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**Abstract**

**Full Text**

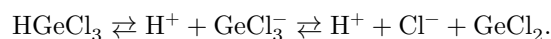
**Chemistry**

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## Study of the Etherates of Trihalogermanes by N.M.R. Spectroscopy

*(Presented by Academician M. I. Kabachnik on 21 VII 1964)*

Trichlorogermane, in contrast to trichlorosilane, is prone to protonation of its hydrogen, which can be explained by the different direction of polarization of these compounds ( $\overset{\delta_+}{\text{H}}\overset{\delta_-}{\text{GeCl}_3}$  and  $\overset{\delta_-}{\text{H}}\overset{\delta_+}{\text{SiCl}_3}$ ) and by the tendency of the former toward dissociation according to the scheme <sup>(1, 2)</sup>:



In this respect  $\text{HGeCl}_3$  is to a considerable extent reminiscent of chloroform, which on alkaline hydrolysis forms dichlorocarbene <sup>(3)</sup>.

**Table 1**

Compound	$\text{CH}_3$ (triplet)	$\text{CH}_2$ (quartet)	M-H (singlet)
$\text{HCCl}_3$	—	—	7.27
$\text{HSiCl}_3$	—	—	6.15
$\text{HGeCl}_3$	—	—	7.62
$(\text{C}_2\text{H}_5)_2\text{O}$	0.86	3.08	—
$(\text{C}_2\text{H}_5)_2\text{O} + \text{HCCl}_3$ (1 : 1)	1.04	3.44	7.63
$(\text{C}_2\text{H}_5)_2\text{O} + \text{HSiCl}_3$ (1 : 1)	1.13	3.39	6.15
$2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HGeCl}_3$	1.48–1.54	4.10–4.26	14.94–15.30
$2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HGeBr}_3$	1.64	4.16	14.00
$2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HGeJ}_3$	1.34	3.92	12.10
$2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HSnCl}_3$	1.70	4.42	12.81
$(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HCl}$ **	1.25	3.54	6.81

Compound	CH <sub>3</sub> (triplet)	CH <sub>2</sub> (quartet)	M–H (singlet)
2(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O · HCl	1.25	3.54	6.83
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	0.90	1.47 and 3.30***	–
2( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O · HGeCl <sub>3</sub>	1.20	1.80 and 4.02***	11.70

Average value of the chemical shift  $\delta$  in ppm for the groups.\*

\* Relative to the signal of tetramethylsilane (TMS), taken as zero.

\*\*  $\delta$  for the liquid (at  $-86^\circ$ ) and gaseous HCl is respectively 2.0 and 0.0 ppm (7).

\*\*\* Respectively for the  $\gamma$ - and  $\beta$ -CH<sub>2</sub> groups (multiplet) and the  $\alpha$ -CH<sub>2</sub> group (triplet).

With weaker bases or other nucleophiles (simple ethers, ketones, aromatic hydrocarbons), HCCl<sub>3</sub> forms associates through hydrogen bonds, for the study of which infrared and especially n.m.r. spectroscopy are widely used (4). In the present work, by the n.m.r. method we studied the molecular complexes of trichlorogermane and other trihalogenides of Group IVB elements with a number of simple ethers; the fact of their formation and their properties were recently reported by us (5, 6).

As can be seen from the data in Table 1, the proton signals of HCCl<sub>3</sub> and HGeCl<sub>3</sub> lie at a noticeably lower field than HSiCl<sub>3</sub> ( $\Delta\delta$  1.1–1.5 ppm), which is in complete agreement with the above-indicated degree of protonation of hydrogen in these trichlorides: HGeCl<sub>3</sub> > HCCl<sub>3</sub>  $\gg$  HSiCl<sub>3</sub>. At the same time, whereas HCCl<sub>3</sub> and HSiCl<sub>3</sub> give narrow singlets with a half-width of  $\sim 1$  cps, the half-width of the singlet signal of trichlorogermane is also  $\sim 7.2$  cps. This fact is apparently a consequence of proton exchange between the covalent (HGeCl<sub>3</sub>) and ionic (H<sup>+</sup> + GeCl<sub>3</sub><sup>-</sup>) forms of trichlorogermane, as well as of the HCl present in it. The etherate obtained from (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, according to material-balance data, elemental analysis, and the n.m.r. spectrum, corresponds to the formula 2(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O · HGeCl<sub>3</sub> (I). The latter is insoluble in excess ether and other solvents, but dissolves HGeCl<sub>3</sub> in itself.

