

$$k_w = (\Delta C_{HA} / \Delta t C_{L_0}) - [k_b C_{H^+} + k_b C_{OH^-}] + \\ [(k_b + k_l) C_{H^+} + k_b C_{OH^-}] (C_{HA} / C_{L_0}) \\ \equiv (\Delta R / \Delta t) - Q + PR$$

where R is C_{HA} / C_{L_0} and Q and P are the two bracketed expressions above. ΔR is the change in R for a time change Δt . The term $(k_w + k'_w)R$ has been omitted from the above equation since only initial hydrolysis rates were measured. Actually the term PR is also almost negligible. Since all experiments gave very similar results, the data for only one are given in Table III. Values of the ionization constants of acetic acid and water at 50° were obtained from the work of Harned and Ehlers⁹ and Walpole,¹⁰ respectively.

TABLE III

SEARCH FOR WATER HYDROLYSIS AT 50°

Initial conditions:

$$C_{L_0} = 0.1438 M; C_{HOAC} = 0.0133 M; C_{NAOAC} = 0.032 M$$

$$C_{H^+} = 7.2 \times 10^{-6} M; C_{OH^-} = 7.7 \times 10^{-9} M$$

$$Q = k_b C_{H^+} + k_b C_{OH^-} = 3.1 \times 10^{-6} \text{ min.}^{-1}$$

$$P = (k_b + k_l) C_{H^+} + k_b C_{OH^-} = 5.6 \times 10^{-6} \text{ min.}^{-1}$$

Rate data:	Δt , min.	$10^6 \Delta R / \Delta t$, min. ⁻¹	$10^6 R$	$10^6 (Q - PR)$, min. ⁻¹	$10^6 k_w$, min. ⁻¹
1435	4.2	0.61	3.1	1.1	
1177	4.5	1.13	3.1	1.4	
3174	4.3	2.48	3.0	1.3	
1465	3.8	3.03	3.0	0.8	

The value of the hydrolysis rate to be expected from the known acid-catalyzed and basic reactions, $Q - PR$, is subject to a fairly large error both from the long extrapolation required to obtain k_b at 50° and from errors in measuring the initial hydrolysis rate. Hence there would be convincing evidence for a water reaction only if the calculated k_w were large compared to $(Q - PR)$. Actually the calculated k_w value is only about a third of $(Q - PR)$ and it may be concluded that no good evidence exists for a direct reaction of this lactone with water.

(9) H. S. Harned and R. W. Ehlers, *THIS JOURNAL*, **55**, 652 (1933).

(10) G. S. Walpole, *J. Chem. Soc.*, **105**, 2501 (1914).

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The Study of Chloroiodides of Silicon, Tin and Germanium Using the Raman Spectra as Proof of Equilibria

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AND MICHEL DELHAYE

RECEIVED NOVEMBER 28, 1951

The chloroiodides of silicon, tin and germanium have a tetrahedral structure and show the following types of Raman spectra: AX_4 four frequencies and one polarized; AX_3Y six frequencies and three polarized; AX_2Y_2 nine frequencies and four polarized.

Earlier work with the chlorobromides of carbon,¹ silicon,² titanium,³ germanium⁴ and tin⁵ led to the present study of the Raman spectra for chloro-

iodides. In the case of the chlorobromides of carbon and silicon three chlorobromides can be isolated whereas for titanium, germanium and tin similar compounds cannot be isolated.

The manner in which the Raman spectra vary was studied^{1,2} for the two series: CCl_4 , CCl_3Br , CCl_2Br_2 , $CClBr_3$, CBr_4 and $SiCl_4$, ..., $SiBr_4$ (Tables I and II). The two spectral patterns have exactly the same shape. Frequency ν_1 , which is the strongest and the most completely polarized, is of

