# INFRARED STUDY OF THE FORMATION OF COMPLEXES OF TRIETHYLSILANE AND TRIETHYLGERMANE WITH ELECTRON-DONATING SOLVENTS *

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## Summary

The integrated intensities of M–H (M = Si, Ge) stretching modes in the IR spectra of triethylsilane and triethylgermane in heptane solution and in the same solvent with added electron-donating solvents have been measured. It was shown that triethylsilane and triethylgermane form complexes of donor-acceptor type (Si and Ge atoms as acceptors) with electron-donating solvents. Solvents with sterically more accessible oxygen atoms as an electron donor solvate triethylsilane and triethylgermane equally. The solvation action of nitrogen-containing electron donors is strongly influenced by steric hindrance of the substituents at the electron donor and acceptor centres.

## Introduction

Electron-donating solvents (D) have an appreciable effect on the reactivity of organometallic compounds [1], and of Si subgroup derivatives in particular. Donor-acceptor complex formation of OMC · D and OMC · $D_2$ types is usually governed by vacant orbitals on the central atom [2]. The general properties of this reaction are widely known; for Si subgroup compounds the complexing abilities increase in the following way: Si < Ge < Sn [3], as well as with an increase of the effective positive charge on the central atom [2,4]. The dependence on the charge is often masked by steric factors of the substituents bonded to the central atom.

The complicating effect of the steric factors is more pronounced in silicon compounds. This is due both to the smaller size of this atom compared to that of the other elements of the subgroup and to the lower complexing ability of silicon compounds. As a consequence, in the case of tin compounds even $Me_4Sn$ (with a small positive charge on the tin atom) is able to form complexes with D [5]. With

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* A Monsieur le Doyen Calas, à l'occasion de son 70e anniversaire.

increase of the positive charge on the tin atom the complexes become more stable [6] and sometimes exist as isolated compounds [7]. Concerning complex formation of silicon compounds with D, the available data lead to conflicting conclusions [8–10]; corresponding data on organogermanium compounds are fragmentary.

Considering the above, the development of a suitable method for studying weak complexes with silicon and germanium derivatives as well as compounds with a small effective positive charge on the central atom is of great importance.

As stated earlier, reliable detection of tin donor-acceptor complexes with D by physical and chemical methods is possible if at least one electron accepting substituent, for example a $CF_3$ group, is situated on the tin atom along with three alkyl groups [5].
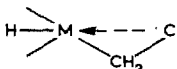
Similarly, trimethylstannyltrifluoromethylacetylene forms donor-acceptor complexes with D [11,12], the tin atom being the acceptor centre. However, the authors failed to detect stable complexes of organosilicon and organogermanium analogues of this stannane either by conductometric nor by calorimetric methods. It is generally believed that complexes of organosilanes and organogermanes are weak. Yet it is known [13,14] that electron-donating solvents exert a catalytic effect on the reactivity of these compounds. This effect is accounted for by the formation of solvent-hydride complexes. Up to now, no complexes have been detected reliably by any physical methods, although the work in this field was begun long ago [15]. However, silane and germane derivatives are extremely suitable for study of their complexes with D by IR spectroscopy.

The M–H (M = Si, Ge) stretching modes in IR spectra are highly characteristic in form [16]. Because of this, the frequencies and intensities of the M–H stretching modes in IR spectra of $R_3MH$ compounds depend only on the electronic effects of the R substituents [17]. This makes it possible to use their frequencies and especially their intensity (which are more sensitive to electronic effects) to study the details of intramolecular interactions in the silane and germane derivatives [18], including those of donor-acceptor type (intramolecular coordination [19]). As a consequence, we considered IR spectroscopy to be an informative method for studying the solvation of silane and germane trialkyl derivatives by electron-donating solvents, D.

## Results and discussion

For present purposes we measured integrated intensities ($A$) of $\nu$(M–H) absorption bands in IR spectra of triethylsilane and triethylgermane in heptane solution and in heptane solution with D added. In doing so, we assumed the following:

1. In complex formation, D → M(H)Alk$_3$, as well as in intramolecular coordination,  [19,20], the excess electron density of the M atom is distributed along the M–C and M–H bonds according to the electronegativities of C and H (which are higher than that of M) and results in an increase in the polarity of these bonds. Therefore, for heptane—D—M(H)Alk$_3$ systems higher integrated intensities of $\nu$(M–H) bands compared to those for heptane—M(H)Alk$_3$ systems would be expected in the IR spectra.

