THE ELECTRONIC EFFECT OF SILYL GROUPS IN DIFFERENT XYZSi–R SYSTEMS*

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Received May 2nd, 1979

The electronic effect parameter σ^* for XYZSi-groups in XYZSi–R compounds as silyl hydrides XYZSiH, alkoxysilanes XYZSiOL (L = alkyl or substituted alkyl), and α-carbofunctional silanes $XYZSiCH_2Y$ (Y = Cl and OL) having X, Y and Z substituents of various electron-donating and electronaccepting ability has been established by a linear regression analysis of the IR and NQR data on these compounds. It is shown that no universal scale of the σ^* constant for silyl XYZSi-groups can be established. The electronic effect transmission of the X, Y and Z substituents through the silicon depends on the type of the intramolecular interaction between the silicon and the R group and the electronic effect parameter of silyl groups should be treated as a variable whose exact value depends on the nature of the particular molecule.

There is only little information on the electronic effect of silyl groups in aliphatic systems. The fact that the electronic effect of X, Y, and Z substituents attached to the silicon controls the electronic effect of the silyl group XYZSi- is, certainly, well understood, and the modification of properties of a molecular center in R by a variation of X, Y and Z substituents was often studied and is well documented for XYZSi–R systems[1–3]. The determination of a scale of the electronic effect parameters for XYZSi-groups in aliphatic systems may, however, be hampered by the mutual influence of the electronegative substituents, X, Y and Z (ref.[4]) and by various intramolecular interactions between the XYZSi-group and the molecular rest R, which was, as to the aliphatic systems, best documented for R = OC_2H_5 and OCH_2CCl_3 (refs[5,6]). Possibility of, or need to take into account the electronic effect variation of some X, Y and Z substituents in some XYZSi-groups with substitution in R decreases even reliability of silyl groups' electronegativities for predicting the silyl groups' electronic effect. Of the electronegativities developed from orbital electronegativities of central atoms of X, Y and Z substituents[7], based upon the covalent boundary potential method of Cordy[8] modified by Wilmshurst,[9] obtained from electronegativities of atoms (groups) composing the X, Y and Z (ref.[10]), or from the Si—H vibrational data[11], the last appear[12] to provide the best scale of the electronic effect of silyl groups.

For the time being neither proposal of a universal scale of the silyl groups' electronic effect has been made, nor the question was posed whether this is possible. In this article we attempt to solve this problem by examination of a number of spectral

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* Part CLXVIII in the series Organosilicon Compounds; Part CLXVII: This Journal *45*, 854 (1980).

data on the XYZSi–R compounds with R = H, OL, and CH_2Y (where L is alkyl and substituted alkyl group and Y designates Cl and OL) in which different intramolecular interactions between the silicon and a center in the R group are known to take place.

RESULTS AND DISCUSSION

Different intramolecular interactions can be experienced by organosilicon compounds XYZSi–R. Besides the polar effect, *i.e.* the combined F and I effect, the mutual polarizability effect[4] plays an important role in X—Si—Y fragments with electronegative or unsaturated X and Y groups, and the so-called back-bonding[1,13] $X \rightleftharpoons Si$ between the silicon and an unsaturated or electronegative group possessing suitable nonbonded occupied molecular orbital takes place as well. Of special importance is also the α-effect[14–19], an intramolecular interaction between the silicon and the heteroatom interposed from the silicon by one carbon atom.

All these interactions can occur within silyl XYZSi-group. In attempting to estimate the electronic effect of different silyl groups in different XYZSi–R systems, the XYZSi–H compounds appear the most suitable to start from, since the interaction between a silyl group and the hydrogen ought to be dominated by polar effect. Proceeding then toward systems with R = OL, and CH_2Y (where Y = Cl and OL), wherein the other intramolecular interactions between silyl and R groups operate, the electronic effect parameter for silyl groups determined in these systems can be compared to that inherent for silyl hydrides XYZSi–H, which can answer whether and/or how the back-bonding and the α-effect moderate the electronic effect of silyl groups.

Silyl Groups in Silyl Hydrides

There is abundant evidence for very strong influence of X, Y and Z substituents on the nature of the hydrogen–silicon bond[20–26] in silyl hydrides XYZSi–H. The only electronic interactions involved in the change of the Si–H bond nature are the polarizability[27] effects. Stretching frequency ν(Si–H) appears[28] worthy to estimate the electronic effect of the XYZSi-group, since, as shown[29] for hydrides XH generally, it correlates rather well with group electronegativities χ_X. Despite that group electronegativities χ_X and σ_I parameter of X groups show some paralels[28], they do not fit sufficiently precised σ_I *vs* χ_X correlation to allow computing σ_I for silyl groups from electronegativity values. The electronic effect parameter of silyl groups can be better approached from the linear relationship between ν(Si–H) and σ^*_{XYZSi-} for the XYZSi–H compounds, provided that at least some σ^*_{XYZSi-}'s are known. The list of Taft σ^* constants for silyl groups found in or assessed from literature and stretching frequency ν(Si–H) in silyl hydrides are given in Table I. Regression analysis employed to establish a linear correlation between these two quantities yields regression line (Eq. (*1*)) which can be subsequently used to estimate σ^* constants of many other silyl XYZSi-groups when ν(Si–H) frequency for XYZSi–H compounds is available[21–23,39,40].

$$\nu(\text{Si–H})^{\text{XYZSi–H}} - \nu(\text{Si–H})^{(\text{CH}_3)_3\text{Si–H}} =$$

$$= (32{\cdot}77 \pm 3{\cdot}60) + (44{\cdot}64 \pm 2{\cdot}25)\,\sigma^*_{\text{XYZSi–}}\,, \quad r = 0{\cdot}989 \qquad (1)$$

An illustration of the electronic effect of silyl XYZSi-groups in silyl hydrides is given in Table II, wherein the $\sigma^*_{\text{XYZSi–}}$ parameters for those silyl groups encountered with more frequently are gathered.