In the IR spectrum of I it is not possible to detect frequencies of either the Ge–H bond (in the region 2000–2200 cm<sup>-1</sup>) or the Ge–O bond (in the region 800–900 cm<sup>-1</sup>). This makes it possible to assume that the formation of I occurs mainly through donor-acceptor interaction of the free electron pairs of the ether oxygens with germyl hydrogen, and not with the vacant *d*-orbitals of the germanium atom. Oxonium compounds are formed in a similar way and, in particular, etherates of hydrogen chloride *n*(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O · *m*HCl, accompanied, according to (8), by a strong bathochromic shift of the H–Cl bond band in the IR spectrum (from  $\sim 2800$  to  $\sim 2400$  cm<sup>-1</sup>).

**Fig. 1.** NMR spectra of etherate I: *a* –freshly prepared, *b* –3 months after preparation

The NMR spectrum of I (Fig. 1a) shows an extremely strong protonation of the germyl hydrogen, close to complete dissociation:  $\delta$  14.9–15.3 ppm, as compared with 7.6 for trichlorogermane itself, whereas for aqueous HCl (signal of the  $\text{H}_3\text{O}^+$  ion) it is 16.6 (7), and for etherates of hydrogen chloride 6.8 ppm (Table 1). The consequence of such a strong interaction of the ether oxygens with the germyl proton is a considerable downfield shift of the signals of the protons of the  $\text{CH}_3$ - and  $\text{CH}_2$ -groups of the ether molecules that are part of I:  $\Delta\delta$  0.7 and 1.2 ppm, respectively, as compared with 0.4 and  $\sim 0.5$  ppm for HCl etherates (Table 1).

A very interesting question is that of the equivalence of the two ether molecules that are part of I. As can be seen from the data in Table 2, when an equimolar amount of  $\text{HGeCl}_3$  is dissolved in I, no molecular complex of it with ether in a 1:1 ratio is formed, but rather a simple mixture of I and  $\text{HGeCl}_3$ , which are in exchange; this is indicated by the broad and sloping signal of the germyl proton (half-width  $\sim 18$  Hz, rate of proton exchange  $\sim 100$  exchanges/sec).

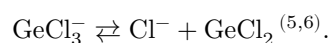
**Table 2**

Compound	$\delta$ in ppm for groups	$\delta$ in ppm for groups	$\delta$ in ppm for groups
Compound	$\text{CH}_3$	$\text{CH}_2$	GeH
$2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HGeCl}_3$ (Ia)	1.48	4.10	14.94
Ia + $\text{HGeCl}_3$ (2 : 1)	1.70	4.40	12.80
Ia + $\text{HGeCl}_3$ (1 : 1)	1.74	4.42	11.24

An attempt to arrive at a complex of composition  $(\text{C}_2\text{H}_5)_2\text{O} : \text{HGeCl}_3 = 1 : 1$  by partial distillation of ether from I also proved unsuccessful. The NMR spectra of samples taken during vacuum distillation of I in a stream of dry  $\text{N}_2$ , up to a decrease in its weight by 63%, proved to be completely identical with the spectrum of the initial I. Thus, during vacuum distillation I decomposes according to the scheme:  $\text{I} \rightarrow \text{GeCl}_2 + 2(\text{C}_2\text{H}_5)_2\text{O} + \text{HCl}$ . In this case, ether and HCl are distilled off—

whereas the remaining I is enriched in germanium dichloride, which, after the distillation is completed, apparently remains in the flask in polymeric form  $(\text{GeCl}_2)_x$ , along with the products of its decomposition—subchlorides  $(\text{Ge}_2\text{Cl}_3)_x$  and  $(\text{GeCl})_x$  (yield 60–70%, germanium dichloride content 55–60%). The presence of a certain amount of  $\text{GeCl}_2$  (5–7%) is apparently also responsible for the color of freshly prepared I, as indicated also by the increased content of Cl and Ge in it. The presence of  $\text{GeCl}_2$  is avoided when  $\text{HGeCl}_3$  is mixed not with ether, but with etherate HCl, which indeed leads to colorless I.

