

THE EFFECTS CONTROLLING THE OXYGEN BASICITY
IN ALKOXYSILANES $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$. THE MUTUAL POLARIZABILITY
EFFECT OF ALKOXY GROUPS ATTACHED TO SILICON*

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Relative basicity of the oxygen in alkoxy silanes $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ having $n = 1-4$ and various electron donating and electron withdrawing groups R measured as $\Delta\nu(\text{OH})$ of phenol due to its interaction with these compounds in CCl_4 is shown to be chiefly controlled by the electronic effect of substituents R. Linear regression analysis of the $\Delta\nu(\text{OH})$ vs n relationship for individual series $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ suggests the operation of the polarizability effect of RO groups becoming more important with increasing electron withdrawing nature of R.

A recent upsurge of interest in substituent effect¹⁻⁴ is apparently related to the possibility of determining molecular parameters free of solvation term. In this regard the Taft equation applied to aliphatic oxygen-containing species offers^{5,6} a simple means to indicate and assess otherwise not easily measurable polarizability effect of a substituent considered^{1,2} to contribute to the substituent's overall electronic effect. We have disclosed⁵⁻⁸ oxygen-containing organosilicon compounds to possess exceptionally suitable conditions for bringing the polarizability effect to life and facilitate the electronic effect variation of a moiety incorporated.

With the hope that our earlier study⁵⁻⁸ on the polarizability effect of groups in oxygen-containing silanes can be easily extended to alkoxy groups we discuss in this note the oxygen basicity in alkoxy silanes $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ with different electron-accepting and electron donating groups R and $n = 1-4$ and try to answer which effect(s) control the oxygen basicity in these compounds.

EXPERIMENTAL

All the compounds, the oxygen basicity of which was measured in this work — $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ with R = $(\text{CH}_3)_3\text{SiCH}_2$, cyclo- C_6H_{11} , $\text{CH}_2=\text{CHCH}_2$, C_6H_5 , Cl_3CCH_2 , Cl_2HCCH_2 and CF_3CH_2 , were prepared by customary procedures: either by a treatment of corresponding chlorosilanes $\text{Cl}_n\text{Si}(\text{CH}_3)_{4-n}$ with equimolar amounts of dry alcohol and pyridine in diethyl

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ether (method *A*), or by a reaction of chlorosilanes with alcohol, hydrogen chloride evolved being removed by bubbling nitrogen into the reaction mixture (method *B*). Alkoxy(methyl)silanes were obtained by rectification and their purity was checked by gas-liquid chromatography. Physical constants of the compounds already reported agreed with literature data. New compounds are presented and characterized in Table I.

Proton acceptor ability (basicity) of the oxygen in (RO)_nSi(CH₃)_{4-n} was obtained from the IR spectra of hydrogen bonds of phenol due to its interaction with these compounds in CCl₄ by usual way⁵.

RESULTS AND DISCUSSION

The published results⁹⁻¹¹ on the oxygen basicity of alkoxysilanes (RO)_nSi(CH₃)_{4-n} and alkoxymethanes (RO)_nC(CH₃)_{4-n} indicate that the oxygen basicity of monoalkoxysilanes is lower and that of tri- and tetraalkoxysilanes is higher than the oxygen basicity of corresponding alkoxymethanes. The oxygen basicity in both species declines with the increasing number of alkoxy groups. An interestingly flatter decrease with alkoxysilanes was ascribed¹⁰ to the lower transmission of the substituent's electronic effect through the silicon and was argued⁹ to be a result of the cooperation of inductive and (*p* - *d*)_n effects. The electronic interactions suggested so far to control the oxygen basicity of alkoxysilanes (RO)_nSi(CH₃)_{4-n} have thus been the inductive effect of RO and R groups and the (*p* - *d*)_n bonding O ≠ Si. We have previously shown⁸ the electronic effect of R substituents in R_nSi(OC₂H₅)_{4-n} (*n* = 1 - 3) to be transmitted to the oxygen better than in R₃COC₂H₅. We have also pointed out⁶⁻⁸ the importance of the polarizability effect in determining the oxygen basicity in such alkoxysilanes as X_n(CH₃)_{3-n}SiOR, XYSi(OC₂H₅)₂ and XSi(OC₂H₅)₃ (X = electro-

