

ELECTRONIC EFFECT OF AND MUTUAL POLARIZABILITY IN GROUPS ATTACHED TO OXYGEN via THEIR C, Si, Ge, AND B ATOMS*

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Relative acidity of triphenylhydroxy substituted germane and stannane is consistent with superior electron donating effect of $(C_6H_5)_3Ge$ and $(C_6H_5)_3Sn$ groups in these compounds. Relative basicity data of alkyl(alkoxy) boranes, methanes, silanes, and germanes $(RO)_nZR_m$ ($Z = B, C, Si,$ and Ge) are compiled. The variation of the electronic effect parameter σ^* of fully alkylated R_mZ -groups upon substitution of their alkyl with ethoxy substituents appears for $Z=B$ and Si to be influenced by mutual polarizability effect of ethoxy substituents. Mutual polarizability of ethoxy substituents attached to carbon and germanium is negligible.

The relative acid and base strengths of triphenylhydroxy¹ and base strengths of triphenylphenoxy² compounds of the Group IV B elements measured as the change in the stretching frequency of H-donor, $\Delta\nu(OH)$, reflect superior electrodonating action of $(C_6H_5)_3Ge$ and $(C_6H_5)_3Sn$ groups attached to the oxygen, since the Taft σ^* parameter of $(CH_3)_3M$ groups in $(C_6H_5)_3MOH$ compounds can be established on the basis of the linear correlation between $\Delta\nu(OH)$ of phenol and σ_X^* for alcohols $X-OH$ (ref.³) to be as 0.51 (C), 0.48 (Si), -0.75 (Ge), and -2.7 (Sn). A decade after the electronegativity of the atom M and π -bonding effects, most pronounced with silicon, weaker with germanium and negligible in other two compounds, were used for the explanation of the relative acidity and basicity first, we stressed^{4,5} the importance of mutual polarizability (MP) of electronegative substituents X constituting $X_nR_{3-n}Si$ groups in alkoxy silanes $X_nR_{3-n}SiOR$ and showed⁶ the extent of the MP effect of alkoxy substituents to be easily estimated from the dependence of the relative oxygen basicity ($\Delta\nu(OH)$ of phenol) of $(RO)_nSiR_{4-n}$ compounds on number of their alkoxy substituents, n.

Compiling the data on the oxygen basicity of alkoxy(alkyl) methanes, silanes, germanes and boranes $(RO)_nZR_m$ ($Z = B, C, Si$ and Ge) we report herein the variation of the electronic effect of fully alkyl substituted methyl, silyl, germyl, and boryl

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groups R_mZ - upon substitution of their alkyls for alkoxy substituents and show how MP of alkoxy substituents in $(RO)_nR_mZ$ groups controls electronic effect parameter σ^* of these groups.

The σ^* parameters for fully alkyl (R_mZ) and diethoxy substituted $((C_2H_5O)_2 \cdot R_{m-2}Z)$ methyl, silyl, germyl, and boryl groups are given in Table I. The boryl group $(n-C_4H_9)_2B$ exhibits electronwithdrawing character¹⁰, while other three groups are electrondonating. Upon the substitution of alkyls in R_mZ groups by two

TABLE I

Comparison of Taft σ^* parameters for some Z groups attached *via* their C, Si, Ge and B atoms to $-OC_2H_5$ moiety

Alkyl substituted group	σ^{*a}	Diethoxy substituted group	σ^{*a}
$(CH_3)_3Ge$	-1.32^b	$(C_2H_5O)_2CH_3Ge$	-0.24^b
$(CH_3)_3C$	-0.30^c	$(C_2H_5O)_2CH_3C$	0.62^d
$(CH_3)_3Si$	-0.14^e	$(C_2H_5O)_2CH_3Si$	0.27^d
$(n-C_4H_9)_2B$	0.43^d	$(C_2H_5O)_2B$	0.50^d

^a Values were established from the $\Delta\nu(OH)$ of phenol (C, Si, B groups) and $\Delta\nu(NH)$ of pyrrol (Ge groups) interacting with $Z-OC_2H_5$ compounds on the basis of linear $\Delta\nu(OH)$ vs σ_X^* correlation with ethyl ethers $X-OC_2H_5$ (ref.⁴); the interrelation of the $\Delta\nu(OH)$ and $\Delta\nu(NH)$ was assumed to be identical as that⁷ between $\Delta\nu(OH)$ of phenol and $\Delta\nu(OH)$ of methanol. ^b From $\Delta\nu(NH)$ values, ref.⁸. ^c Ref.⁹. ^d Ref.¹⁰. ^e Ref.¹¹.

