{OH})_2]^{2-}$ reported for aqueous solution¹⁷. The numbering of the normal modes is based on orientation of the molecule with the Ge-O₂ atoms in the *xz* plane. The descriptions of the skeletal deformations are only very approximate. The methyl rocking vibrations $\nu_5, \nu_{12}, \nu_{17}$, and ν_{25} were too weak to be identified. It is also possible that one or more of these may be masked by the small amount of scattering from the sample tube at *ca.* 825 cm^{-1} , although they are quite low in intensity in neat $(\text{CH}_3)_2\text{GeCl}_2$ as well. Both the symmetrical and antisymmetrical Ge-(OH)₂ stretching vibrations are assigned to the line at 673 cm^{-1} as a result of its almost complete depolarization. The comparable stretching vibrations of $[(\text{CH}_3)_2\text{Sn}(\text{OH})_4]^{2-}$ at 555 cm^{-1} (ref. 18) are very similar in line width and polarization. The torsional modes ν_{14} and ν_{20} would not be expected to cause scattering under the conditions of these experiments.

The spectrum was also determined for a solution prepared by adding sufficient

$[(\text{CH}_3)_2\text{GeO}]_4$ to 11.7 M nitric acid to give 4.35 M $(\text{CH}_3)_2\text{Ge}(\text{IV})$. Aside from the presence of nitrate lines, the only differences in this spectrum from that of $(\text{CH}_3)_2\text{Ge}(\text{OH})_2$ in water were a reduction in intensity of the line at 673 cm^{-1} assigned to $\text{Ge}(\text{OH})_2$ bond stretching and a *ca.* 10 cm^{-1} shift of the antisymmetric $\text{Ge}-\text{C}_2$ stretch toward higher frequencies. No changes were observed in the relative intensities of the symmetrical and antisymmetrical $\text{Ge}-\text{C}_2$ stretching vibrations.

There are several pronounced differences in the hydrolytic behavior of $(\text{CH}_3)_2\text{GeCl}_2$ and $(\text{CH}_3)_2\text{SnCl}_2$ which reflect characteristic changes in the chemistry of germanium(IV) and tin(IV). Both of these dichlorides exist in the liquid state as tetrahedral molecules^{14,19}. Hydrolysis of the germanium compound even in strongly acidic solution produces tetrahedral $(\text{CH}_3)_2\text{Ge}(\text{OH})_2$ with strong germanium-oxygen bonds. With the tin compound, the only organometallic species present in aqueous solutions at pH values less than about 2 is the aquo-ion $[(\text{CH}_3)_2\text{Sn}]^{2+}$ which has a linear $\text{C}-\text{Sn}-\text{C}$ skeleton²⁰. No Raman lines attributable to $\text{Sn}-\text{OH}_2$ bonds are observed. Rehybridization of the di²¹- and tri-organotin²² compounds with expansion of the coordination number of tin from four to five or six appears to be very common when ligands with highly electronegative donor atoms are substituted for less electronegative ones. With germanium compounds, this appears to be rarely if ever the case. Thus tetrahedral $(\text{CH}_3)_3\text{GeClO}_4$ is a rather typical molecular liquid²³, while the tin atom in $(\text{CH}_3)_3\text{SnClO}_4$ is five coordinate^{24,25}.

The physical properties of $(\text{CH}_3)_2\text{PbCl}_2$ suggest that expansion of the coordination number of lead from four to six has already occurred with the solid chloride⁷, and the Raman and infrared spectra of crystalline $(\text{CH}_3)_2\text{PbCl}_2$ support a structure with linear $[\text{H}_2\text{C}-\text{Pb}-\text{CH}_2]^{2+}$ ions. The very low Raman intensities of the lead-chlorine bond stretching vibrations indicates that these bonds are probably highly polar³⁰. The compound $(\text{CH}_3)_2\text{PbCl}_2$ is only slightly soluble in water, but Raman studies on solutions of $(\text{CH}_3)_2\text{Pb}(\text{NO}_3)_2$ and $(\text{CH}_3)_2\text{Pb}(\text{ClO}_4)_2$ indicate that the solutions contain linear $[(\text{CH}_3)_2\text{Pb}]^{2+}$ aquo-ions^{7,27}. With these solutions, there is some evidence for a very low intensity line attributable to $\text{Pb}-\text{OH}_2$ bond stretching.