2. Complex formation or solvation may be considered as an interaction of Lewis acids and bases and can be classified on the principle of hard and soft acids and

bases [21,22]. Typical example of a hard acid and base interaction is the formation of hydrogen bonds. Hence, some properties of hydrogen bond formation can be applied to complexes of donor-acceptor type. This assumption is well founded since the intermolecular hydrogen bond represents a type of electron-acceptor interaction [23,24]. The equation $-\Delta H = a\Delta A^{1/2}$, derived by Iogansen [25] for the intensity of intermolecular hydrogen bonds is likely to hold for complexes of donor-acceptor type. In this case, the increased values of the intensity $(\Delta A^{1/2})$ on complex formation, $\Delta A^{1/2} = A^{1/2}_{\text{comp.}} - A^{1/2}_{\text{accept.}}$ may be looked upon as being proportional to the enthalpies of complex formation $(-\Delta H)$.

Intermolecular interactions in solutions can be divided into two groups: universal —which exist between all the molecules without exception, and specific—which result in the formation of weak or strong chemical bonds. The first type of interaction is determined by two independent properties of the medium, expressed in terms of functions of dielectric constant $\gamma$ [22] and refractive index $P$ [22]. The contribution of the universal interaction to the spectroscopic parameters is appreciable only in a medium where specific solvation may be ignored [26]. Specific solvation is determined by the acidity (electrophility) and basicity (nucleophility) of the solvents. The total basicity of solvent D is sometimes estimated [26] from Scale B (the shift of phenol stretching mode frequency (O–H) in IR spectra when it forms hydrogen bond with D). But more careful analysis indicates that basicity and $B$ are proportional only for closely related compounds [27].

Experimental data and parameters characteristic of intermolecular interactions are presented in Table 1. One can see from the Table that there is no correlation between $A^{1/2}$ and parameters of non-specific solvation (polarity function $\gamma = \epsilon - 1/2\epsilon + 1$ and polarizability function $P = n^2 - 1/n^2 + 2$). This indicates that the dominant contribution in the increase of the integrated intensity is not influenced by

TABLE 1

$\Delta A^{1/2}$ VALUES IN THE IR SPECTRA OF THE COMPOUNDS STUDIED AND $\gamma$, $P$, $B$, $DN$ AND $\beta$ PARAMETERS OF THE DONOR SOLVENTS

| Number | Donor solvent (D) | $\Delta A^{1/2}$(Ge–H) | $\Delta A^{1/2}$(Si–H) | $\gamma$ [26] | $P$ [26] | $B$ [26] | $DN$ [28] | $\beta$ [29] |
|--------|-------------------|------------------------|------------------------|---------------|----------|----------|-----------|--------------|
| 1 | Anisole | 0.01 | – | 0.3447 | 0.39417 | 155 | 8.3 | 0.24 |
| 2 | Acetonitrile | 0.02 | 0.02 | 0.4803 | 0.28568 | 160 | 14.1 | 0.31 |
| 3 | Dioxane | – | 0.02 | 0.2231 | 0.33845 | 237 | 14.8 | 0.37 |
| 4 | Nitrobenzene | 0.04 | 0.02 | 0.4788 | 0.41465 | 67 | 4.4 | 0.39 |
| 5 | Diethyl ether | 0.05 | 0.04 | 0.3449 | 0.29323 | 280 | 19.2 | 0.47 |
| 6 | Acetone | 0.04 | 0.04 | 0.4647 | 0.29734 | 224 | 17.0 | 0.48 |
| 7 | Acetophenone | 0.05 | 0.03 | 0.4581 | 0.40409 | 202 | 18.6 | 0.49 |
| 8 | Tetrahydrofuran | 0.07 | 0.06 | 0.4049 | 0.32916 | 287 | 20.0 | 0.55 |
| 9 | Pyridine | 0.06 | 0.03 | 0.4414 | 0.39026 | 472 | 33.1 | 0.64 |
| 10 | Dimethylformamide | 0.08 | 0.00 | 0.4798 | 0.34143 | 291 | 26.6 | 0.69 |
| 11 | Triethylamine | 0.08 | 0.05 | 0.2432 | 0.32496 | 650 | 30.7 | 0.71 |
| 12 | Hexamethylphosphoramide | 0.15 | 0.14 | 0.4751 | 0.36027 | 470 | 38.8 | 1.05 |
| 13 | Benzene | 0.03 | 0.02 | 0.2306 | 0.38523 | 48 | 0.1 | 0.10 |
| 14 | Toluene | 0.02 | 0.03 | 0.2395 | 0.38285 | 58 | – | – |
| 15 | Mesitylene | 0.02 | 0.00 | 0.2301 | 0.38427 | 77 | – | – |
| 16 | Dimethylaniline | 0.06 | 0.00 | 0.3641 | 0.41656 | 422 | – | – |

