MUTUAL POLARIZABILITY EFFECT OF SOME SUBSTITUENTS BONDED TO SILICON*

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The oxygen relative basicity of ethoxysilanes $XSi(CH_3)_n(OC_2H_5)_{3-n}$, $X_n(CH_3)_{3-n}SiOC_2H_5$ and $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$ with X = F, Cl, Br, C_2H_5O, C_6H_5 and CH_2=CH was measured as $\Delta\nu(OH)$ of phenol due to interaction with these compounds in CCl_4. The $\Delta\nu(OH)$ data are analysed by means of Taft equation and reveal X groups to exert strongly reduced $-I$ effect in all the above ethoxysilanes. The reduction of $-I$ effect of the substituents X is proposed to arise from their mutual polarizability effect.

There has been much dispute concerning the bonding between silicon and electronegative element or electronegative (unsaturated) group (further X), and the two effects, inductive effect of X and back-bonding X $\rightleftharpoons$ Si are claimed to control molecular features of molecules R_nSiX_{4-n} (refs[1-3]). Our results[4,5] on oxygen basicity of the alkoxysilanes $R_1R_2R_3SiOR$ with $R = C_2H_5$ and Cl_3CCH_2 suggest electron-withdrawing $R_1R_2R_3Si$ groups in ethoxysilanes $(R = C_2H_5)$ to affect the oxygen in 2,2,2--trichloroethoxysilanes $(R = Cl_3CCH_2)$ by electron-donating action and this finding was explained by an enormous polarization of silyl groups[5] that is, at least in part, due to polarizability effect of R_1, R_2, and R_3 substituents.

With a view to disclose a role of polarizability effect of substituents attached to silicon, this note reports analysis of the oxygen basicity data in ethoxysilanes $XSi(CH_3)_n(OC_2H_5)_{3-n}$, $X_n(CH_3)_{3-n}SiOC_2H_5$ and $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$, measured as $\Delta\nu(OH)$ of phenol due to interaction with these ethoxysilanes, by means of the Taft equation[5].

EXPERIMENTAL

Ethoxysilanes $XSi(CH_3)_n(OC_2H_5)_{3-n}$ with $n = 0-2$ and X = F, Cl, Br, C_2H_5O, C_6H_5, and CH_2=CH, further $X_n(CH_3)_{3-n}SiOC_2H_5$ having $n = 1-3$ and X = C_6H_5, Br, and further $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$ with $n = 1-2$ and X = Cl, C_6H_5, and CH_2=CHCH$_2$(CH$_3$)$_2$. .SiOC$_2$H$_5$ and $C_6H_5CH_2Si(CH_3)_2(OC_2H_5)$ have been prepared by a treatment of corresponding chloro- or bromosilanes with ethanol. All the compounds have been already reported[7,8].

Dichloromethyl ethyl ether was prepared according to the procedure[9]. Purity of all the compounds was checked by gas–liquid chromatography and their identity proved by elemental analysis or NMR spectroscopy.

Relative oxygen basicity of ethoxysilanes was determined from the IR spectra of hydrogen bonds of phenol interacting with ethoxysilanes in CCl_4, as already described[10].

RESULTS AND DISCUSSION

The oxygen basicity measurements of ethoxysilanes $(CH_3)_nSi(OC_2H_5)_{4-n}$ in CCl_4 using phenol as reference acid have shown[11] that the ethoxysilanes are weaker bases than ethers and that as the number of alkoxy groups on silicon increases, the basicity declines, but less so than in the case of alkoxymethanes $(CH_3)_nC(OC_2H_5)_{4-n}$. The result is that $CH_3Si(OC_2H_5)_3$ and $Si(OC_2H_5)_4$ are more basic than their carbon analogues. The findings were explained[11] by electron back-donation from the oxygen to the silicon and by the fact that "π-bonding capacity of silicon tends to become saturated as the number of donor atoms increases". An extent of back-donation in Si—X was considered to be dependent on the nature of substituents attached to the same silicon also in other papers[1,2,12]. Meanwhile, solvation phenomena in diluted solutions of phenol and alkoxysilane in CCl_4 were deduced[13] to influence the equilibrium between phenol and oxygen-containing solute and their complex unimportantly and the relationship between oxygen basicity $(\Delta v(OH))$ and electronic substituent parameter $\sum \sigma^*$ (see Eq. (1)) was proved to be valid for many oxygen-containing species as alcohols[14,15], ethers[14,16], alkoxysilanes[17] and

