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APPLICATION OF ELECTRONIC AND IR SPECTROSCOPY TO THE DETERMINATION OF σ_p-, σ_p^+- AND σ_R^0-CONSTANTS OF SOME ORGANOSILICON AND ORGANOGERMANIUM SUBSTITUENTS *

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Summary

The σ_p- and σ_p^+- constants of some silicon- and germanium-containing substituents have been determined from electronic absorption spectroscopy data of charge-transfer (CT) complexes of phenylgermanes, benzylsilanes and benzylgermanes with tetracyanoethylene (TCNE). Resonance constants of corresponding substituents have been determined from the integrated intensity values of aromatic ring stretching modes (IR spectroscopy data) of benzylsilanes and benzylgermanes. It is shown that the effect of d_π—p_π interaction in phenylgermanes remains practically unchanged in the course of the transition from the ground state to the CT state. The high negative values of σ_p^+-constants for benzylorganosilicon and benzylorganogermanium substituents indicate the presence of considerable σ, π-conjugation in the CT state of benzylsilanes and benzylgermanes. This effect is also established for the ground state of the above mentioned compounds from their σ_R^0-values. The effect of σ,π-conjugation is displayed in greater degree in the ground state as well as in the CT state in benzylgermanes as compared with benzylsilanes.

Introduction

Various correlation equations of the Hammet type are widely used in the investigation of intramolecular electronic effects and for the separation of electronic effects into inductive and conjugative components. Despite some objections against the application of Hammet equations (e.g. ref. 1), their produc-

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

tivity for resolving a wide range of problems in theoretical organic and organometallic chemistry is quite evident.

There are extensive and properly systematized data on Hammet σ-constant values and their analogs for various organic substituents [e.g. 2,3]. However, information concerning the σ-constants of organometallic substituents (for organosilicon and organogermanium in particular) is far less extensive. The investigation of electronic effects of organosilicon and organogermanium substituents (σ-constants on various scales are generally regarded as their quantitative measure) is both of theoretical (e.g. information on d_π—p_π interactions) and of applied value (for the estimation of substituents influence on reaction rates or reaction equilibria for the investigation of reaction mechanisms).

The little information available on σ-constants of substituents containing Group IVB elements is almost exclusively concerned with organosilicon substituents. Thus, polar effects of silyl groups of the type $(CH_3)_{3-n}X_nSi$ (X = Cl, Br, OCH_3, $OSi(CH_3)_3$ etc. [4,5] have been systematically studied. The authors have calculated the σ-constant values by the classical physico-chemical method: a reactivity study of substituted benzoic acids. These data made it possible to consider the relative contributions of inductive and conjugative effects of some silyl substituents, the σ-value dependence versus the number of X substituents, as well as the role of d_π—p_π interaction. The procedure most widely used to determine σ-constant values, involving investigation of reactivities, is very time consuming and it requires quite a number of chemicals, organometallic synthesis being in most cases a difficult problem. This procedure is only applicable to σ-constant determination of those substituents that do not react with carboxyls, otherwise it is necessary to select another reaction series. Thus, it is in some cases necessary to use several physico-chemical methods to determine reactivity constant.

Bazant, Rochow and coworkers [e.g. 5] have reported values of σ-constants obtained in the course of a classical benzoic acids reactivity investigation supplemented with potentiometric titrations and an NMR procedure. Inductive σ^*-constants were determined by use of IR spectroscopy to measure basicities of organometallic compounds [e.g. 6]. Traven et al. [7] have determined σ^--constants of phenylpolisilanes by potentiometric titration of substituted *N,N*-dimethylanilines. It was concluded that the acceptor properties of silylalkyl substituents in the ground state resulting from d_π—p_π interaction are independent of the number of silicon atoms in the chain. The values of σ_R^0-constants of the SiX_3 series can be measured by ^{13}C NMR of phenylsilane derivatives [9].