When the sensitivity of ν(Si–H) frequency in silyl hydrides to the variation of substituents attached to silicon had been recognized, the electronic effect of X, Y and Z substituents in XYZSi–H system was examined on the ground of ν(Si–H) *vs* $\sigma^*_{\text{X,Y,Z}}$ relationship. Deviations from the correlation line for alkoxy, halogeno, dialkylamino

TABLE I

Taft σ^* Parameter for Silyl Groups and Stretching Frequency ν(Si—H) in Silyl Hydrides

XYZSi-Group	$\sigma^*_{\text{XYZSi–}}$					ν(Si—H)[f]
	a	*b*	*c*	*d*	*e*	
$(C_2H_5)Si$	−1·10	—	—	−0·93	−1·01	2 097
$(CH_3)_3Si$	−0·72	−0·81	−1·38	−0·85	−0·93	2 118
$C_6H_5(CH_3)_2Si$	—	−0·87	—	—	−0·87	2 120
$(CH_3)_3SiO(CH_3)_2Si$	—	−0·81	—	—	−0·81	2 115
$(C_6H_5)_3Si$	−0·53	—	−0·59	—	—0·56	2 126
$Cl(CH_3)_2Si$	0·32	—	—	—	0·32	2 168
H_3Si	0·87	—	—	—	0·87	2 175
Cl_2CH_3Si	1·30	—	—	—	1·30	2 213
Br_3Si	1·80	—	2·71	—	2·26	2 236
Cl_3Si	2·27	—	2·74	—	2·51	2 258
F_3Si	3·53	—	2·99	—	3·26	2 315

[a] In XYZSi—H, calculated from force constant of Si—H bond[30]. [b] Determined[31] from ionization constant of silylacetic acid $XYZSiCH_2CO_2H$ (ref.[32]). [c] Calculated from σ_m and σ_p constants as $\sigma_I = (\sigma_m - \alpha\sigma_p)/(1 - \alpha)$ (ref.[33]) and $\sigma^* = 6{\cdot}23\sigma_I$ (ref.[31]), σ_m and σ_p were obtained from ionization of $(CH_3)_3Si—C_6H_4—CO_2H$ (refs[34,35]), reaction of $(C_6H_5)_3Si—C_6H_4CO_2H$ with diphenyldiazomethane (ref.[36]), and from ^{19}F-NMR chemical shift of $X_3Si—C_6H_4F$ (X = F, Cl, Br, ref.[37]). [d] Derived[38] from stretching vibration ν(Si—H) of $((CH_3)_3Si)_3SiH$ and $((C_2H_5)_3.Si)_3.SiH$. [e] Average value. [f] In cm^{-1} (ref.[39] and refs therein).

and for unsaturated groups like phenyl of vinyl have been considered[39,41] consistent with the presence of $(p-d)_\pi$ back-donation and competition for d-orbitals of silicon by the chloro- and alkoxy-substituents. Meanwhile, the new interpretation[4] of reduced −I effect of electronegative or unsaturated substituents bonded to silicon has been put forward. Commenting herein only on the electronic effect of the whole silyl XYZSi-group, we will stress following facts emerging from Tables I and II.

1) Trialkylsilyl groups are, apparently due to the higher electropositivity of silicon when compared to carbon, greater electrodonors than trialkylmethyl groups. From this viewpoint interestingly electronwithdrawing ability of H_3Si group obviously results from the $\overset{\delta+}{\mathrm{Si}}—\overset{\delta-}{\mathrm{H}}$ bond polarity[20,27].

2) The electrondonating character of silyl groups survives also in the case of $X(CH_3)_2Si$-groups with rather strong electronwithdrawing X like allyl, vinyl, benzyl, phenyl, halogenoalkyl, alkoxy and dimethylamino substituent. Three unsaturated (phenyl or vinyl) or $(CH_3)_2N$-substituents on silicon are still not able enough to break

TABLE II

Taft σ^* Parameter for Silyl Groups in Silyl Hydrides[a]