The data on the distillation of I and the dissolution of  $\text{HGeCl}_3$  in it, as well as the presence in the NMR spectrum of I for the ethyl groups of only 7 lines (a quartet for  $\text{CH}_2$  and a triplet for  $\text{CH}_3$ ), indicate a symmetrical structure of I and equivalence of both ether molecules included in its composition. This requirement is satisfied by  $[(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{H} \dots \text{O}(\text{C}_2\text{H}_5)_2]^+\text{GeCl}_3^-$  or  $[(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{H} \leftarrow \text{O}(\text{C}_2\text{H}_5)_2]^+\text{GeCl}_3^-$ . The indicated structure explains the tendency of trichlorogermane etherates to act in many reactions as sources of germanium dichloride, which is due in this case to the particular ease of dissociation:



The process of “aging” of trichlorogermane etherates is also very characteristic. Initially insoluble I, on storage for 1-3 days ( $\sim 20^\circ$ ), becomes soluble in ether and other organic solvents. At the same time, there is a gradual shift of the signal of the germyl proton (and, to a lesser degree, of the ether proton signals) toward stronger fields—up to 10.2 ppm 3 months after preparation (Fig. 1b). Along with this, weak quartets with  $\delta \sim 4.1$  and  $\sim 2.3$  ppm (Fig. 1b) additionally appear in the spectrum of the “old” (soluble) etherate; these are associated with the formation, during the “aging” process, of  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_2\text{H}_5\text{GeCl}_3$ , which is confirmed by the identity of the NMR spectrum of “old” I with the spectrum of freshly prepared I containing added amounts of these compounds. The decomposition of I is considerably accelerated by increasing the temperature.

Thus, the shift, accompanying the “aging” process of I, of the resonance signals of its protons into the region of stronger field is explained by a dilution effect of I by decomposition products, as well as by the appearance of proton exchange between I and  $\text{C}_2\text{H}_5\text{OH}$ . Indeed, as seen from Table 3, dilution of soluble (“old”) etherate I with ether or  $\text{CCl}_4$  causes an even sharper shift of the signal of the germyl proton toward stronger field (the  $\delta$  values for the protons of the  $\text{CH}_3$ - and  $\text{CH}_2$ -groups, equal to 1.34 and 3.54 ppm, respectively, remain almost unchanged). All these facts also indicate interaction of the individual particles of I with one another and the complex structure of etherates as a whole.

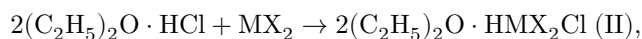
**Table 3**

Compound	$\delta$ , ppm, for the group Ge—H
$2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HGeCl}_3$ (Ib)*	10.20
Ib + $(\text{C}_2\text{H}_5)_2\text{O}$ (1 : 1)	9.90
Ib + $(\text{C}_2\text{H}_5)_2\text{O}$ (1 : 3)	9.00
Ib + $(\text{C}_2\text{H}_5)_2\text{O}$ (1 : 15)	7.06
Ib + $\text{CCl}_4$ (1 : 3)	9.18

\* Age—3 months.

Similar I etherates are formed by  $\text{HGeCl}_3$  also with other simple ethers, comparative NMR-spectral data for which are given in Table 1. However, in contrast to dialkyl ethers, tetrahydrofuran gives with  $\text{HGeCl}_3$  only soluble etherates ( $\delta_{\text{GeH}} \approx 14.2$  ppm).

In addition to trichlorogermane etherates, we obtained and studied etherates of a number of other trihalogermanes. The etherate of tribromogermane  $2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HGeBr}_3$  ( $n_D^{20} \sim 1.527$ ,  $d_4^{20} \sim 1.404$ ) was obtained by mixing  $\text{HGeBr}_3$  with an excess of ether, while etherates II were obtained by dissolving  $\text{GeI}_2$  or  $\text{SnCl}_2$  in  $\text{HCl}$  etherate:



where M is Ge or Sn, and X is I or Cl. These etherates are likewise insoluble in ether, colored oily liquids; in their NMR spectra (Table 1) and other properties they are very similar to I.  $(\text{GeCl}_2)_x$  likewise dissolves readily in etherate  $\text{HCl}$ , again forming I.