electrostatic or dispersion forces. There are some literature data on the insignificant role of non-specific solvation in complex formation. When studying the relationship between the enthalpy of complex formation (acceptor $CHCl_3$) and Gutmann donor numbers DN [28] of donor compounds, multiparameter correlation enables one to speak of the practical insignificance of polarity parameter and the low significance of the polarizability factor [30]. The polarizability factor is especially important in donor molecules with conjugated $\pi$-electron systems [22]. Hence, the contribution of the universal interaction to the increased intensity, $\Delta A^{1/2}$, is significant only when aromatic hydrocarbons are used as D (compounds 13–15, Table 1).

The energy of the intermolecular interaction is determined in most cases by the basicity of the ligand and by steric factors [31]. Parameter $B$, as a measure of the electron-donating ability [26], leads to the relationship $\Delta A^{1/2} = f(B)$, shown in Fig. 1. From Fig. 1 it is clear that there is no common relationship between $\Delta A^{1/2}$ and $B$ for both silanes and germanes. Each type of electron-donor centre (N or O) is characterized by a separate straight line, as expected from literature data [27,32]. Lines I and II correspond to D with an O atom as the electron-donor centre. Lines III and IV correspond to solvents with an N atom as the electron-donor centre. It is evident from Fig. 1 that oxygen-containing solvents solvate triethylsilane and triethylgermane to approximately equal degrees (the higher solvation of organoger-manium compounds follows from the corresponding arrangement of lines I and II) but to a significantly higher degree compared to nitrogen-containing solvents. This is in agreement with literature data [31], from which it follows that a strong base,
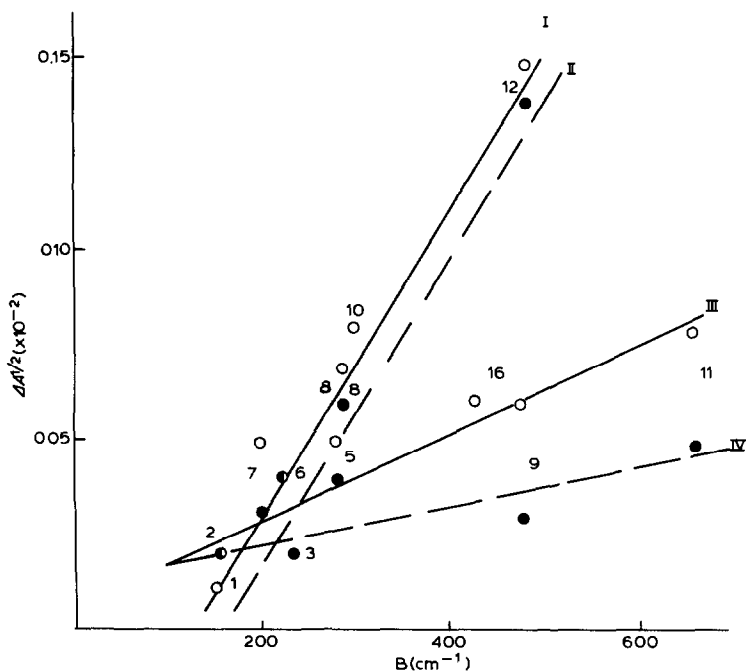