$$\Delta v(OH) = \varrho \cdot \sum \sigma^* + C \qquad (1)$$

siloxanes[17]. Proton accepting ability of oxygen measured from the IR spectra of hydrogen bonds of phenol can thus provide an information on electronic effect of substituents bonded to oxygen.

Four correlations $\Delta v(OH)$ vs $\sum \sigma^*$ parameter are given in Table I, and three of them, concerning the ethoxysilanes $R_1R_2R_3SiOC_2H_5$, $R_1R_2Si(OC_2H_5)_2$ and $R_1Si(OC_2H_5)_3$ include only compounds with substituents R_1, R_2, and R_3 uncapable of back-bonding or uncapable of the intramolecular interaction termed the α-effect (refs[18,19] and refs therein). A perusal of Table I reveals that transmission of electronic effect of substituents R_1, R_2, and R_3 through the silicon is greater than that through carbon (the ϱ^* constant for $R_1R_2R_3COC_2H_5$ is about twice less than that for $R_1R_2R_3SiOC_2$.H_5 and $R_1R_2Si(OC_2H_5)_2$ and still less than that for $R_1Si(OC_2H_5)_3^*$). Silicon pos-

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*   The opposite situation is encountered[20] with $R_1R_2R_3MCH_2Cl$ compounds (M = Si, C). The higher transmission of electronic effect through carbon relative to silicon was ascribed[19] to the α-effect.

sesses empty low-lying $3d$ orbitals which, utilized in $(p-d)_\pi$ bonding may be reason for high electronic effect transmission, since they can make the Si—O bond more polarizable[21]. The results given below are supportive of this opinion. Further we shall

TABLE I

Parameters of Correlations with Eq. (1)

Set	$-\varrho^*$	h^a	r^b	C	l^c	n^d
$R_1R_2R_3COC_2H_5^e$	32·96	1·41	0·984	299·17	3·63	10
$R_1R_2R_3SiOC_2H_5^f$	62·01	2·99	0·988	273·11	1·16	13
$R_1R_2Si(OC_2H_5)_2^g$	63·00	4·12	0·992	257·91	1·77	6
$R_1Si(OC_2H_5)_3^h$	48·20	4·46	0·988	238·60	1·62	6

^{a} Standard error of ϱ^*; ^{b} correlation coefficient; ^{c} standard error of C; ^{d} number of points in set; ^{e} R_1, R_2, R_3: H, H, CH_3; H, H, C_2H_5; H, CH_3, CH_3; CH_3, CH_3, CH_3; H, H, CH_2Cl; H, H, Cl; C_2H_5O, CH_3, H; C_2H_5O, CH_3, CH_3; $CH_2=CH$, H, H, (all from ref.[16]); Cl, Cl, H ($\Delta\nu(OH) = 103$ cm^{-1}); ^{f} R_1, R_2, R_3: CH_3, i-C_3H_7, i-C_3H_7; n-C_3H_7, n-C_3H_7, n-C_3H_7; CH_3, n-C_4H_9, n-C_4H_9; CH_3, n-C_3H_7, n-C_3H_7, i-C_3H_7; CH_3, CH_3, n-C_4H_9; CH_3, CH_3, n-C_3H_7; CH_3, CH_3, CH_3; CH_3, CH_3, $CF_3(CH_2)_2$; CH_3, $CF_3(CH_2)_2$, $CF_3(CH_2)_2$; $CF_3(CH_2)_2$, CF_3.$(CH_2)_2$, $CF_3(CH_2)_2$ (all ref.[17]); $H_2C=CHCH_2$, CH_3, CH_3 ($\Delta\nu(OH) = 259$ cm^{-1}); $C_6H_5CH_2$, CH_3, CH_3 ($\Delta\nu(OH) = 260$ cm^{-1}); ^{g} R_1, R_2: n-C_3H_7; n-C_3H_7; n-C_4H_9, CH_3; C_2H_5, CH_3; CH_3, CH_3; $Cl(CH_2)_2$, CH_3; $Cl(CH_2)_2$, $Cl(CH_2)_2$ (all ref.[19]); ^{h} R_1: n-C_4H_9, n-C_3H_7, CH_3, $Cl(CH_2)_2$, $Cl(CH_2)_3$, Cl_2CHCH_2 (all ref.[19]).

