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INFRARED STUDY OF INTRAMOLECULAR COORDINATION IN (CHLOROMETHYL)- AND (DICHLOROMETHYL)-GERMANES

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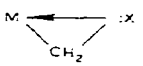
Summary

Frequencies (ν) and integrated intensities (A) of Ge—H stretching modes in the IR spectra of (diorgano)germanes containing $GeCH_2Cl$ and $GeCHCl_2$ fragments have been measured. Anomalous values of ν and A (compared to those expected from the inductive effect only) are explained by intramolecular coordination between chlorine and germanium atoms. The enthalpy of intramolecular coordination ($-\Delta H$) has been determined by IR spectroscopy. The enthalpy of intramolecular coordination is shown to increase with the acceptor properties of the substituents bonded to the germanium atom in (diorgano)- and (triorgano)-germanes.

Introduction

The electronic intramolecular interaction in systems of  type (M = Si, Ge, Sn, X = halide) has been studied in recent years [1—3]. This interest arose from the fact that intramolecular coordination appeared to be a driving force for different rearrangements and for many elimination reactions in organometallic compounds. Spectroscopic data [2,4—7] show that with any R_i and M in $(R_i)_3MCH_2Cl$ compounds, the electron density at the chlorine atom in the CH_2Cl fragment is always lower than that of corresponding carbon analogue. The anomalously high mobility of the chlorine atom in the CH_2Cl fragment towards interaction with nucleophilic reagents [8] also indicates a characteristic distribution of electron density in the molecules of organometallic compounds.

There are some data from the spectroscopic study of intramolecular coordina-

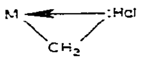
TABLE 1

IR DATA

No	Compound	$\Sigma\sigma^*$	ν(Ge–H) (cm^{-1})		$A^{1/2} \times 10^2$ (mol^{-1} l)$^{1/2}$ cm^{-1}		Composition (%)		Enthalpy, $-\Delta H$, (kJ/mol) ±0,5
			ν_c	ν_f	$A_c^{1/2}$	$A_f^{1/2}$	C_c	C_f	
I	$(C_2H_5)_2HGeCH_2Cl$ [a]	0,85							2,1
II	$(CH_3)_2HGeCH_2Cl$ [a]	1,05							3,3
III	$(C_4H_9)H_2GeCH_2Cl$	1,41	2053	2076	1,85	1,51	30	70	4,6
IV	$(C_2H_5)H_2GeCH_2Cl$	1,44	2054	2078	1,86	1,50	30	70	4,6
V	$(CH_3)H_2GeCH_2Cl$	1,54	2064	2085	1,84	1,49	30	70	5,3
VI	$CH_3(C_6H_5)HGeCH_2Cl$ [a]	1,65							4,2
VII	$(C_2H_5)_2HGeCHCl_2$ [a]	1,74							5,0
VIII	$(C_4H_9)H_2GeCHCl_2$	2,30	2075	2094	1,84	1,33	45	55	7,4
IX	$(C_2H_5)H_2GeCHCl_2$	2,33	2074	2095	1,82	1,32	45	55	7,8
X	$(C_2H_5)ClHGeCH_2Cl$ [a]	3,85							4,6

[a] Ref. 3.

tion that have been appeared recently in the literature. The published data allow us to draw some conclusions concerning this effect. An interaction of



type is indicated by the following facts.

1. The lower polarity of the C—Cl bond in chloromethylsilane compared to that in ethyl chloride [2].
2. The similar character of the dipole moment change in compounds of $H_2(CH_3)SiX$ and H_3SiCH_2X (X = Cl, Br, I) types [9].
3. The non-equivalence of Sn—Cl bonds in the $SnCl_3$ group and the nonlinearity of NQR ^{35}Cl dependence on n in compounds of $Cl_nSn(CH_2Cl)_{4-n}$ type [4].
4. The weak NQR ^{35}Cl sensitivity to the inductive effect of the substituents in $R_2(R_3Si)CCl$ compounds compared to that in analogous organic compounds [10].
5. The lower, compared to that expected, inductive constant σ^* for the chloromethyl fragment in $(R_i)_3SiCH_2Cl$ compounds [11].
6. The decrease of stretching mode frequency ν(M—H) (M = Si, Ge) in the IR spectra of compounds containing chloromethyl fragments [3,12,13].
7. The increase of the integrated intensity of the ν(M—H) stretching mode in molecules participating in intramolecular coordination [3,13].