Fig. 1. Plot of $\Delta A^{1/2}$ vs. $B(\bullet)$ for $Et_3SiH$ and ($\bigcirc$) for $Et_3GeH$. The numbering of the points refers to the numbering of the compounds in Table 1.

triethylamine, can, in some cases, be less active in complex formation than oxygen bases which are known to be weak. This is, probably, due to weak steric hindrance in complex formation with an O atom as the electron-donor centre. Indeed, the Van der Waals radius of O is 1.40 Å, and that of N is 1.15 Å. However, slight differences in the steric accessibility of the acceptor centres (Si and Ge atoms) in the compounds studied exerted no influence on the energy of intermolecular interaction (Fig. 1, lines I and II).

Although $\Delta A^{1/2}$ for N-containing bases is less than that for O-containing bases, complex formation between triethylsilane and triethylgermane with N-containing D differs greatly (Fig. 1, lines IV and III): N-containing bases are more effective in solvation of triethylgermane. Thus, despite its high $B$ value, $N,N$-dimethylaniline does not solvate triethylsilane and acts as an inert solvent. Apparently, steric hindrances of the donor and acceptor molecules have as much influence on the formation of complexes of silane and germane derivatives than the basicity of the electron-donor molecules does. For example, the $B$ values for hexamethylphosphoramide and pyridine are practically the same (Table 1, Fig. 1), yet $A^{1/2}$ for hexamethylphosphoramide is twice that for pyridine. From the data presented in ref. 9 it follows that steric factors have an appreciable effect on the D → silane interaction. Study of the effect of complex formation on the frequency of Si–H stretching modes in IR spectra has shown that significant interaction of trimethoxy- and triethoxy-silanes with D occurs only when there is little steric hindrance in the molecules of the solvents ($Me_2C=O$, $Me_2S=O$, $Me_3P=O$). Yet, tripropyloxy- and triisopropyloxy-silanes with bulky PrO and i-PrO groups practically do not interact with the solvents D [9].

From a comparison of the orders of solvating abilities for $Et_3SiH$: hexamethylphosphoramide > THF > triethylamine > acetone > pyridine > acetonitrile; for $Et_3GeH$: hexamethylphosphoramide > triethylamine > THF > pyridine > acetone > acetonitrile; and for $Me_3SnC\equiv CCF_3$ [11]: hexamethylphosphoramide > pyridine > acetonitrile > acetone, it follows that the properties of the donor depend also on the nature of the acceptor. Hexamethylphosphoramide is the only exception and is the universal solvating agent for all the compounds studied. Other solvents have no constant order of solvating ability.

The relationship between $\Delta A^{1/2}$ and $B$ suggests the following. First, triethylgermane is solvated by bases D to a greater degree than triethylsilane is. Second, for any given organometallic compound there is no unique relationship between $\Delta A^{1/2}$ and $B$. Third, for a given donor (N or O) and acceptor (Si or Ge) centre there is an approximately linear relationship between $\Delta A^{1/2}$ and $B$. Consequently, without great steric hindrance the interaction between $Et_3SiH(Et_3GeH)$ and D is of specific donor-acceptor character.