Electronic absorption spectroscopy of π,π-CT complexes is a convenient physico-chemical method of measuring reactivity constants of organometallic substituents. It follows from Mulliken's theory of donor-acceptor interaction [8] that it is possible to define reactivity constants in terms of the interaction between substituents and an electron deficient center on the benzene ring with the Brown-Okamoto σ^+-constants (see below). This makes it possible to give an account of substituent electronic properties in the CT state. In the work quoted above [7], σ^+-constant values were determined for various silicon containing substituents involving one or two silicon atoms. In so doing the authors made use of the correlation between CT frequency (ν_{CT}) of monosubstituted benzene-TCNE complexes and σ^+-constant values. It turned out that, as distinguished from the ground state, in the CT state the substituents possess increasing electron-donor ability with increase of the number of silicon atoms. Treilor et al. [10] reported essential data on electronic effects in the CT state of benzyl substituents of the type CH_2MPh_3 (M = C, Si, Ge, Sn, Pb) assuming the presence of σ, π-conjugation.

Results and discussion

Previously [11], the reactivity constants of some organosilicon and organogermanium substituents had been measured by electronic absorption spectroscopy of CT complexes. It has been shown that one can classify the substituents in accordance with their degree of conjugation with the benzene ring on passing from the ground state to the CT state in combination with their electron-donor properties in the ground state from IR spectroscopy. In the work discussed here this procedure was partially employed for measuring σ-constants not previously estimated, mainly for organosilicon and organogermanium substituents. It is of interest to single out the resonance component from the overal electronic effect of organometallic substituents with a view to estimating the contribution of conjugation with the aromatic ring in the ground state.

Let us consider briefly the theoretical justification for σ-constant determination by electronic absorption spectroscopy of CT complexes.

For weak complexes of the π, π-type the CT band position is in linear relationship with the donor ionisation potential I_D, this has been confirmed experimentally [8]. For most benzene derivatives the linear relationships between I_D and the sum of σ_p^+-Brown-Okamoto constants of substituents, as well as between CT band frequency (ν_{CT}) of complexes with TCNE and I_D have been established [12]. From these relationships the following equation is obtained [11],

$$\sigma_p^+ = \frac{\nu_{CT} - 24800}{5260} \tag{1}$$

Equation 1 allows us to calculate σ_p^+-constants for any substituents (including organometallic ones) from experimental values of ν_{CT}. It was also confirmed that the increase of conjugation from the ground state to the CT state is not characteristic of substituents possessing negative conjugation effects with benzene ring. The values of σ_p- and σ_p^+-constants for such substituents were close to each other. Therefore, a linear correlation between ν_{CT} and σ_p-Hammet constants was suggested:

$$\sigma_p = \frac{\nu_{CT} - 23900}{1000} \tag{2}$$

Equation 2 does not, however, allow calculation of σ_p-constants for benzyl and other substituents exhibiting an increase of σ, π-conjugation in the CT state, accounted for by the presence in the CT state of an electron $+E$ effect.

The relationships 1 and 2 were used for the calculation of organosilicon and organogermanium substituent σ_p-constants, presented in Tables 1 and 2.

It is known, that the σ_p- constant represents a sum of the contributions of inductive (σ_I) and conjugative (resonance, σ_R) substituent effects.

$$\sigma_p = \sigma_I + \sigma_R \tag{3}$$

TABLE 1

CALCULATED σ_p^- AND σ_p^+-VALUES OF SOME ORGANOGERMANIUM SUBSTITUENTS (C_6H_5R)