TABLE I

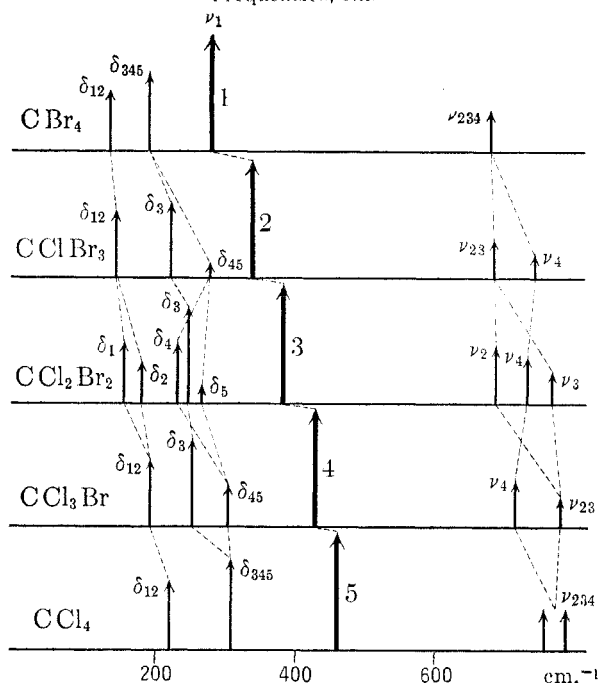
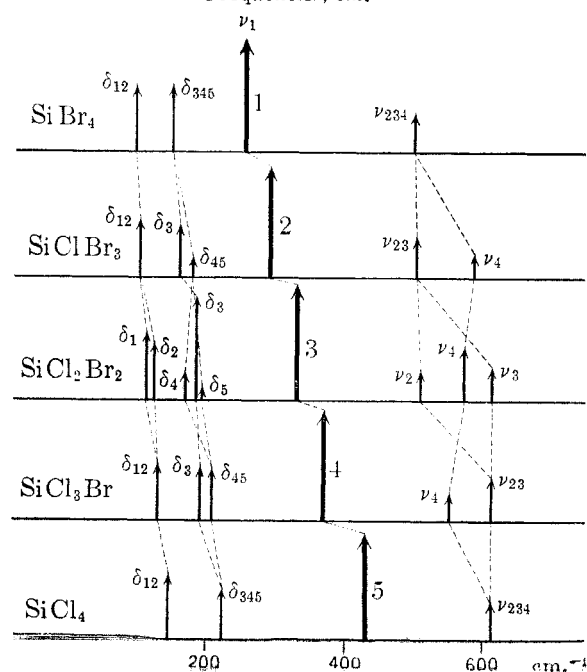
Frequencies, cm.⁻¹

TABLE II

Frequencies, cm.⁻¹

(1) M.-L. Delwaulle and F. Francois, *Compt. rend.*, **214**, 226 (1942).

(2) M.-L. Delwaulle and F. Francois, *ibid.*, **219**, 335 (1944).

(3) M.-L. Delwaulle and F. Francois, *ibid.*, **220**, 173 (1945).

(4) M.-L. Delwaulle and F. Francois, *ibid.*, **227**, 1229 (1948).

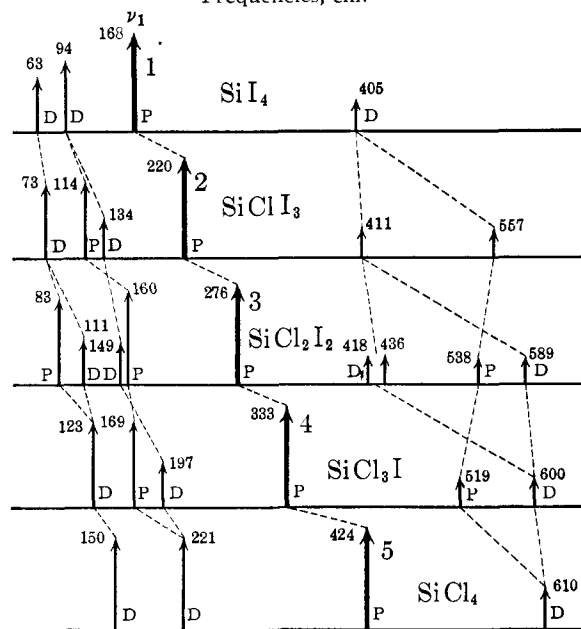
(5) M.-L. Delwaulle and F. Francois, *ibid.*, **219**, 84 (1944).

particular interest because it shifts toward the exciting line as bromine replaces chlorine. In the carbon series the locations for frequency ν_1 are at 459, 418, 370, 328 and 268 cm^{-1} .

Mixtures of ACl_4 and ABr_4 where A is titanium, germanium or tin, not only show the Raman frequencies of ACl_4 and ABr_4 but also show new frequencies with three highly polarized lines between the ν_1 frequencies of ACl_4 and ABr_4 . These three lines were: at 326, 294, 263 for titanium [389 TiCl_4 , 235 TiBr_4]; at 309, 281, 257, for germanium [396 GeCl_4 , 235 GeBr_4] and at 270, 250, 235 for tin [367 SnCl_4 , 220 SnBr_4]. The study of a large number of mixtures establishes the identification of almost all the frequencies of ACl_3Br , ACl_2Br_2 and AClBr_3 .^{3,4,5}

In the case of the chloriodides, the authors isolated the three chloriodides of silicon but not those of germanium and tin. The Raman spectra for the three chloriodides of silicon (SiClI_3 , SiCl_2I_2 , SiCl_3I) were obtained and photographed for the first time. The pattern of the Raman lines for this series [SiI_4 , ..., SiCl_4] (Table III) has exactly the same shape as that of the above series [SiCl_4 , ..., SiBr_4] (Table II). Knowledge of these Raman spectra is useful in the control of the preparation of the chloriodides.