As noted above, the usefulness of parameter $B$ for explaining the changes in $\Delta A^{1/2}$ is limited. Parameter B, as a measure of the relative electron-donating properties of D, is not universal. It is well known [27,32,33] that this parameter applies only to series of D compounds with unchanged donor centre. Considering this, we chose two other parameters and correlated them with $\Delta A^{1/2}$. The values are the donor numbers ($DN$) of Gutmann [28] and parameter $\beta$ [29]. An analysis of the relationship between these values is given in ref. 34. According to Gutmann [28], in the donor-acceptor approach general medium effects are described in terms of electron donating and accepting properties of the solvents. As an quantitative
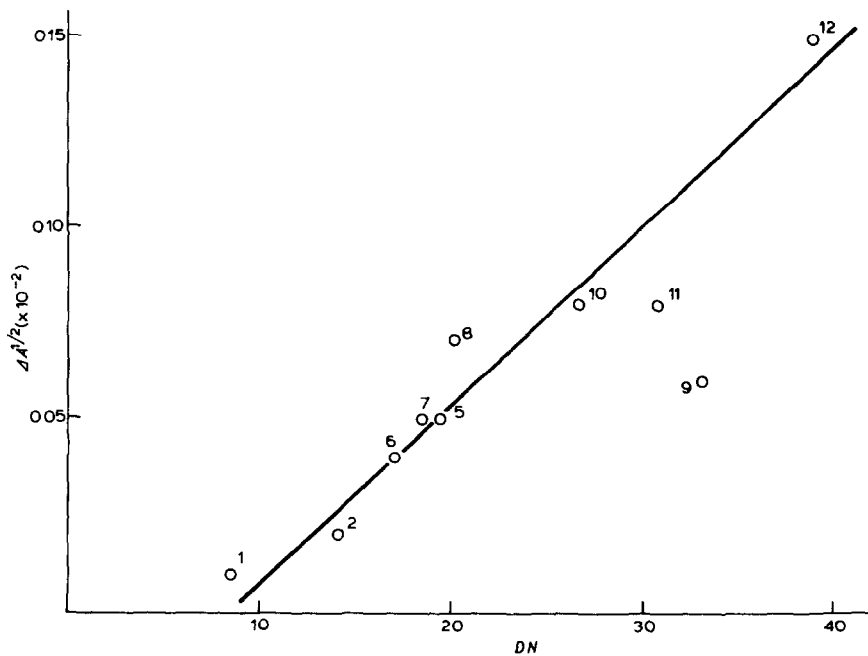
Fig. 2. Plot of $\Delta A^{1/2}$ (Ge–H) vs. Gutmann's $DN$ parameters.
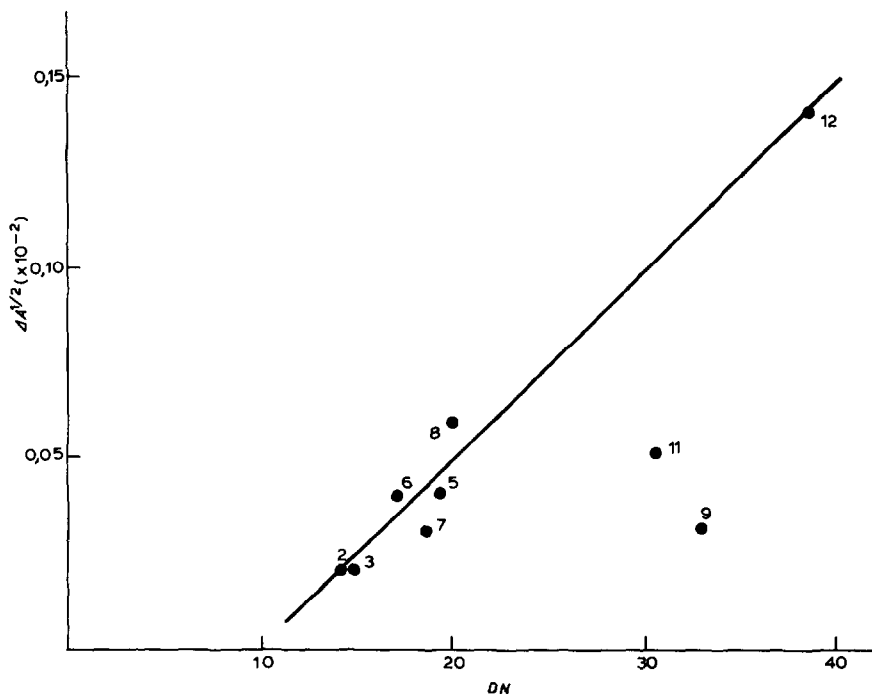