Group	σ^*	Group	σ^*
$(i\text{-}C_3H_7)_3Si$	−1·41 ± 0·16	$(CH_3)_2N(CH_3)_2Si$	−0·76 ± 0·12
$(n\text{-}C_3H_7)_3Si$	−1·14 ± 0·15	$((CH_3)_2N)_2CH_3Si$	−0·91 ± 0·14
$(C_2H_5)_3Si$	−1·20 ± 0·16	$((CH_3)_2N)_3Si$	−0·87 ± 0·13
$(CH_3)_3Si$	−0·73 ± 0·13	$C_2H_5O(CH_3)_2Si$	−0·82 ± 0·14
$CH_3(CH_2{=}CHCH_2)_2Si$	−0·58 ± 0·06	$Cl_2CH(CH_3)_2Si$	0·12 ± 0·09
$CF_3CH_2CH_2(CH_3)_2Si$	−0·62 ± 0·05	$(C_2H_5O)_2CH_3Si$	0·32 ± 0·10
$(CF_3CH_2CH_2)_2CH_3Si$	−0·42 ± 0·06	$(C_2H_5O)_3Si$	1·00 ± 0·14
$(C_6H_5CH_2)_3Si$	−0·47 ± 0·07	$Cl(CH_3)_2Si$	0·39 ± 0·10
$ICH_2(CH_3)_2Si$	−0·42 ± 0·06	Cl_2CH_3Si	1·39 ± 0·17
$BrCH_2(CH_3)_2Si$	−0·35 ± 0·06	Cl_3Si	2·40 ± 0·22
$ClCH_2(CH_3)_2Si$	−0·29 ± 0·07	Br_3Si	1·91 ± 0·19
$C_6H_5(CH_3)_2Si$	−0·69 ± 0·05	F_3Si	3·68 ± 0·29
$CH_2{=}CH(CH_3)_2Si$	−0·60 ± 0·05	$(C_2H_5O)_2ClSi$	1·98 ± 0·19
$(C_6H_5)_2CH_3Si$	−0·60 ± 0·05	$(C_2H_5O)Cl_2Si$	2·58 ± 0·23
$(C_6H_5)_3Si$	−0·55 ± 0·05	$(C_6H_5O)_3Si$	2·07 ± 0·20
$(CH_2{=}CH)_3Si$	−0·38 ± 0·07	H_3Si	0·54 ± 0·12

[a] The σ^* parameter for silyl groups was established from ν(Si—H) values reported in refs[21–23,39,41].

down +I effect of silyl group, which is of all the instances the most surprising fact for the $((CH_3)_2N)_3Si$-group.

TABLE III

Taft σ^* Parameter for Silyl Groups Attached to OC_2H_5 Moiety[a]

Group	σ^*	Group	σ^*
$(n\text{-}C_3H_7)_3Si$	−0·27 ± 0·05	$F(CH_3)_2Si$	0·36 ± 0·06
$CH_3(n\text{-}C_4H_9)_2Si$	−0·24 ± 0·05	$ClCH_2(CH_3)C_2H_5OSi$	0·38 ± 0·06
$CH_3(n\text{-}C_3H_7)_2Si$	−0·24 ± 0·05	$BrCH_2(CH_3)C_2H_5OSi$	0·38 ± 0·06
$(CH_3)_3Si(CH_3)_2Si$	−0·23 ± 0·05	$CH_2{=}CH(C_2H_5O)_2Si$	0·39 ± 0·06
$n\text{-}C_4H_9(CH_3)_2Si$	−0·20 ± 0·05	$C_2H_5O(C_6H_5)_2Si$	0·41 ± 0·06
$n\text{-}C_3H_7(CH_3)_2Si$	−0·20 ± 0·05	$C_6H_5(C_2H_5O)_2Si$	0·43 ± 0·06
$(CH_3)_3Si$	−0·15 ± 0·05	$(C_2H_5O)_3Si$	0·45 ± 0·06
$CH_2{=}CH(CH_3)_2Si$	−0·10 ± 0·05	$(C_6H_5)_3Si$	0·45 ± 0·06
$C_2H_5O(n\text{-}C_3H_7)_2Si$	−0·06 ± 0·03	$Br(CH_3)_2Si$	0·47 ± 0·06
$C_6H_5(CH_3)_2Si$	−0·02 ± 0·03	$ClCH_2CH_2(C_2H_5O)_2Si$	0·48 ± 0·06
$n\text{-}C_4H_9(CH_3)C_2H_5OSi$	−0·01 ± 0·03	$ICH_2(C_2H_5O)_2Si$	0·51 ± 0·06
$CH_3(C_2H_5)C_2H_5OSi$	0·00 ± 0·03	$(F_3CCH_2CH_2)_3Si$	0·54 ± 0·07
$CH_2{=}CHCH_2(CH_3)_2Si$	0·06 ± 0·03	$BrCH_2(C_2H_5O)_2Si$	0·54 ± 0·07
$C_6H_5CH_2(CH_3)_2Si$	0·06 ± 0·03	$ClCH_2(C_2H_5O)_2Si$	0·54 ± 0·07
$C_2H_5O(CH_3)_2Si$	0·08 ± 0·03	$Cl_2CHCH_2(C_2H_5O)_2Si$	0·56 ± 0·07
$F_3CCH_2CH_2(CH_3)_2Si$	0·10 ± 0·04	$Cl(CH_3)_2Si$	0·57 ± 0·07
$H(CH_3)_2Si$	0·12 ± 0·04	$C_2H_5O(ClCH_2CH_2)_2Si$	0·58 ± 0·07
$CH_3(C_2H_5O)C_6H_5Si$	0·14 ± 0·04	$H(C_2H_5O)_2Si$	0·58 ± 0·07
$CH_3(C_2H_5O)CH_2{=}CHSi$	0·15 ± 0·04	$F(C_2H_5O)CH_3Si$	0·66 ± 0·07
$n\text{-}C_4H_9(C_2H_5O)_2Si$	0·18 ± 0·04	$Cl(C_2H_5O)CH_3Si$	0·76 ± 0·09
$CH_3(C_2H_5)_2Si$	0·19 ± 0·04	$Cl_2CH(C_2H_5O)_2Si$	0·82 ± 0·09
$n\text{-}C_3H_7(C_2H_5O)_2Si$	0·20 ± 0·04	$F(C_2H_5O)_2Si$	0·83 ± 0·09
$ICH_2(CH_3)_2Si$	0·20 ± 0·04	$Cl(C_2H_5O)_2Si$	0·84 ± 0·09
$ClCH_2(CH_3)_2Si$	0·23 ± 0·05	$Br(C_2H_5O)_2Si$	0·98 ± 0·10
$ClCH_2CH_2(CH_3)C_2H_5OSi$	0·25 ± 0·05	$Cl_3C(C_2H_5O)_2Si$	1·10 ± 0·11
$CH_3(C_2H_5O)_2Si$	0·27 ± 0·05	Cl_2CH_3Si	1·26 ± 0·11
$CH_3(F_3CCH_2CH_2)_2Si$	0·29 ± 0·05	$Cl_2(C_4H_4S)Si$	1·38 ± 0·12
$H(C_2H_5O)CH_3Si$	0·31 ± 0·06	Br_3Si	1·39 ± 0·12
$ClCH_2CH_2CH_2(C_2H_5O)_2Si$	0·32 ± 0·06	$Cl_2(C_2H_5O)Si$	1·46 ± 0·14
$HC{\equiv}C(CH_3)_2Si$	0·32 ± 0·06	HCl_2Si	1·49 ± 0·14
$BrCH_2(CH_3)_2Si$	0·33 ± 0·06	Cl_3Si	1·77 ± 0·15
$ICH_2(CH_3)C_2H_5OSi$	0·34 ± 0·06		