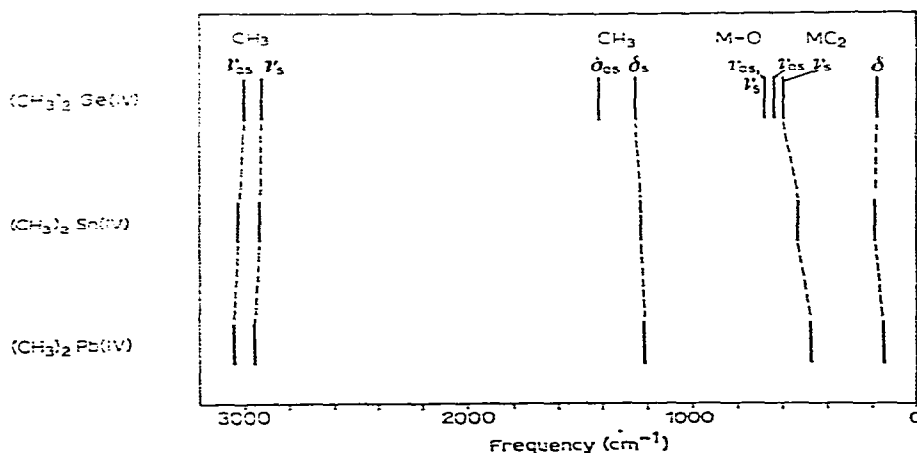


Fig. 2. Correlation chart for the Raman frequencies of $(\text{CH}_3)_2\text{Ge}(\text{IV})$, $(\text{CH}_3)_2\text{Sn}(\text{IV})$, and $(\text{CH}_3)_2\text{Pb}(\text{IV})$ in acidic aqueous solution.

Fig. 2 shows a correlation chart for the Raman active frequencies of the dimethylgermanium tin, and lead species present in acidic aqueous solution.

It is of interest that the vibrations of the dimethylgermanium moiety in $(\text{CH}_3)_2\text{Ge}(\text{OH})_2$ are so similar to those in $(\text{CH}_3)_2\text{GeCl}_2$ and that those involving Ge-(OH)₂ bond stretching are so alike in $(\text{CH}_3)_2\text{Ge}(\text{OH})_2$ and $[\text{O}_2\text{Ge}(\text{OH})_2]^{2-}$. These vibrational frequencies have all of the characteristics of good group frequencies. The same properties have been observed for the vibrations of the Si-C₂ moiety which change little in the series $(\text{CH}_3)_2\text{SiF}_2$, $(\text{CH}_3)_2\text{SiCl}_2$, $(\text{CH}_3)_2\text{SiBr}_2$ ²⁸, and $(\text{OH})(\text{CH}_3)_2\text{-SiOSi}(\text{CH}_3)_2(\text{OH})$ ²⁹ where there should be appreciable changes in the extent of π bonding to silicon.

The dimethylgermanium(IV) moiety can be regarded as an extremely strong and "hard" Lewis acid which appears, with only few if any exceptions, in tetrahedral, typically covalent molecules. The corresponding dimethyltin(IV) moiety is a much weaker Lewis acid. It occurs in many covalent molecules where the tin atom has a coordination number of 4, but it also occurs in compounds with a coordination number of six in the presence of highly electronegative ligands. Thus, the polarization of a given ligand is lessened by expansion of the coordination number. Finally, the dimethyllead(IV) moiety is a very weak Lewis acid in so far as "hard" bases are concerned, and it probably occurs frequently in compounds where the lead atom is at least six-coordinate. The weaker acidity compared to tin would appear to result from the larger lead "core". These observations point up the difficulties inherent in comparisons of structures and reaction mechanisms of diorganogermanium(IV), -tin(IV), and -lead(IV) compounds. In the presence of polar solvents or other electronegative ligands, the geometry about alkyl germanium moieties remains essentially tetrahedral, while for tin and lead the diorgano moiety becomes linear and the coordination number of the metal is greater than four.

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SUMMARY

Raman spectra have been obtained on aqueous solutions prepared from $[(\text{CH}_3)_2\text{GeO}]_4$. The solutions have been shown to contain tetrahedral $(\text{CH}_3)_2\text{Ge}(\text{OH})_2$ and vibrational assignments have been made. The equilibrium constants for the hydrolysis of dimethylgermanium, tin, and lead compounds have been compared and discussed in terms of the structures and hybridization of the species present in acidic aqueous solutions.

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