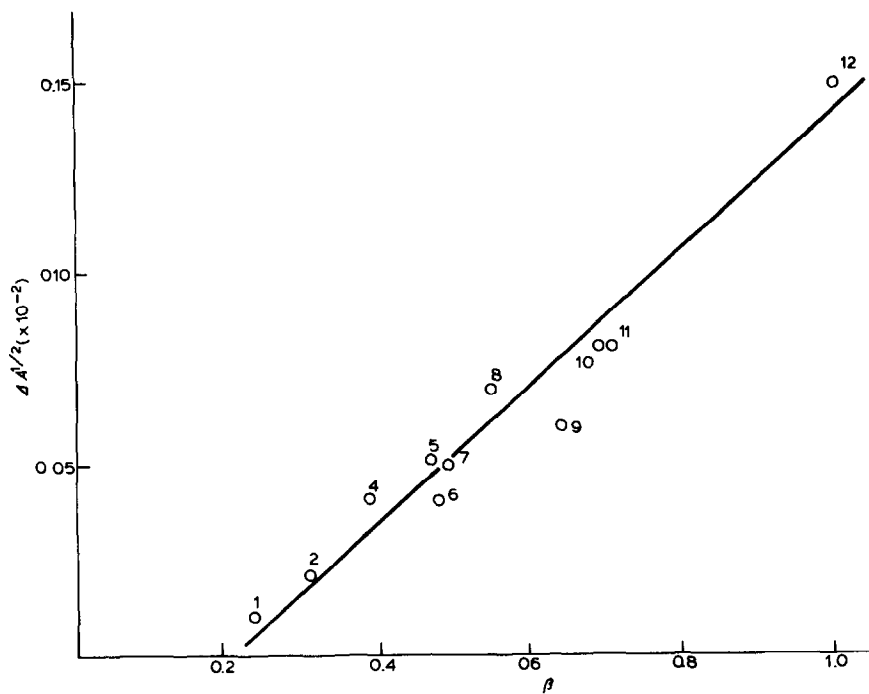Fig. 3. Plot of $\Delta A^{1/2}$ (Si–H) vs. Gutmann's $DN$ parameters.

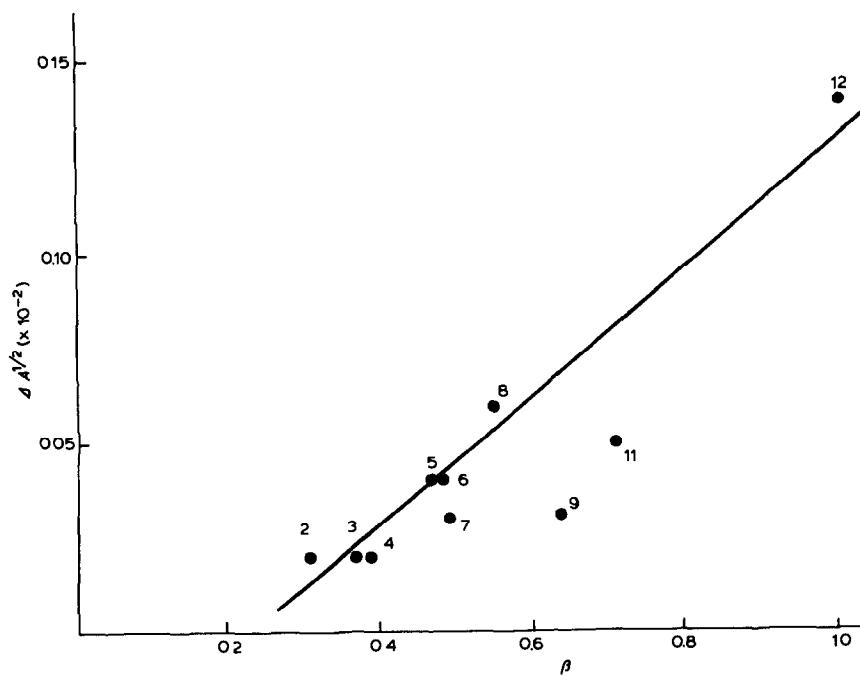Fig. 4. Plot of $\Delta A^{1/2}$ (Ge–H) vs. $\beta$ parameters.



Fig. 5. Plot of $\Delta A^{1/2}$ (Si–H) vs. $\beta$ parameters.

measure of the electron donating properties of the solvent, a scale of empirical *DN* parameters has been advanced. *DN* is defined as the negative enthalpy ($-\Delta H$ kcal/mol) of the interaction of basic solvents with the nonprotic Lewis acid $SbCl_5$ in dilute solution in 1,2-dichloroethane. *DN* values for the bases used are given in Table 1.