There are different points of view concerning the mechanism of intramolecular coordination [1,3,6,7,14]. In most cases [1,3,4,9,13] (*p*—*d*) σ interaction, upon which the lone electron pair of the X atom shifts into the vacant d_γ orbital of the M atom, is suggested. The validity of this proposed mechanism is based on the experimental evidence of electronic density shift from the CH_2Cl fragment of the M atom and on the fact that the Si subgroup elements are known to participate in the formation of additional σ bonds, transforming into five- and six-valent states [15].

In an earlier report [3], we have shown that the investigation of the frequency and integrated intensity of Ge—H stretching modes in the IR spectra of trisubstituted germanes provides significant data on intramolecular coordination. The aim of this work was to study intramolecular coordination in disubstituted germanes containing chloro- and dichloro-methyl fragments, and to investigate the dependence of intramolecular coordination enthalpy on the effective charge on the Ge atom.

Results and discussion

The values of the frequencies (ν) and integrated intensities (A) of the Ge—H stretching modes of the compounds investigated are given in Table 1. It is evident that the ν(Ge—H) band has a doublet character. As in the case of silane derivatives [12,13] and triorganogermanes [3], this is caused by intramolecular coordination between chlorine and germanium atoms (α-effect). At first sight the doublet character of ν(Ge—H) bands in diorganogermanes containing $>GeH_2$ fragments, might be explained by the existence of two bands characteristic of two types of stretching vibrations: symmetrical (ν_s) and asymmetrical (ν_{as}). However, much of the experimental evidence concerning ν(Ge—H) in diorgano-

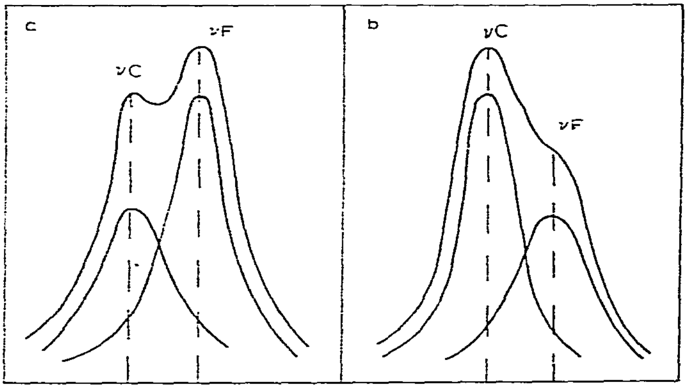


Fig. 1. Form of absorption bands of the ν(Ge—H) stretching mode in the IR spectra of the compounds investigated (solvent is heptane): a) compounds III, IV, V, b) compounds VIII, IX.

germanes [16,17], together with calculated data available [18], indicate that the difference between ν_s and ν_{as} values is generally very small. Therefore, there is one band for both symmetrical and asymmetrical stretching vibrations in the experimental spectrum, as indicated by the significantly great intensity of the band in diorganogermanes compared to that in triorganogermanes. In triorganogermanes [3] and diorganogermanes (Fig. 1) containing chloromethyl substituents, the ν(Ge—H) absorption band has a doublet character, differing markedly from other tri- and di-organogermanes. Intramolecular coordination in chloromethyl derivatives is responsible for the doublet character of the ν(Ge—H) bands. The assignment of ν(Ge—H) bands to coordinated (ν_c) and "free" (ν_f) forms has been studied in detail [3,12,13].