No.	substituent R	ν_{CT}, (cm^{-1})	σ_p	σ_p^+
1	$OGe(OC_6H_5)(CH_3)_2$	21300	—	−0.86
2	$Ge(SCH_3)_3$	23400	—	−0.27
3	$Ge(C_6H_5)(n\text{-}C_6H_{13})_2$	24800	0.09	0.00
4	$Ge(C_6H_5)_2(n\text{-}C_6H_{13})$	24900	0.10	0.02
5	$Ge(CH{=}CHC_4H_9)_3$	24900	0.10	0.02
6	$Ge(C_6H_5)_2CH_2CH{=}CHCH_3$	25000	0.11	0.04
7	$Ge(C_6H_5)_2CH_2OCH_3$	25000	0.11	0.04
8	$Ge(C_6H_5)_2H$	25000	0.11	0.04
9	$Ge(C_6H_5)HBr$	25300	0.14	0.10
10	$Ge(C_6H_5)Cl[(CH_2)_4COCH_3]$	25300	0.14	0.10
11	$GeHCl[(CH_2)_5CH_3]$	25400	0.15	0.11
12	$Ge(C_6H_5)_3$	25400	0.15	0.11
13	$Ge(C_6H_5)_2[(CH_2)_4COCH_3]$	25500	0.16	0.13
14	$Ge(C_6H_5)HCl$	25500	0.16	0.13

or, alternatively, [2]:

$$\sigma_p = \sigma_I + \sigma_R^0 + (\sigma_p - \sigma^0) \quad (4)$$

where the σ_R^0-constant represents the set of conjugative and inductive substituent effects and the value $(\sigma_p - \sigma^0)$ enables estimation of the contribution of direct polar conjugation (through resonance). The value σ_R^0 can be estimated by IR spectroscopy, as proposed by Katritzky et al. [13,14], on the basis of integrated intensity value (A) calculations of benzene-derivative absorption bands in the 1600 cm^{-1} region, associated with aromatic ring stretching modes:

$$\sigma_R^0 = \sqrt{\frac{A - 100}{17600}} \quad (5)$$

The σ_R^0-values obtained for the benzylorganosilicon and benzylorganogermani-

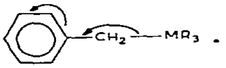
TABLE 2

CALCULATED σ_R^0- AND σ_p^+-VALUES OF SILICON AND GERMANIUM-CONTAINING SUBSTITUENTS (C_6H_5R)

No	substituent	A, (mole^{-1} l cm^2)	ν_{CT} (cm^{-1})	σ_R^0	σ_p
1	$CH_2Si(CH_2C_6H_5)_2CH_3$	1140	19700	−0.24	−0.97
2	$CH_2Si(CH_2C_6H_5)HCH_3$	904	20000	−0.21	−0.91
3	$CH_2SiH(C_2H_5)_2$	1030	20200	−0.23	−0.87
4	$CH_2Si(CH_2C_6H_5)HC_2H_5$	970	20400	−0.22	−0.84
5	$CH_2Si(CH_3)_3$	948	20800	−0.17	−0.76
6	$CH_2SiH(C(CH_3)_3)_2$	954	20900	−0.22	−0.74
7	$CH_2Ge(CH_3)_3$	1060	19200	−0.23	−1.01
8	$CH_2GeH_2C_2H_5$	1070	19300	−0.24	−1.05
9	$CH_2Ge(CH_2C_6H_5)_2H$	1129	19400	−0.24	−1.03
10	$CH_2Ge(CH_2C_6H_5)H_2$	993	19800	−0.23	−0.95
11	$CH_2Ge(CH_2C_6H_5)HC_2H_5$	1080	20000	−0.24	−0.91
12	$CH_2Ge(OC_2H_5)_3$	1076	22000	−0.24	−0.53

um substituents studied are presented in Table 2.