[a] The σ^* parameter has been established from the relative basicity of the oxygen in $XYZSi$—OC_2H_5 compounds reported in papers[4,5,16,27,42,44–51] and from a linear correlation between the oxygen basicity and σ^* of X groups in X—OC_2H_5 (ref.[43]).

3) The reversal of electronic effect of silyl group from donating to withdrawing is realised by one Cl_2CH, Cl or by two C_2H_5O-substituents.

4) The ethoxy group and chlorine synergetically increase electronwithdrawing nature of silyl groups.

5) Electronwithdrawing nature of the F_3Si, Cl_3Si and Br_3Si groups is better discerned than that of their carbon analogues. Similarly, the triphenoxysilyl group is much more powerful electronacceptor than triethoxysilyl group.

Silyl Groups Attached to Oxygen

The σ^* parameter of the electronic effect of silyl XYZSi-groups attached to the oxygen in alkoxysilanes XYZSi–OL can be easily estimated[5] from the phenol hydrogen bonded OH stretching frequency shift ($\Delta\nu$(OH)) measured[42] in CCl_4 and from linear correlations between the $\Delta\nu$(OH) and known σ^* parameters of X groups for ethers X—O—L (ref.[43]). Many silyl groups attached to the oxygen in alkoxysilanes XYZSi–OL have been shown[5,6] to vary their electronic effect with L. Our attention will be therefore arrested to several systems XYZSi–OL where L = C_2H_5, CH_3, CH_2=$CHCH_2$, $Cl(CH_2)_2$, HC≡CCH_2 and Cl_3CHH_2, and σ^*_{XYZSi-} will be estimated from the linear $\Delta\nu$(OH) *vs* σ^*_X correlations fitted by the appropriate X–OL sets.

TABLE IV

Taft σ^* Parameter for Silyl Groups in Methoxysilanes XYZSi—OCH_3[a]

Group	σ^*	Group	σ^*
$(CH_3)_3Si(CH_3)_2Si$	−0·24 ± 0·05	$(CH_3O)_3Si$	0·46 ± 0·07
$(CH_3)_3Si$	−0·11 ± 0·05	$ClCH_2CH_2(CH_3)O)_2Si$	0·48 ± 0·07
$CH_3O(CH_3)_2Si$	0·04 ± 0·04	$ICH_2(CH_3O)_2Si$	0·50 ± 0·07
$H(CH_3)_2Si$	0·05 ± 0·04	$Cl_2CHCH_2(CH_3O)_2Si$	0·54 ± 0·08
c-$C_6H_{11}(CH_3O)_2Si$	0·24 ± 0·05	$ClCH_2(CH_3O)_2Si$	0·59 ± 0·08
$CH_3(CH_3O)_2Si$	0·28 ± 0·05	$BrCH_2(CH_3O)_2Si$	0·60 ± 0·08
HC≡$C(CH_3)_2Si$	0·32 ± 0·06	H_3Si	0·65 ± 0·09
$H_2(CH_3)Si$	0·32 ± 0·06	$Cl_2CH(CH_3O)_2Si$	0·77 ± 0·09
$ClCH_2CH_2CH_2(CH_3O)_2Si$	0·33 ± 0·06	$Cl(CH_3O)_2Si$	0·92 ± 0·10
CH_2=$CHCH_2(CH_3O)_2Si$	0·35 ± 0·06	$Cl_3C(CH_3O)_2Si$	1·02 ± 0·12
$C_6H_5(CH_3O)_2Si$	0·42 ± 0·07		

[a] The σ^* parameter was established from the relative oxygen basicity in methoxysilanes $XYZSiOCH_3$, reported in papers[45,49,50,52–54] and from linear correlation between $\Delta\nu$(OH) and σ^* of X groups in X—OCH_3 (ref.[43]).