In the absence of intramolecular coordination, the substituents bonded to the Ge atom influence the polarity of the Ge—H bond by an inductive mechanism only. This allows the integrated intensities of ν(Ge—H) absorption bands to be determined for molecules not involving intramolecular coordination ($A_f^{1/2}$) from the equation obtained previously for the compounds of R_2GeH_2 type

$$A_{ind}^{1/2} = 1.79 - 0.2\,\Sigma\sigma^* \text{ [16]} \tag{1}$$

$A_f^{1/2}$ values were used to calculate the concentration of molecules in "free" (C_f) and coordinated (C_c) forms. It follows from Table 1 that the integrated intensity of coordinated molecules ($A_c^{1/2}$) is in all cases 0.3—0.5 $\times$ 10^2 $\text{mol}^{-1/2}\ \text{l}^{1/2}\ \text{cm}^{-1}$ higher than that of "free" molecules ($A_f^{1/2}$). This is explained by the fact that chloro- and dichloro-methyl groups exhibit both electron-acceptor (—I effect) and electron-donor (α effect) properties (donating lone electron pairs of the Cl atom onto the vacant 4*d* orbitals of the Ge atom). This process is accompanied by a rise of Ge—H bond polarity, as was discussed previously [3,13]. As a consequence, $A_c^{1/2}$ values increase and become much higher than the values of $A_f^{1/2}$.

The shapes of the ν(Ge—H) absorption bands in the IR spectra of the germanes in heptane solution are shown in Fig. 1. It can be seen that for compounds III—V (the proportion of coordinated molecules is about 30%) the peak intensities of ν_c(Ge—H) are lower than those of ν_f(Ge—H). The higher integrated intensity of the coordinated form in compounds VIII and IX, and the greater concentration of coordinated molecules (~45%) lead to a higher peak intensity of ν_c compared to that of ν_f. As in the case of triorganogermanes [3], the shapes of ν(Ge—H) bands in compounds III—V, VIII and IX are affected by solvent. On consecutive addition of carbon tetrachloride or toluene to the heptane solution of the compound investigated, a regular change of the peak intensity ratio of ν_c and ν_f bands takes place. Partial disturbance of coordination in this case results in a decrease of ν_c peak intensity and in the increase of ν_f peak intensity.

We have estimated the enthalpy ($-\Delta H$) of intramolecular coordination in the diorganogermanes (compounds III—V, VIII and IX). It follows from the data in Table 1 that the intramolecular coordination enthalpy in tri- and di-organogermanes depends on the character of the substituents bonded to the Ge atom. The enthalpy of intramolecular coordination increases from 2.1 to 7.8 kJ/mol with a rise of acceptor properties of the substituents from 0.85 to 2.33 (according to σ^* Taft constants). Correlation of $-\Delta H$ values with the sum of Taft inductive constants ($\Sigma\sigma^*$) of the substituents in tri- [3] and di-organogermanes (compounds I—V, VII and IX; Table 1) results in the linear equation:

$$-\Delta H = 3.5\ \Sigma\sigma^* - 0.6 \qquad (r = 0.985;\ s = \pm 0.3) \tag{2}$$

In diorganogermanes one of hydrogen atoms was treated as a substituent.

Relationships similar to eq. 2 are well known for intermolecular complexes formed by organometallic compounds and electron donors. Thus, for example, for intermolecular complexes formed by organochlorostannanes of Cl_nSnR_{4-n} type with acetone (eq. 3) or tributylphosphine oxide (eq. 4), the following relations are true [19]:

$$-\Delta H = 1.03\ \Sigma\sigma^* - 0.23 \tag{3}$$

$$-\Delta H = 2.29\ \Sigma\sigma^* + 0.59 \tag{4}$$

where $\Sigma\sigma^*$ is the sum of inductive Taft constants for substituents bonded to the tin atom.

It can be seen from relations 2—4, that the enthalpy of the intermolecular donor-acceptor bond, as well as the enthalpy of intramolecular coordination in chloromethylgermanes, increases linearly with increasing acceptor properties of the substituents bonded to the central element on which coordination occurs.

Increase of substituents acceptor abilities results in an increase of the positive charge on the central atom, and hence in a decrease of the diffusion of vacant *nd* orbitals, which, in its turn, favours overlapping of *nd* orbitals with lone electron pairs of the donor centre (the Cl atom in CH_2Cl and $CHCl_2$ fragments in the case of intramolecular coordination), i.e. it increases the strength of donor-acceptor bond and its enthalpy.