According to a great deal of the data published in the literature, including those obtained by study of CT complexes of arylsilanes and arylgermanes [e.g. 11], silyl and germyl substituents, regardless of appreciable inductive +I- effect (e.g. for $Si(CH_3)_3$ group $\sigma^\star$ = —0.915), exhibit acceptor properties. The latter is traditionally explained by d_π—p_π interaction [16] consisting of partial delocalization of electronic density from the ring onto vacant *nd*-orbitals of the silicon or germanium atoms (—M effect in ground state). Accordingly, the σ_p- and σ_p^+-constants of essentially all organogermanium substituents (except 1 and 2) have small similar positive values. Evidently, this indicates practically permanent d_π—p_π interaction in both ground and CT states. It is worth noting that comparison of σ_p- and σ_p^+-values of some substituents in Table 1 with corresponding values of their organosilicon analogues [11] indicates a fall of d_π—p_π interaction on transition from silicon to germanium. The presence of heteroatoms (oxygen, sulphur) with lone electron pairs in substituents 1 and 2 defines substantial electron-donor properties of the corresponding phenylgermanes in the CT state; for compounds with substituent 1 they are almost as high as for benzylgermanes (vide infra). The d_π—p_π interaction in Ge—phenyl bonds of these compounds is missing and in accordance with the remark mentioned above, calculation of σ_p-constant values by the method used here is impossible. Our estimation of σ_R^0-constants of some substituents listed in Table 1 indicates that their values are close to zero (similar data have been obtained [9] for silyl substituents). Hence, conjugation effects of such substituents with the ring in the ground state are poorly defined. The exception is once again fragment 1 in Table 1 with its roughly estimated value of σ_R^0 of about —0.6. On the whole, however, it will be noted that with variation of the organic part of fragment R, the ν_{CT}-value of the corresponding compounds alters only slightly, due to the practically similar σ_p- and σ_p^+-values, demonstrating the small variation in structure of organogermanium substituents.

Let us now consider electronic effects of substituents in benzyl derivatives of silicon and germanium (Table 2). Calculated σ_R^0-constants for substituents of CH_2MR_3 type (M = Si, Ge) have large negative values. Thus, the fragments under consideration in the ground state already exhibit a significant positive conjugation effect with the benzene ring, and the main component of the latter seems to be a mesomeric +M-effect (σ, π-conjugation) . The appearance of an electron-deficient center on the aromatic ring by excitation of the CT complex leads to a further increase of this effect, evolving in the CT state into the electromeric +E-effect of substituents [17]. Large negative values of σ_p^+-constants in comparison with σ_R^0-constants are a confirmation of this. The compounds presented in Table 1 (vide supra) also possess a significant +E-effect in the CT state, but the reason for this is the presence of *n*, σ-conjugation of the lone electron pair of oxygen with the aromatic system.

Comparison of σ_R^0- and σ_p^+-values of the silicon- and germanium-containing substituents presented in Table 2 allows us to draw the following conclusions. The σ_R^0-constants featuring, as noted above, the effect of σ,π-conjugation in the ground state are somewhat higher in absolute value for germanium-containing substituents, resulting from higher Ge—C bond polarizability compared with the Si—C bond. The σ_p^+-constant values of germanium-containing substituents possess essentially higher negative values compared with silicon-containing substituents, indicating an increase of σ, π-conjugation in the CT state, due to the presence of the positive charge on the aromatic ring in the excited state of the CT complex. This conclusion is in accordance with the literature data.

Experimental

The electronic absorption spectra were measured on a Perkin-Elmer 402 spectrophotometer in the 300—850 nm region. A solution of the compounds studied in CH_2Cl_2 (0.5 mole/l) and a solution of tetracyanoethylene in CH_2Cl_2 (0.05 mole/l) were mixed in 3 : 1 in volume ratio to record the spectra. The cell path was 1 cm.

IR spectra of the compounds studied were measured on a Perkin-Elmer 577 spectrophotometer in the 1600 cm^{-1} region, in heptane and carbon tetrachloride solution. A CaF_2 cell with a path length of 0.5—1 mm was used. The integrated intensity A was calculated as given below [14]:

$$A = 1.57(d_{max}K\ \Delta\nu_{1/2}/cl)$$

where d_{max} = absorbance maximum of absorption band; $\Delta\nu_{1/2}$ = half-width of band; c = concentration (mole l^{-1}); l = cell path (cm).

The solvents were purified by the usual methods and the purity checked by GLC.

The compounds $(PhCH_2)_2GeHEt$, $PhCH_2GeH_2Et$ and $PhGe(CH{=}CHBu)_3$ were prepared according the following methods.