A large body of data on the relative oxygen basicity, $\Delta\nu(OH)$, have been determined for ethoxysilanes $XYZSi-OC_2H_5$ (refs[4,5,16,27,42,44-51]). From all these $\Delta\nu(OH)$ values established σ^* parameters for silyl groups in ethoxysilanes are compiled in Table III. From this table following inferences can be drawn.

1) Trialkylsilyl groups are electrondonating in ethoxysilanes, even though apparently less than in silyl hydrides.

2) Other silyl groups retain electrondonating character only in the case of some $(alkyl)_2XSi$-groups with X = electronwithdrawing substituent as C_6H_5, $CH_2{=}CH$, or C_2H_5O. Somewhat startling is the higher electronwithdrawing ability of $XCH_2.(CH_3)_2Si$ than that of $X(CH_3)_2Si$-groups for X = vinyl and phenyl.

3) There is no more synergistic action of C_2H_5O and Cl substituents increasing electronwithdrawing nature of silyl group in ethoxysilanes.

4) Taking $(CH_3)_3Si$ group as one and Cl_3Si group as the second end-point of silyl group's scale, the difference between them in σ^* units is markedly lesser for ethoxysilanes (1·92) than for silyl hydrides (3·13). The ability of both silyl electrodonors and electronacceptors is somewhat reduced when they are attached to oxygen. Thus, *e.g.* electronwithdrawing action of $X(CH_3)_2Si$ groups with X = C_2H_5O and Cl in ethoxysilanes is higher than that in the Si–H system, electronwithdrawing action of the X_2CH_3Si groups in the both systems is very alike, and electronwithdrawing action of the X_3Si groups in ethoxysilanes is lower than in silyl hydrides. Despite that, σ^*'s for $(C_6H_5)_n(CH_3)_{3-n}Si$ groups attached to OC_2H_5 differ more significantly than when attached to hydrogen.

TABLE V

Taft σ^* Values of Alkoxy(methyl)silyl Groups $(LO)_n(CH_3)_{3-n}Si$ in Alkoxysilanes $(LO)_n(CH_3)_{3-n}Si{-}OL$[a]

L	$LO(CH_3)_2Si$	$(LO)_2CH_3Si$	$(LO)_3Si$
C_2H_5	0·08 ± 0·03	0·27 ± 0·05	0·45 ± 0·06
CH_3	0·04 ± 0·04	0·28 ± 0·05	0·46 ± 0·07
$CH_2{=}CHCH_2$	0·12 ± 0·04	0·39 ± 0·05	0·61 ± 0·06
$ClCH_2CH_2$	0·15 ± 0·05	0·42 ± 0·06	0·68 ± 0·08
$HC{\equiv}CCH_2$	0·14 ± 0·05	0·55 ± 0·08	1·03 ± 0·13

[a] The σ^* parameter was established from the oxygen relative basicity of alkoxysilanes $(LO)_n.(CH_3)_{3-n}SiOL$ reported in papers[42,52,55,56] and from linear correlations[43] between $\Delta\nu(OH)$ and σ^* of X groups in X—O—L (L = CH_3, C_2H_5, $CH_2{=}CHCH_2$, $ClCH_2CH_2$ and $HC{\equiv}CCH_2$).

The relative basicity of the ether-like oxygen in compounds R—O—R′ has been shown[5,6,43] to be controlled by total electronic effect of R and R′ groups, that is by a blend of their polar and polarizability effects. Many in ethoxysilanes XYZSi–OC_2H_5 electronwithdrawing silyl groups act in 2,2,2-trichloroethoxysilanes XYZSi–OCH_2CCl_3 as electrondonors, apparently due to an enormous role of the polarizability component of their electronic effect[5]. Therefore, the analysis of the oxygen basicity in alkoxysilanes XYZSi–OL with different L appears to be of interest in order to find whether the electronic effect of silyl groups XYZSi is modified by L. The electronic effect parameter for silyl groups can be, similarly as for XYZSi–OC_2H_5, assessed from appropriate $\Delta\nu(OH)$ *vs* σ^*_X correlation lines[27,43] for X—O—L with L = methyl, allyl, 2-chloroethyl and propargyl, provided that $\Delta\nu(OH)$ for XYZSi–OL are known.

As for the methoxysilanes XYZSi–OCH_3, the $\Delta\nu(OH)$'s reported[45,49,50,52–54] allow to assess σ^* parameter for XYZSi-groups (Table IV) which indicate that electronic effect of silyl groups attached to OCH_3 observes the same rules as that of silyl groups attached to OC_2H_5 moiety.