If the inductive effect of the substituents bonded to the central element is dominating, and if steric hindrance has no marked influence on the formation of the donor-acceptor bond, a simple relationship might be expected between $-\Delta H$ values and the σ^* parameters, characteristic of the I effect. Similar linear relationships have been observed for intermolecular organochlorostannane complexes [19] and for intramolecular complexes in the chloromethylgermanes studied. The similarity in relationships is believed to indicate not only a formal analogy between intermolecular donor-acceptor bonds and intramolecular coor-

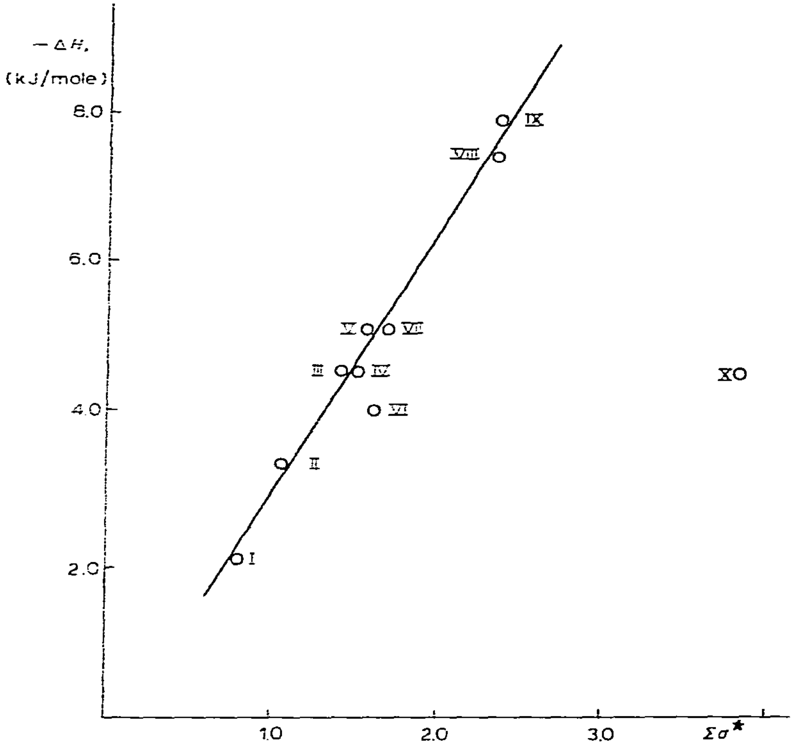


Fig. 2. The relationship between —ΔH and Σσ* of the substituents in di- and triorganogermanes.

dination, but also a common mechanism for the two processes. This mechanism is confirmed as being (*p*—*d*) σ interaction, the value of which (enthalpy —Δ*H*) is determined by overlap integrals of donor *p* orbitals and acceptor *nd* orbitals. Overlap integrals depend on the central atom charge, which is, in its turn, depends on the electronic effects of the substituents at the central element. The above-mentioned relationships 2—4 refer to the case when —Δ*H* is influenced by the inductive effect only. If the substituents bonded to the central atom exert both inductive and resonance effects, some deviations from the linear relationships of eqs. 2—4 are observed. They are found for (chloromethyl)methylphenylgermane and (chloromethyl)ethylchlorogermane (compounds VI, X; Table 1, Fig. 2). The enthalpy of intramolecular coordination in these compounds is small compared to that expected from equation 2. Deviations of the points, corresponding to the straight line —Δ*H* — Σσ* (Fig. 2), are 1.1 and 8.4 kJ/mol for (chloromethyl)methylphenylgermane and (chloromethyl)ethylchlorogermane, respectively. The decrease of —Δ*H* values for intramolecular coordination in these compounds is probably due to (*p*—*d*) π interaction in Ge—Ph and Ge—Cl bonds. The effect of the (*p*—*d*) π interaction consist in a partial transfer of π-electrons from the aromatic ring or lone electron pairs of Cl atom to the vacant 4*d* orbitals of the Ge atom. This effect is directed opposite to the —I effect of the phenyl group and the Cl atom and formally leads to a decrease of acceptor properties of the substituents. This decrease is responsible for the smaller values of $-\Delta H$ in compounds VI and X, compared to those calculated by equation 2. The effect of $(p-d)\ \pi$ interaction is more pronounced in the Ge—Cl bond than in the Ge—Ph fragment [16]. Hence, the deviation of the point corresponding to (chloromethyl)ethylchlorogermane is much greater than that of the point for (chloromethyl)methylphenylgermane (Fig. 3).