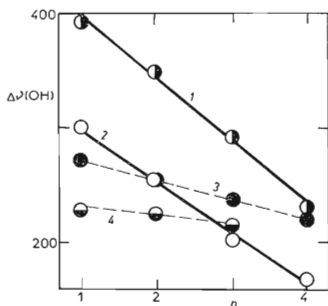


FIG. 1

The phenol $\Delta\nu(OH) - n$ dependence for $(C_2H_5O)_nGe(CH_3)_{4-n}$ (1), $(C_2H_5O)_n \cdot C(CH_3)_{4-n}$ (2), $(C_2H_5O)_nSi(CH_3)_{4-n}$ (3) and $(n-C_4H_9O)_nB(n-C_4H_9)_{3-n}$ (4)

C_2H_5O substituents electronwithdrawing character of the boryl group appears almost unaltered, while electrondonating ability of other three groups decreases. The germyl group still remains electrondonating, but the methyl and the silyl group become possessing electronaccepting behaviour. This variation of electronic effect of the R_mZ groups upon their substitution is to be best discussed in relation to the variation of relative oxygen basicity of $(RO)_nZR_m$ compounds with number of RO substituents, n (Fig. 1). The linear character of this dependence (Eq. (1)) allows to get

$$\Delta\nu(OH) = a - b \cdot n \quad (1)$$

following values for parameter b :

$(n-C_4H_9O)_nB(n-C_4H_9)_{3-n}$	7.5
$(C_2H_5O)_nSi(CH_3)_{4-n}$	18
$(C_2H_5O)_nC(CH_3)_{4-n}$	46
$(C_2H_5O)_nGe(CH_3)_{4-n}$	57

They can be discussed as was done previously⁶ for alkoxyasilanes in which $-I$ effect of RO substituents was determined¹² to be reduced. The low b parameter with Si and B compounds indicates that alkoxy substituent attached to silicon and boron are prone to synergistic interaction $RO \leftarrow M \rightarrow OR$ that increases the oxygen basicity over that affected solely by inductive effect of alkoxy substituents. The electronwithdrawing action of alkoxy substituents in B and Si compounds is thus reduced owing to MP of ethoxy substituents. We can thus say that MP effect with Si and B compounds is important. The opposite situation is seen with C and Ge compounds for which the relationship $\Delta\nu(OH)$ vs n gets steeper character and ethoxy substituents have constant $-I$ effect⁵.

Herein presented data correct our earlier presented¹⁰ view that MP effect in orthoborates is of low importance, and seem to be supportive of the fact that MP effect is facilitated by vacant ($2p$ B, $3d$ Si) orbitals. The resolution of a mode of such facilitation needs, however, further data, since very important MP effect of $(CH_3)_3SiO$ substituents exists¹³ in $((CH_3)_3SiO)_nSi(CH_3)_{4-n}$, where there is a lack¹⁴ of conjugation between the two $(p-d)_\pi$ bonds of the Si—O—Si system.

EXPERIMENTAL

Di-*n*-butyl *n*-butylboronate¹⁵ and *n*-butyl di-*n*-butylborinate¹⁶ were prepared as reported. Their oxygen basicity in CCl_4 was measured with phenol as described¹⁰ and was found to be for both $n-C_4H_9(n-C_4H_9O)_2B$ and $(n-C_4H_9)_2(n-C_4H_9O)B$ compounds $227 \pm 7 \text{ cm}^{-1}$.

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