Despite the fact the *DN* scale is widely used, still it has been criticized [34]. The change in enthalpy of complex formation (*DN*) is not linearly related, in the general case, to the change in Gibbs free energy ($\Delta G$) of the same process. Therefore, it is not quite correct to correlate the properties of the complexes determined by the change in Gibbs free energy with the parameter *DN*. The $\beta$ scale [29] does not suffer from these shortcomings. It is defined as the ability of the solvent D to donate a lone electron pair in the formation of hydrogen bonds [29] and complexes with Lewis acids [34].

We correlated the $\Delta A^{1/2}$ values to parameters *DN* and $\beta$. The following relationships were found (Figs. 2–5).

$$\Delta A^{1/2} = 0.0047\ DN - 0.04\ (Et_3GeH, r = 0.984, s = \pm 0.008) \tag{1}$$

(compounds **1,2,5,6,7,8,10** and **12**)

$$\Delta A^{1/2} = 0.0049\ DN - 0.05\ (Et_3SiH, r = 0.984, s = \pm 0.008) \tag{2}$$

(compounds **2,3,5,6,7,8** and **12**)

$$\Delta A^{1/2} = 0.168\ \beta - 0.03\ (Et_3GeH, r = 0.989, s = \pm 0.006) \tag{3}$$

(compounds **1,2,3,4,5,6,7,8,10,11** and **12**)

$$\Delta A^{1/2} = 0.173\ \beta - 0.04\ (Et_3SiH, r = 0.986, s = \pm 0.007) \tag{4}$$

(compounds **2,3,4,5,6,7,8** and **12**)

Solvents with $DN < 10$ (benzene, nitrobenzene) do not obey eqs. 1 and 2. As noted above, the polarizability factor is pronounced in conjugated $\pi$-systems [22]. Because of this, in the case of benzene and nitrobenzene the contribution of nonspecific interaction to $\Delta A^{1/2}$ may cause points **4** and **13** to deviate from the correlation straight lines. It should be also borne in mind that *DN* is determined for the hard acid $SbCl_5$ and that for soft acids *DN* may be quite different. Points **9** and **11**, corresponding to pyridine and triethylamine, also deviate from the correlation lines (Figs. 2 and 3). The greatest deviation is observed for the points corresponding to complexes with triethylsilane (Fig. 3). This deviation is likely to result from steric hindrance preventing the donor and acceptor centres of the interacting molecules being brought together. The effect of steric hindrance in triethylsilane is more significant than that in triethylgermane.

It has been shown [34] that *DN* is related linearly to the $\beta$ scale.

$$DN = -0.17 + 38.4\ \beta \tag{5}$$

Pyridine does not obey this correlation, i.e. it does not obey eq. 5. Some deviation is observed also for the point corresponding to triethylamine, even though the *DN* value for $Et_3N$ was corrected from 61 [28] to 30.7 [34]. Therefore, when $\Delta A^{1/2}$ is correlated with the $\beta$ scale, the points corresponding to solvate complexes of $M(H)Et_3$ with pyridine and triethylamine would also be expected to deviate from the correlation lines.

It is seen from Figs. 4 and 5 that with $Et_3GeH$ almost all the points obey the unique relationship (eq. 3). Only a slight deviation is observed for point **9** (pyridine). In the case of $Et_3SiH$, significant deviation from the correlation dependence (eq. 4) is observed for points **9** (pyridine) and **11** (triethylamine). This is most likely due to steric hindrance of complex formation.

Thus, the interaction of triethylsilane and triethylgermane with D is of donor-acceptor type. Steric hindrance in complex formation change the orders of relative donating abilities depending on the type of acceptor centre (Si and Ge), but do not change the present conclusions as a whole.

## Experimental

IR spectra were recorded on a UR-20 spectrophotometer. Heptane solutions of triethylsilane and triethylgermane and similar solutions with electron-donating solvents added were used to obtain the spectra. The concentrations of organometallic compounds were $0.05-0.06$ mol $l^{-1}$; and concentration of the addition agents were $0.5-0.6$ mol $l^{-1}$. All measurements were referred to heptane. The cell path was 0.602 mm. The integrated intensity of M–H stretching modes $A$ ($mol^{-1} l cm^{-2} \times 10^4$) was measured by Iogansen's method [35]. The error in $A^{1/2}$ was within 0.02, which compares favorably with reported data [35,36].

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