TABLE II

$\Delta\nu(OH)$, in cm^{-1}, for $R'R''R'''SiOC_2H_5^a$

R'	R''	R'''	$\Delta\nu(OH)$
CH_3	CH_3	CH_3	271^b (273)
Cl	CH_3	CH_3	207^c (93)
Cl	Cl	CH_3	136^c (^{d})
Cl	Cl	Cl	84^c (^{d})
C_2H_5O	CH_3	CH_3	257^b (180)
C_2H_5O	C_2H_5O	CH_3	237^b (87)
C_2H_5O	C_2H_5O	C_2H_5O	219^b (^{d})

^{a} Values in parentheses relate to the $\Delta\nu(OH)$ derived from the $\Delta\nu(OH)$ vs $\sum\sigma^*$ plot for $R_1R_2R_3$.$SiOC_2H_5$ having $R_1, R_2,$ and R_3 uncapable of back-bonding and the α-effect (the second entry of Table I) presumed that σ^* of CH_3, Cl, and C_2H_5O are 0, 2·9, and 1·5 respectively. ^{b} Ref.[11], ^{c} Ref.[4]. ^{d} Negative value.

pay our attention to ethoxysilanes that have electronegative or unsaturated substituents bonded directly to silicon.

The decisively nonadditive effect of successive substitution of a molecular moiety by electron-withdrawing substituents on equilibrium data of molecules derived by such a substitution is called "saturation effect" (refs[22-25]). This effect is also seen with ethoxysilanes in Table II, where the experimentally found $\Delta v(OH)$ data for $R'R''R'''SiOC_2H_5$ are compared with those calculated from the $\Delta v(OH)$ vs $\sum \sigma^*$ relationship including only such $R_1R_2R_3SiOC_2H_5$ that have R_1, R_2, and R_3 uncapable of the α-effect or back-bonding. The oxygen basicity of ethoxymethanes $R_1R_2R_3COC_2H_5$ appears to be in harmony with substituent parameter $\sum \sigma^*_{R_1R_2R_3}$. (The $\Delta v(OH)$ data for $ClH_2COC_2H_5$ and $Cl_2HCOC_2H_5$ are consonant with Eq. (1) (Table I)). On the other hand, the experimental $\Delta v(OH)$ data for $R'R''R'''SiOC_2H_5$ with R' to $R''' = CH_3$, Cl and OC_2H_5 differ quite considerably from the $\Delta v(OH)$ data derived, the difference being enhanced with increasing number of Cl or OC_2H_5 substituents. The experimental $\Delta v(OH)$ is always higher. Saturation effect is thus much more important with organosilicon compounds, and electron-withdrawing ability of Cl and OC_2H_5 substituents is reduced irrespective of their number at silicon.

The question to be answered now is whether this quite apparent reduction of $-I$ effect of Cl, C_2H_5O and also other (see later) substituents directly bonded to silicon is in relation to the ability of these substituents to be involved in back-bonding. Tables III — V provide evidence that this is not so. Tabulated σ^* constants of electronegative

TABLE III

Wavenumber Shifts, $\Delta v(OH)$ in cm^{-1}, of Phenol Due to Interaction with $XSi(CH_3)_n(OC_2H_5)_{3-n}$ in CCl_4 and σ^* of Substituents X in $XSi(CH_3)_n(OC_2H_5)_{3-n}$