TABLE III
Frequencies, cm^{-1}



The chloriodides of silicon were at first prepared by causing silicon tetrachloride to react with hydrogen iodide gas at red heat (Besson⁶).⁷ Figure 1A shows the microphotometer record of the Raman spectrum for the product of the above reaction and indicates that the percentage of silicon iodotrichloride formed was very small. The frequencies (ν_1) can be seen for both SiCl_3I and SiCl_4 .

In order to prepare sufficient amounts of chloro-

(6) A. Besson, *Compt. rend.*, **112**, 611, 1314 (1898).

(7) In order to isolate the chloriodides the product of the reaction must be distilled through a fractionating column. The reaction must be repeated many times to obtain sufficient product.

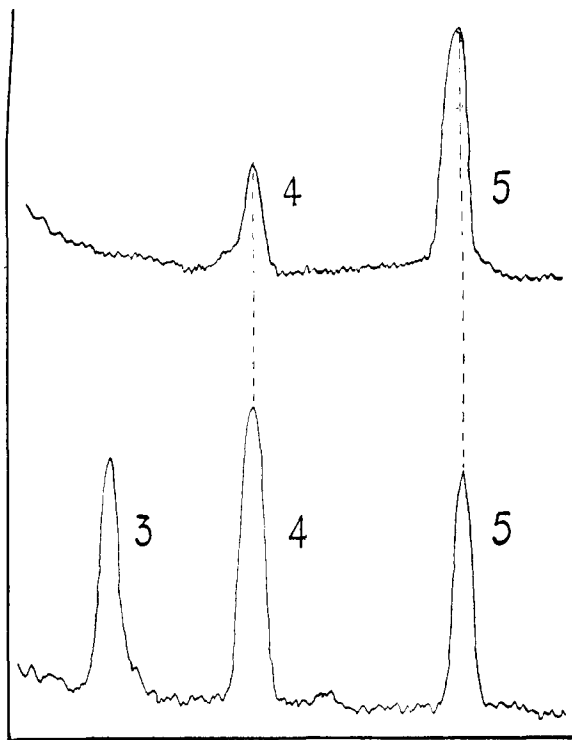
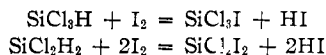


Fig. 1.—Raman spectra of silicon chloriodides: upper, $\text{SiCl}_4 + \text{IH}$ at 450° ; lower (B) $\text{Si} + \text{HCl} + \text{I}_2$ at 550° .

iodides the authors treated finely divided silicon with iodine and hydrogen chloride gas at 550° .^{8,9} When hydrogen chloride reacts with silicon in this form, SiCl_4 , SiCl_3H and a small amount of SiCl_2H_2 are formed. It is assumed that iodine reacts with SiCl_3H and SiCl_2H_2 according to the equations



The hydrogen iodide thus formed could react to give further replacement of chlorine by iodine. This was found to be true.

The Raman spectrum (Fig. 1B) for the liquid thus obtained indicated a large amount of silicon trichloriodide¹⁰ and a considerable amount of both silicon dichloriodide and silicon tetrachloride. One can see the ν_1 frequencies for each compound. When the mixture obtained by the above method is fractionally distilled, a small amount of silicon triiodochloride and silicon tetraiodide can be identified in the highest boiling fractions. It is interesting to note that iodine can replace hydrogen in silicon derivatives. Substitution by iodine occurs less readily than substitution by bromine.

Silicon trichloriodide is unstable toward heat, forming silicon tetrachloride, silicon dichloriodide and silicon tetraiodide. Figure 2 shows the microphotometer record of the Raman spectra for the material formed (by heating trichloriodide) at 325° (A) and at 400° (B).

Silicon trichloriodide reacts more rapidly with hydrogen iodide than does silicon tetrachloride. Figure 3 shows the microphotometer record of the

(8) The silicon was obtained by treating an alloy of silicon and aluminum with HCl .

(9) Silicon chlorobromides were made by a similar method at 360° .

(10) Yield 50% by volume.