Experimental

The compounds were prepared according by the following reactions

$(C_4H_9)H_2GeCHCl_2$:

$$(C_4H_9)H_2GeCl + CHCl_2Li \xrightarrow[Et_2O/THF]{-95^\circ C} (C_4H_9)H_2GeCHCl_2 + LiCl$$

$(C_4H_9)H_2GeCH_2Cl$:

$$(C_4H_9)H_2GeCHCl_2 + Bu_3SnH \rightarrow (C_4H_9)H_2Ge(CH_2Cl) + Bu_3SnCl$$

$(C_2H_5)H_2GeCHCl_2$:

$$(C_2H_5)H_2GeCl + CHCl_2Li \xrightarrow[Et_2O/THF]{-95^\circ C} (C_2H_5)H_2GeCHCl_2 + LiCl$$

The compounds described in this paper were characterized using standard analytical techniques: GLC (Aerograph 90P, Varian 1200, SE 30) and NMR Varian T 60).

$(C_4H_9)H_2GeCHCl_2$

$BuGeH_2Cl$ (16.70 g, 0.10 mol) was added dropwise at —95° C to $CHCl_2Li$ (0.095 mol), freshly prepared by Kobrich's method [20]. The mixture was maintained at —95° C for 2 h and then warmed up to room temperature. After hydrolysis and pentane extraction, the solution obtained was dried over Na_2SO_4 and then distilled, giving $BuGeH_2CHCl_2$, (10.36 g, 48% yield). B.p. 65° C/ 15 mmHg, NMR (ppm): $\delta(GeH_2)$ 4.54 (quart), $\delta(CH)$ 5.60 ppm (t).

$(C_4H_9)H_2GeCH_2Cl$

Bu_3SnH (3.24 g, 0.011 mol) was added to $BuGeH_2CHCl_2$ (2.41 g, 0.011 mol). An exothermic reaction took place and the mixture was then refluxed for 1 h. Distillation in the presence of catalytic amounts of galvinoxyl and hydroquinone gave $BuGeH_2CH_2Cl$, (1.51 g, 75% yield). B.p. 44—46° C/11 mmHg, NMR (ppm): $\delta(GeH_2)$ 4.08 (quint), $\delta(CH_2)$ 3.03 ppm (t).

$(C_2H_5)H_2GeCHCl_2$

$EtGeH_2Cl$ (1 g, 0.136 mol) was added dropwise at —95° C to freshly prepared $CHCl_2Li$ (0.120 mol). The mixture was maintained at —95° C for 2 h and then warmed up to room temperature. After hydrolysis and pentane extraction, the solution was dried over Na_2SO_4 and then distilled giving $EtGeH_2CHCl_2$ (8.06 g, 43% yield). B.p. 59° C/40 mmHg, NMR (ppm): $\delta(GeH_2)$ 4.52 (m), $\delta(CH)$ 5.62 ppm (t).

IR spectra

IR spectra were recorded on a Zeiss UR-20 spectrophotometer. Heptane solutions of the compounds studied (concentration 0.05—0.08 mol/l) were used to obtain the spectra. Procedures for the determination of concentration (C_f and C_c) as well as of the integrated intensities ($A_f^{1/2}$ and $A_c^{1/2}$) are described in detail in ref. 3. The integrated intensity were determined by the method given in ref. 21. For the enthalpy ($-\Delta H$) measurements, the temperature dependence of the integrated absorbance of absorption bands corresponding to molecules of "free" and coordinated forms was studied.

The purity of the compounds studied was checked by GLC.

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