X	$n = 0$		$n = 1$		$n = 2$		$\sigma^{*,b}$
	$\Delta v(OH)$	$\sigma^{*,a}$	$\Delta v(OH)$	$\sigma^{*,a}$	$\Delta v(OH)$	$\sigma^{*,a}$	
F	180	$1 \cdot 22 \pm 0 \cdot 14$	198	$0 \cdot 95 \pm 0 \cdot 10$	228^c	$0 \cdot 73 \pm 0 \cdot 05$	$3 \cdot 1$
Cl	179	$1 \cdot 24 \pm 0 \cdot 14$	187	$1 \cdot 13 \pm 0 \cdot 10$	207^d	$1 \cdot 07 \pm 0 \cdot 07$	$2 \cdot 9$
Br	165	$1 \cdot 53 \pm 0 \cdot 16$	—	—	217^c	$0 \cdot 90 \pm 0 \cdot 07$	$2 \cdot 8$
C_2H_5O	219^e	$0 \cdot 41 \pm 0 \cdot 07$	237^e	$0 \cdot 33 \pm 0 \cdot 05$	257^e	$0 \cdot 26 \pm 0 \cdot 03$	$1 \cdot 5$
C_6H_5	221	$0 \cdot 37 \pm 0 \cdot 07$	251	$0 \cdot 11 \pm 0 \cdot 04$	267	$0 \cdot 10 \pm 0 \cdot 02$	$0 \cdot 6$
$CH_2{=}CH$	225	$0 \cdot 28 \pm 0 \cdot 05$	250	$0 \cdot 13 \pm 0 \cdot 03$	276	$-0 \cdot 05 \pm 0 \cdot 02$	$0 \cdot 6$

^{a} Derived from the $\Delta v(OH)$ of $XSi(CH_3)_n(OC_2H_5)_{3-n}$ and the $\Delta v(OH)$ vs $\sum \sigma^*$ plot for $R_1R_2R_3$. .$SiOC_2H_5$, $R_1R_2Si(OC_2H_5)_2$, and $R_1Si(OC_2H_5)_3$ having R_1, R_2, and R_3 uncapable of back bonding (the second, the third, and the fourth entries of Table I). ^{b} Assumed in organic compounds[26]. ^{c} Slightly impure ethoxysilane. ^{d} Ref.[4]. ^{e} Ref.[11].

TABLE IV

Wavenumber Shifts, $\Delta v(OH)$ in cm^{-1}, of Phenol Due to Interaction with $X_n(CH_3)_{3-n}SiOC_2H_5$ in CCl$_4$ and Values of σ^* of Substituents X in $X_n(CH_3)_{3-n}SiOC_2H_5$

X	n	$\Delta v(OH)$	$\sigma^{*,a}$	$\sigma^{*,b}$
Cl	1	207^c	1·07 ± 0·07	2·9
	2	136^c	1·11 ± 0·06	
	3	84^c	1·02 ± 0·06	
C$_2$H$_5$O	1	257^d	0·26 ± 0·03	1·5
	2	237^d	0·29 ± 0·03	
	3	219^d	0·29 ± 0·02	
C$_6$H$_5$	1	267	0·10 ± 0·02	0·6
	2	246	0·22 ± 0·02	
	3	219	0·29 ± 0·02	
Br	1	217	0·90 ± 0·07	2·8
	3	123^e	0·81 ± 0·04	

^{a} Derived from the $\Delta v(OH)$ of $X_n(CH_3)_{3-n}SiOC_2H_5$ and the $\Delta v(OH)$ vs $\sum \sigma^*$ plot for $R_1R_2R_3$.SiOC$_2$H$_5$ having R_1, R_2, and R_3 uncapable of back bonding (the second entry of Table I). ^{b} Assumed in organic compounds[26]. ^{c} Ref.[4]. ^{d} Ref.[11]. ^{e} Slightly impure compound.