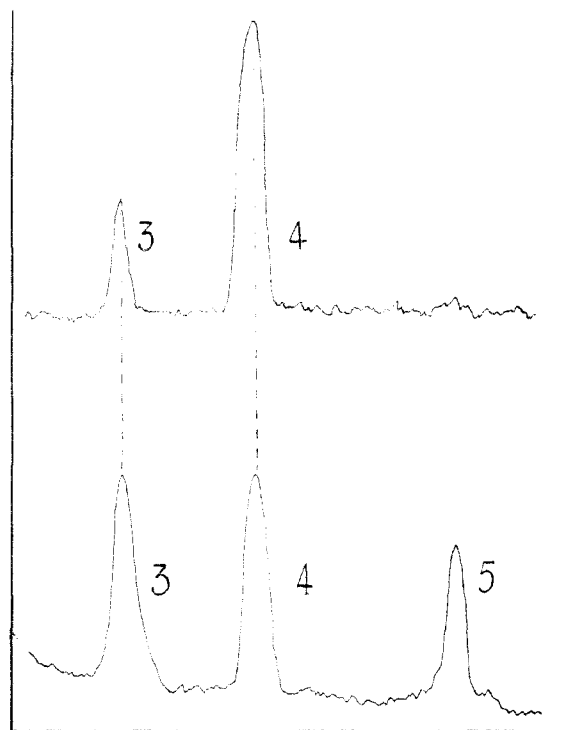


Fig. 2.—Raman spectra for silicon chloriodides: (A) upper, SiCl_3I at 325° ; (B) lower, SiCl_3I at 400° .

Raman spectrum for the liquid obtained by treating silicon trichloriodide with hydrogen iodide at 325° . The first chlorine is the most difficult to replace.

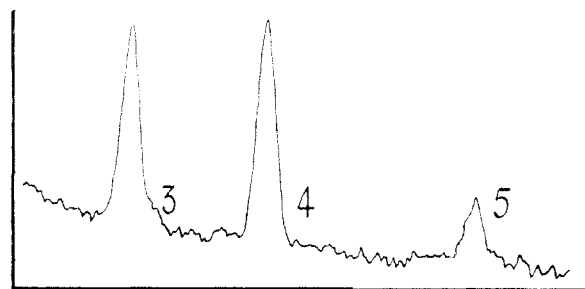


Fig. 3.—Raman spectrum for silicon chloriodides: $\text{SiCl}_3\text{I} + \text{HI}$ at 325° .

Chloriodides of tin were described early in the literature but were later disproved (Lenormand,¹¹ Auger,¹² Räder¹³). There is no record in the literature of the chloriodides of germanium. However germanium and tin chloriodides exist but cannot be isolated. They can be prepared by either causing germanium tetrachloride or stannic chloride to react with hydrogen iodide or by mixing the halides AsCl_4 and AsI_4 either in the pure form or in a solvent such as carbon disulfide. The reaction, which takes place when AsCl_4 and AsBr_4 are mixed, is more rapid for tin than for germanium.¹⁴ For the same element (germanium or tin) the chlorine-bromine exchange reaction proceeds faster than does

the chlorine-iodine exchange reaction. The study of Raman spectra for these mixtures or solutions definitely shows, as in the case of the chlorobromides of Ge and Sn, the existence of new molecules. Tables IV and V show the ν_1 frequencies of the three chloriodides of germanium and tin and similar frequencies for the chlorobromides. The pattern of the lines is unchanged when we replace chlorine by iodine, instead of chlorine by bromine. There is also great similarity between the spectra for the germanium and tin compounds.

TABLE IV

ν_1 frequencies, cm^{-1}

161	190	222	258	396
GeI_4 1	2	3	4	GeCl_4 5
235	257	281	309	396
GeBr_4 1	2	3	4	GeCl_4 5

TABLE V

ν_1 frequencies, cm^{-1}

153	172	195	215	367
SnI_4 1	2	3	4	SnCl_4 5
220	235	250	270	367
SnBr_4 1	2	3	4	SnCl_4 5

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Methylsulfur Trichloride and Analogous Compounds^{1,2}

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FREDERIC T. MARTIN

RECEIVED JUNE 25, 1952

In a recent paper from this Laboratory the preparation and reactions of methylsulfur trichloride were reported.³ The reaction between methyl disulfide and chlorine was described as

(1) This paper describes work done on Project NR-055-165 under Contract Nonr-647(00) with the Office of Naval Research, United States Navy.

(2) Taken in part from the Master's Thesis of Kay Robert Brower.

(3) K. R. Brower and I. B. Douglass, *THIS JOURNAL*, **73**, 5787 (1951).

(11) M. C. Lenormand, *J. pharm. chim.*, **8**, 249 (1898).

(12) V. Auger, *Compt. rend.*, **149**, 860 (1909).

(13) M. G. Räder, *Z. anorg. Chem.*, **130**, 325 (1923).

(14) M. L. Delvaux, *Compt. rend.*, **232**, 54 (1951).