The electronic effect parameter σ^*_{XYZSi} for silyl groups in other alkoxysilanes XYZSiOL is given in Tables V and VI. A perusal of Table V reveals how is the electronic effect of $(LO)_n(CH_3)_{3-n}$ Si groups influenced by the nature of L and by the number of LO-substituents. The inclining number of the LO-substituents increases electronwithdrawing ability of $(LO)_n(CH_3)_{3-n}Si$ group, the increase being more pronounced with more electronwithdrawing substituent L. There is therefore possible to discern σ^* values for the individual $LO(CH_3)_2Si$, $(LO)_2CH_3Si$, or $(LO)_3Si$ groups, and, interestingly enough, the differences between σ^*'s within the individual

TABLE VI

Taft σ^* Values[a] of $Cl_n(CH_3)_{3-n}Si$ Groups in $Cl_n(CH_3)_{3-n}Si$—OL and the Oxygen Basicity[b] in These Compounds

L	n = 1		n = 2		n = 3	
	σ^*	$\Delta\nu(OH)$	σ^*	$\Delta\nu(OH)$	σ^*	$\Delta\nu(OH)$
C_2H_5	0·57 ± 0·07	207	1·26 ± 0·11	136	1·77 ± 0·15	84
$ClCH_2CH_2$	0·61 ± 0·08	161	1·02 ± 0·11	120	1·03 ± 0·11	119
Cl_3CCH_2	—	115	—	120	—	130

[a] The σ^* parameter has been established from relative oxygen basicity in $Cl_n(CH_3)_{3-n}SiOL$ (ref.[6]) and from linear correlation $\Delta\nu(OH)$ *vs* σ^*_X for X—OL (refs[43,51]). [b] In cm^{-1}.

$LO(CH_3)_2Si$, $(LO)_2CH_3Si$, and $(LO)_3Si$ silyl group sets become more apparent with increasing number of LO substituents.

Table VI confirms the earlier reported fact[5,6] that electronwithdrawing ability of silyl groups in alkoxysilanes XYZSi–OL depends on the nature of L. Thus electronwithdrawing ability of $Cl_n(CH_3)_{3-n}Si$ groups with $n = 2, 3$ in $Cl_n(CH_3)_{3-n}SiOL$ declines when going from $L = C_2H_5$ *via* $L = ClCH_2CH_2$ to $L = Cl_3CCH_2$ and the decrease in electronwithdrawing ability of $Cl_n(CH_3)_{3-n}Si$ groups is facilitated by their chlorine atoms.

Silyl Groups in Silyl–CH_2Cl *System*

The ^{35}Cl-NQR frequency of various substituted methyl chlorides XCH_2Cl (excepting those having two electronegative atoms with unshared electron pair bonded to the same carbon atom) bear a linear relationship to the σ^* parameter of X groups[57]. Following compounds XCH_2Cl (X = CH_3CO, $ClCH_2$, C_6H_5O, $CH_3CO_2CH_2$, HCO_2CH_2, C_6H_5, $C_6H_5CH{=}CH$ $H_2C{=}CH$, CH_3OCH_2, C_3H_7, $Cl(CH_2)_2$, C_2H_5, $Cl(CH_2)_3$, CH_3, n-C_4H_9 (all ref.[57]), $(CH_3)_3C$, i-C_3H_7 (ref.[14]) have been employed in order to establish a linear correlation between ^{35}Cl–NQR frequency (ν^{77}) and known σ^* of X (Eq. (*2*)). Eq. (*2*) can be

$$\nu^{77} = (33\cdot04 \pm 0\cdot11) + (1\cdot19 \pm 0\cdot16)\,.\,\sigma^*_X \qquad (2)$$

TABLE VII

Taft σ^* Parameter for Silyl XYZSi-Groups Attached to CH_2Cl[a]

Group	σ^*_{XYZSi-}	Group	σ^*_{XYZSi-}
$N(CH_2CH_2O)_3Si$[b]	−0·28 ± 0·05	$(C_6H_5)_3Si$	1·41 ± 0·24
$H(CH_3)_2Si$	0·97 ± 0·20	$Cl(CH_3)_2Si$	1·50 ± 0·26
$(CH_3)_3Si$	1·08 ± 0·21	$C_6H_5O(CH_3)_2Si$	1·55 ± 0·26
$CH_3SiO(CH_3)_2Si$	1·11 ± 0·22	$(C_2H_5O)_3Si$	1·75 ± 0·29
$ClCH_2(CH_3)_2Si$	1·24 ± 0·23	$(CH_3CO_2)_3Si$	2·47 ± 0·38
$CH_3CO_2(CH_3)_2Si$	1·26 ± 0·23	$C_6H_5Cl_2Si$	2·51 ± 0·38
$Cl(CH_2Cl)CH_3Si$	1·26 ± 0·23	CH_3F_2Si	2·51 ± 0·38
$CH_3(C_2H_5O)_2Si$	1·30 ± 0·24	CH_3Cl_2Si	2·58 ± 0·39
$CH_3(C_2H_5)_2Si$	1·30 ± 0·24	Cl_3Si	3·15 ± 0·46
$F(CH_3)_2Si$	1·36 ± 0·24	F_3Si	3·23 ± 0·46
$C_2H_5O(CH_3)_2Si$	1·39 ± 0·24	$(SCN_3)Si$	3·45 ± 0·50

[a] All ν^{77} values for $XYZSiCH_2Cl$ from ref.[57]. [b] Ref.[58].

used to estimate σ^* constant for silyl groups from ν^{77} values reported[57,58] for XYZSi–CH_2Cl compounds. As shown in Table VII, the σ^* parameters of silyl groups attached to CH_2Cl create (by their values) quite different scale with regard to that for the XYZSi–H or the XYZSi–OL systems.