## Experimental Part

The NMR spectra were recorded on a high-resolution spectrometer of the JNM-C-60 type (60 MHz) at  $\sim 23^\circ$ . The values of the chemical shifts  $\delta$  are given in ppm relative to the TMS signal, taken as zero.

**Etherates of trichlorogermane.** 104 g of an azeotropic mixture of  $\text{HGeCl}_3$  and  $\text{GeCl}_4$  ( $\sim 2 : 1$ ) were added over 5 min to 155 g abs. diethyl ether with stirring and efficient cooling. This produced two layers, the lower of which was a mobile oily liquid of light yellow-green color, insoluble in ether and other organic solvents. Yield 131.5 g,  $n_D^{20} \sim 1.497$ ,  $d_4^{20} \sim 1.255$ ; it decomposes on distillation.

Found, %: C 28.38; 28.81; H 6.46; 6.49; Cl\* 34.00; 33.71; Ge 24.90, 25.20  
 $\text{C}_8\text{H}_{21}\text{Cl}_3\text{GeO}_2$ . Calculated, %: C 29.27; H 6.44; Cl 32.41; Ge 22.11

The NMR spectrum of this compound (Fig. 1a) indicates the presence in it of three types of protons in the ratio 12 : 8 : 1 (from integration data; accuracy  $\pm 5\%$ ), which corresponds to the composition  $2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HGeCl}_3$  (I).

By distillation of the upper layer remaining after separation of etherate I, we isolated only excess  $(\text{C}_2\text{H}_5)_2\text{O}$  and  $\text{GeCl}_4$  (yield 27.5 g).

In a similar manner, an etherate of trichlorogermane with di-*n*-butyl ether of composition  $2(\text{C}_4\text{H}_9)_2\text{O} \cdot \text{HGeCl}_3$  (III) was prepared;  $n_D^{20}$  1.474,  $d_4^{20}$  1.173.

**Decomposition of trichlorogermane etherates.** 104.5 g of etherate I were boiled with a reflux condenser for 30 h (the temperature rose from 47 to 65°). After removal of ether and a mixture of  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{HGeCl}_3$  (yields, according to gas-liquid chromatography,\*\* respectively 4.6 and 8.2 g), 25.5 g (39%) of ethyltrichlorogermane, b.p. 32° (7 mm), were isolated. Boiling 26 g of etherate III (110–130°, 12 h) gives 4 g (35%) of *n*- $\text{C}_4\text{H}_9\text{GeCl}_3$ .

**Preparation of germanium dichloride.** 25.5 g of etherate I were carefully evaporated under the vacuum of a water-jet pump ( $p \sim 20$  mm Hg) at  $0^\circ$  (2–2.5 h). When the temperature was raised to  $50\text{--}60^\circ$ , a yellow, finely crystalline precipitate immediately began to form, which was dried for 2 h at  $50\text{--}60^\circ/1$  mm. Yield 7.1 g (61%, calculated as  $\text{GeCl}_2$ ), sublimation point  $\sim 140^\circ$ ; according to elemental analysis, the ratio  $\text{Ge} : \text{Cl} = 1 : 1.52$ . The latter reacts with  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  (on heating to  $50^\circ$ ) and with  $\text{CH}_3\text{OCH}_2\text{Cl}$  (exothermically at  $\sim 20^\circ$ ), giving, in yields of 54–56%, respectively,  $\text{C}_6\text{H}_5\text{CH}_2\text{GeCl}_3$  and  $\text{CH}_3\text{OCH}_2\text{GeCl}_3$ .

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\* Titrimetrically found: 33.0; 33.6%.

\*\* Column  $0.4 \times 200$  cm with 15% polymethylphenylsiloxane on diatomaceous brick,  $100^\circ$ , carrier gas—helium.

*Note: Figure translations are in progress. See original paper for figures.*

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