TABLE V

Wavenumber Shift, $\Delta v(OH)$ in cm^{-1}, of Phenol Due to Interaction with $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$ in CCl$_4$ and Value of σ^* of Substituents X in $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$

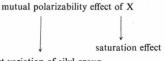| R	n	$\Delta v(OH)$	$\sigma^{*,a}$	$\sigma^{*,b}$
Cl	1	187	1·14 ± 0·09	2·9
	2	115	1·13 ± 0·09	
C$_2$H$_5$O	1	237^c	0·33 ± 0·05	1·5
	2	219^c	0·31 ± 0·03	
C$_6$H$_5$	1	251	0·11 ± 0·04	0·6
	2	223	0·28 ± 0·03	

^{a} Derived from the $\Delta v(OH)$ of $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$ and the $\Delta v(OH)$ vs $\sum \sigma^*$ plot for $R_1R_2Si(OC_2H_5)_2$ having R_1 and R_2 uncapable of back-bonding (the third entry of Table I). ^{b} Assumed in organic compounds[26]. ^{c} Ref.[11].

or unsaturated substituent X bonded to silicon in ethoxysilanes have been derived from appropriate $\Delta v(OH)$ *vs* $\sum \sigma^*$ plots for $R_{4-n}Si(OC_2H_5)_n$ having R uncapable of the α-effect or back bonding (Table I). They show that $-I$ effect of X, *i.e.* F, Cl, Br, C_2H_5O, C_6H_5, and $CH_2=CH$, is reduced in all the $XSi(CH_3)_n(OC_2H_5)_{3-n}$ (Table III), $X_n(CH_3)_{3-n}SiOC_2H_5$ (Table IV), and $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$ (Table V) irrespective of number of ethoxy or X groups. The X substituents can be divided into two groups according to magnitude of their $-I$ effect in different ethoxysilanes. The C_2H_5O, and Cl exert the same $-I$ effect (their σ^* is about the same) in all $XSi(CH_3)_n$.$(OC_2H_5)_{3-n}$, $X_n(CH_3)_{3-n}SiOC_2H_5$ and $X_n(CH_3)_{2-n}Si(OC_2H_5)_2$. On the other hand, $-I$ effect of F, C_6H_5, and $CH_2=CH$ depends on number of these substituents or ethoxy groups attached to the silicon. Their already reduced $-I$ effect further diminishes with decreasing number of X or C_2H_5O substituents in the above three types of ethoxysilanes. Bromine appears to possess the same behaviour in Br_n.$(CH_3)_{3-n}SiOC_2H_5$, but its $-I$ effect decreases with decreasing number of C_2H_5O groups in $BrSi(CH_3)_n(OC_2H_5)_{3-n}$. However, the $\Delta v(OH)$ for bromo(ethoxy)silanes are likely less precise due to the fact that these compounds were isolated as not perfectly pure.

The reduction of $-I$ effect of substituents X is significant both for the substituents capable of back-bonding $(F, C_6H_5, OC_2H_5, CH_2=CH)$ and those (Cl, Br) which are known to be involved in back-bonding only weakly. Hence, back-bonding, operative in silanes having one electronegative or unsaturated substitutent attached directly to silicon, turns out to be of minor, if any, importance in ethoxysilanes that have more these substituents on silicon. Therefore, we presume mutual polarizability effect of the X substituents to be responsible for the reduction of their $-I$ effect in studied ethoxysilanes. This suggestion, already supported in our previous paper[5], can be advocated by the great transmission of electronic effect through silicon in ethoxysilanes (Table I).

In summary then, we attempt to generalize our results reported here and in papers[4,5] by the Scheme 1. Provided that X stands for an easily polarizable electronegative or unsaturated substituent (which appears not to be the case of Cl_2CH

<div align="center">mutual polarizability effect of X</div>

<div align="center">saturation effect</div>

electronic effect variation of silyl group

SCHEME 1

group[5]) and R designates an alkyl group, mutual polarizability effect of substituents X attached to silicon results in saturation effect with X_nSiR_{4-n} compounds $(n \geqq 2)$ and

can, moreover, support polar effect variation of silyl group $X_nR_{3-n}Si$— in X_nR_{3-n}.
.Si—Y compounds having a strongly electron-withdrawing and hardly polarizable
group Y $\left(\text{as is the case of the } OCH_2CCl_3 \text{ group}^{4,5}\right)$.

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