The only electrondonating silyl group attached to CH_2Cl is $N(CH_2CH_2O)_3Si$ group. As was reported[58], there takes place the intramolecular coordination interaction between the silicon and the nitrogen in $\overrightarrow{N(CH_2CH_2O)_3Si}$ group responsible for a great σ-electron density on chlorine. All the other silyl groups are significantly electronwithdrawing, which, compared to their electronic effect in the silyl hydrides or in the alkoxysilanes, is very striking. However, such an unusual electronic effect of silyl groups can be well comprehended in terms of the intramolecular interaction between the silicon and the chlorine in the XYZSi–CH_2Cl systems shifting electron density from chlorine to silicon[14–16]. Evidently, this interaction is strong enough to force trialkylsilyl and some other electrondonating silyl groups to behave as strong electron acceptors.

The difference between $(CH_3)_3Si$ and Cl_3Si groups in σ^* units is significantly lesser in the XYZSi–CH_2Cl system (2·07) than in the XYZSi–H system (3·13). Additionally, the differences between the same σ^*_{XYZSi-}'s in the both systems (Table VIII) decrease when going from $(CH_3)_3Si$ to Cl_3Si group (down the column of Table VIII), which

TABLE VIII

Comparison of the Electronic Effect of Silyl Groups in Silyl Hydrides and Chloromethylsilanes

Group	σ^*_{XYZSi-}		$\Delta\sigma^*$
	XYZSi—H	XYZSiCH$_2$Cl	
R_3Si	−1·13[a]	1·30[b]	2·43
$C_2H_5O(CH_3)_2Si$	−0·81	1·39	2·20
$(CH_3)_3Si$	−0·73	1·08	1·81
$(C_6H_5)_3Si$	−0·55	1·41	1·96
$ClCH_2(CH_3)_2Si$	−0·28	1·24	1·52
$F(CH_3)_2Si$	0·19	1·36	1·17
$CH_3(C_2H_5O)_2Si$	0·32	1·30	0·88
$Cl(CH_3)_2Si$	0·39	1·50	1·11
$(C_2H_5O)_3Si$	1·02	1·75	0·73
Cl_2CH_3Si	1·40	2·58	1·18
Cl_3Si	2·40	3·15	0·75

[a] $(n\text{-}C_3H_7)_3Si$. [b] $CH_3(n\text{-}C_3H_7)_2Si$.

implicates that the silicon–chlorine interaction diminishes in this direction. This is in perfect accordance with the analysis of the α-effect presented earlier[16].

Silyl Groups Attached to CH_2OL *Moiety*

Herein we attempt to analyse the oxygen basicity in α-carbofunctional silanes $XYZSi–CH_2OL$ (L = H, alkyl or trimethylsilyl group). Some of these compounds can be regarded[18,53,59,60] to experience the intramolecular interaction termed the α-effect[14–16] shifting electron density from the oxygen to the silicon. From the Δν(OH) values derived σ* parameters for the $XYZSiCH_2$ an XYZSi groups in $XYZSi–CH_2OL$ compounds are seen in Table IX.

As for the $XYZSiCH_2$ groups attached to the OL moiety only $(CH_3)_3SiCH_2$ group appears electrondonating. Its +I effect is very alike to that exerted in the $(CH_3)_3SiCH_2CO_2R$ (R = H, alkyl) compounds[32,66]. However, $(CH_3)_3SiCH_2$ group in the ground state of the $(CH_3)_3SiCH_2OL$ system was found electronwithdrawing[64] and its electrondonating ability inferred from the Δν(OH) values can be attributed[18] to the change of its electronic effect in $(CH_3)_3SiCH_2OL\cdots HOC_6H_5$ complex. As for

TABLE IX

The Oxygen Basicity in $XYZSiCH_2OL$ and $\sigma^*_{XYZSi(CH_2)_n}$ Parameter in These Compounds

XYZSi	L	Δν(OH)[a]	$\sigma^*_{XYZSi(CH_2)_n}$[b]	
			n = 1	n = 0
$(CH_3)_3Si$	C_2H_5	293	−0·27 ± 0·05	−0·76 ± 0·14
	CH_3	278	−0·19 ± 0·05	−0·53 ± 0·14
	H	246	−0·27 ± 0·05	−0·76 ± 0·14
	$(CH_3)_3Si$	293	−0·25 ± 0·04	−0·86 ± 0·11
H_3Si	CH_3	246	0·10 ± 0·03	0·27 ± 0·08
	CH_3	227[c]	0·27 ± 0·05	0·76 ± 0·14
$(C_6H_5)_3Si$	CH_3	132	1·13 ± 0·13	3·17 ± 0·36
	CH_3	161	0·87 ± 0·10	2·44 ± 0·28
	CH_3	155[d]	0·92 ± 0·11	2·59 ± 0·31