Preparation of $(PhCH_2)_2GeHEt$

$(PhCH_2)_2GeHCl$. $HgCl_2$ (17.65 g, 0.065 mol) was added dropwise to $(PhCH_2)_2GeH_2$ (20 g, 0.078 mol). After 24 h at room temperature with stirring the crystalline product formed was extracted with 20 cm^3 of C_6H_6. Its recrystallisation gave to 14.20 g of $(PhCH_2)_2GeHCl$ (62.5% yield) m.p. 59°C.

$(PhCH_2)_2GeHEt$. A solution of $(PhCH_2)_2GeHCl$ (12 g, 0.041 mol.) in 30 cm^3 of C_6H_6 was added dropwise to EtMgBr (0.0474 mol) in ether. The mixture was refluxed for 2 h. After hydrolysis, extraction and concentration the residue obtained was distilled to give $(PhCH_2)_2GeHEt$, 8.25 g (70.5% yield), B.p.: 138—142°C/5 × 10^{-2} mmHg. NMR (δ, ppm) (C_6D_6): $(PhCH_2)_2GeClH$: Ge—H = 5.51(q); CH_2 = 2.36(d). $(PhCH_2)_2GeEtH$: Ge—H = 4.18(q); CH_2 = 2.18(d); C_2H_5 = 0.6—1(m).

Preparation of $PhCH_2GeH_2Et$

$EtGeClH_2$ (12 g, 0.085 mol) was added to an ether solution of $PhCH_2MgCl$ (0.17 mol) at 0°C. The mixture was then refluxed for 1 h. After hydrolysis, extraction and concentration the residue obtained gave after distillation $PhCH_2GeH_2Et$ (11.45 g, 69.5% yield). B.p.: 82—84°C/14 mmHg. NMR (δ, ppm) (C_6D_6): GeH_2 = 3.94(q); CH_2 = 2.28(t); C_2H_5 = 0.70—1.20(m).

Preparation of $PhGe(CH{=}CHBu)_3$

Phenylgermane, $PhGeH_3$, (0.010 mol) and $BuC{\equiv}CH$ (0.030 mol) were heated

TABLE 3

IR AND NMR CHARACTERISTICS OF THE ISOMERS $PhGe(\overset{A}{C}H{=}\overset{B}{C}H{-}\overset{X_2}{C}H_2{-}Pr)_3$

isomeric forms	ABX_2	$\delta(A)$ [a] (ppm)	$\delta(B)$ [a] (ppm)	$\nu A - \nu B$ (cm^{-1})	$J(AB)$ (Hz)	$\delta(X_2)$ (ppm)	$J(AX)$ (Hz)	$J(BX)$ (Hz)
I	AB *cis*	5.70	6.43	44	12.5	2.10	1.25	7
II	AB *cis*	5.80	6.40	36	12.5	2.10	1.25	7
	AB *trans*	5.92	5.92	—	17.5	2.10	—	—
III	AB *cis*	5.86	6.38	31	12.5	2.10	1.25	7
	AB *trans*	5.92	5.92	—	17.5	2.10	—	—
IV	AB *trans*	5.92	5.92	—	18	2.10	—	—

[a] Solvent CCl_4.

in a Carius tube for 4 h at 80°C with a catalytic amount of azoisobutyronitrile. The reaction quantitatively gave $PhGe(CH{=}CHBu)_3$. B.p. = 126°C/10^{-3} mmHg. For IR and NMR characteristics see Table 3.

Other germanium-containing compounds were synthesized following literature methods: $Ph_2Ge(n\text{-}hexyl)_2$, $Ph_3Ge(n\text{-}hexyl)$, Ph_2BrGeH, $PhClGeH(CH_2)_5CH$ Ph_2ClGeH [17]; Ph_4Ge [18]; $Ph_3Ge(CH_2)_4COCH_3$ [19]; $PhGe(SMe)_3$ [20]; $Ph_3GeCH_2OCH_3$ [21]; $PhGe(CH{=}CHC_4H_9)_3$, $(PhCH_2)_3GeH$ and $(PhCH_2)_2GeH_2$ [22].

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