[a] Δν(OH) of phenol, in cm^{-1}, from refs[18,51,53,59–64]. [b] Parameter σ^*_{XYZSi-} has been established from Δν(OH) of phenol for $XYZSiCH_2OL$ and from linear correlations Δν(OH) *vs* σ^*_X for X—OL (L = H, CH_3, C_2H_5, ref.[43] and L = $(CH_3)_3Si$, ref.[65]); σ^*_{XYZSi-} has been derived as 2·8. $\sigma^*_{XYZSiCH_2-}$. [c] Obtained from Δν(OH) of methanol (ref.[59]) according to the equation $\Delta\nu(OH)^{C_6H_5OH} = 1{\cdot}76 . \Delta\nu(OH)^{CH_3OH} + 21{\cdot}0$ (ref.[61]). [d] Obtained from Δν(OH) of pyrrol (ref.[60]) according to the above equation since it interelates Δν(OH) of phenol and Δν(OH) of pyrrol as well.

the silylmethyl group H_3SiCH_2, this is slightly electronwithdrawing. Provided that the α-effect is also involved in the ground state of H_3SiCH_2OL, the difference between the two values for $\sigma^*_{H_3SiCH_2}$ inferred from the interaction of $H_3SiCH_2OCH_3$ with phenol and with methanol (more positive value) might follow from a higher willingness of H_3SiCH_2 group to reduce the α-effect during the interaction of $H_3SiCH_2OCH_3$ with stronger acid (C_6H_5OH).

Both the $(C_6H_5)_3SiCH_2$ and Cl_3SiCH_2 groups are electron withdrawing. Interestingly, their −I effect is very alike, which obviously results from an important role of the α-effect in the $(C_6H_5)_3SiCH_2OCH_3$ compound. As to the electronic effect parameter σ^*_{XYZSi-}, its value for $(CH_3)_3Si$ group is about the same as that in $(CH_3)_3Si$–H system, and the values for H_3Si, $(C_6H_5)_3Si$ and Cl_3Si groups can be commented on as above: the high σ^* of $(C_6H_5)_3Si$ speaks in favor of a pronounced involvement of $(C_6H_5)_3Si$ group in the α-effect.

CONCLUSION

There appears impossible to establish a universal scale of the electronic effect parameter for silyl XYZSi-groups in such XYZSi–R system in which different intramolecular interactions between the silicon and the R groups operate. The silyl groups' electronic effect in silyl hydrides XYZSi–H, wherein the silyl groups influence the hydrogen atom chiefly by pure polar effect, serves as a good standard to be compared with the electronic effect of silyl groups exerted in other XYZSi–R systems. Besides the many pecularities of the electronic effect of silyl groups within individual XYZSi–H, XYZSi–OL (L = alkyl or substituted alkyl) and XYZSi–CH_2Y (Y = OL or Cl) systems, the marked reduction of both electrondonating and electronwithdrawing ability of silyl groups is observed in alkoxysilanes XYZSi–OL, where polar effect lumped together with back-donation operates between the silicon and the oxygen. An increase in electronwithdrawing ability of silyl groups takes place in α-carbofunctional silanes $XYZSiCH_2Y$. This increase, caused by the α-effect, diminishes with increasing electronwithdrawing ability of XYZSi-group. Some differences in the electronic effect in the different XYZSi–R systems can be apprehended in terms of the X, Y and Z's electronic effect transmission through the silicon. As for silyl hydrides, Eq. (*3*) was derived taking the first eight silyl groups from Table II into account. As for the ethoxysilanes,

$$\sigma^*_{XYZSi-} = -(0{\cdot}90 \pm 0{\cdot}63) + (0{\cdot}78 \pm 0{\cdot}18) \sum\sigma^*_{X,Y,Z} \qquad (3)$$

(Eq. (*4*)), all the values of silyl groups' electronic parameter from Table III were considered, presuming the electronic effect of unsaturated (vinyl, phenyl), hydrogen and electronegative (X and XCH_2 where X = halogen and ethoxy group) substituents directly attached to silicon as determined before[4,17,27]. The same presumption allowed to obtain equation (*5*) for

$$\sigma^*_{\mathrm{XYZSi-}} = -(0{\cdot}09 \pm 0{\cdot}01) + (0{\cdot}57 \pm 0{\cdot}01) \,.\, \sum\sigma^*_{\mathrm{X,Y,Z}} \qquad (4)$$

$$\sigma^*_{\mathrm{XYZSi-}} = (1{\cdot}55 \pm 0{\cdot}21) + (0{\cdot}29 \pm 0{\cdot}10) \,.\, \sum\sigma^*_{\mathrm{X,Y,Z}} \qquad (5)$$

chloromethylsilanes. There appears that the transmission of the electronic effect of X, Y and Z substituents through the silicon is the most effective in silyl hydrides ($z = 0{\cdot}78$), and decreases when proceeding *via* the alkoxysilanes ($z = 0{\cdot}57$) to chloromethylsilanes ($z = 0{\cdot}29$), which means that it is controlled by the involvement of the silicon atom in the back-bonding or in the α-effect.

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Translated by the author (J. P.).