TABLE I
Yields and Physical Constants of New (RO)_nSi(CH₃)_{4-n}

Compound	B.p. °C/Torr	n _D ²⁰	Yield, %	Method
[(CH ₃) ₃ SiCH ₂ O] ₂ Si(CH ₃) ₂	126/55	1.4128	96	<i>B</i>
[(CH ₃) ₃ SiCH ₂ O] ₃ SiCH ₃	127/25	1.4194	85	<i>A</i>
[(CH ₃) ₃ SiCH ₂ O] ₄ Si	128/19	1.4231	80	<i>A</i>
(cyclo-C ₆ H ₁₁ O) ₃ SiCH ₃	179/4.5	1.4690	47	<i>B</i>
(Cl ₃ CCH ₂ O) ₂ Si(CH ₃) ₂	80/0.1	1.4779	78	<i>B</i>
(Cl ₃ CCH ₂ O) ₃ SiCH ₃	124/0.1	1.4925	73	<i>B</i>
(Cl ₂ CHCH ₂ O) ₂ Si(CH ₃) ₂	106/2.5	1.4649	74	<i>B</i>
(Cl ₂ CHCH ₂ O) ₃ SiCH ₃	145/0.8	1.4807	69	<i>B</i>
(Cl ₂ CHCH ₂ O) ₄ Si	185/0.5	1.4888	37	<i>B</i>

TABLE II

Wavenumber Shift, $\Delta\nu(\text{OH})$ in cm^{-1} , of Phenol Due to Interaction with $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ in CCl_4

R	n			
	1	2	3	4
$(\text{CH}_3)_3\text{SiCH}_2$	293 ^a	276	255	239
cyclo- C_6H_{11}	281	271	254	238
C_2H_5 ^b	271	257	237	219
CH_3 ^c	269	252	226	202
$\text{CH}_2=\text{CHCH}_2$	256 ^a	236	210	188
ClCH_2CH_2 ^d	233	206	180	154
$\text{HC}\equiv\text{CCH}_2$ ^e	227	197	166	129
C_6H_5 ^f	176	141	105	109
$(\text{CH}_3)_3\text{Si}$ ^g	168	158	145	140
Cl_2CHCH_2	193 ^a	156	127	108
Cl_3CCH_2	135 ^a	112	111	110
F_3CCH_2	167 ^h	117	—	—

^a Ref.¹², ^b Ref.⁹, ^c Ref.¹⁰, ^d Ref.¹³, ^e Ref.¹¹; ^f Some of the values differ from those reported in paper¹⁴, ^g Ref.¹⁵, ^h Ref.¹⁶.

TABLE III

Results of Correlation with Eq. (I) for $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$

R	a	b
$(\text{CH}_3)_3\text{SiCH}_2$	311.5 ± 2.1	18.3 ± 0.5
cyclo- C_6H_{11}	297.5 ± 3.3	14.6 ± 1.2
C_2H_5	290.0 ± 2.1	17.6 ± 0.5
CH_3	294.0 ± 3.9	22.7 ± 1.4
$\text{CH}_2=\text{CHCH}_2$	280.0 ± 2.1	23.0 ± 0.5
ClCH_2CH_2	259.0 ± 0.9	26.3 ± 0.3
$\text{HC}\equiv\text{CCH}_2$	261.0 ± 2.7	32.5 ± 1.0
C_6H_5 ^a	211.7 ± 0.0	35.5 ± 0.0
Cl_2CHCH_2 ^a	224.7	33.0
$(\text{CH}_3)_3\text{Si}$	177.0 ± 3.3	9.7 ± 1.2
Cl_3CCH_2 ^b	158.0	23.0
F_3CCH_2 ^b	217.0	50.0

^a For $n = 1-3$; ^b for $n = 1-2$.

negative or unsaturated substituent), which implies that this effect can, to some extent, control also oxygen basicity in $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$. The oxygen basicity data $-\Delta\nu(\text{OH})$ for the $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ compounds, gathered in Table II, are for most of these silanes linearly dependent on n (Table III). This observation has not yet been stated in a more general sense. The substituents' X, Y, and Z electronic effect transmission through the silicon in $\text{XYZSiOC}_2\text{H}_5$ is higher⁸ than that in $\text{XYZCOC}_2\text{H}_5$. Moreover, there takes place no flattening of the slope of the $\Delta\nu(\text{OH})$ vs n plot with $(\text{cyclo-C}_6\text{H}_{11}\text{O})_n\text{Si}(\text{CH}_3)_{4-n}$ compounds wherein the oxygen is significantly shielded by bulky $\text{cyclo-C}_6\text{H}_{11}$ group. Consequently, the oxygen basicity trends with $(\text{RO})_n$. $\text{Si}(\text{CH}_3)_{4-n}$ are not markedly influenced by the steric effect of R groups and are mainly affected by the change in the electronic effect of $(\text{RO})_{n-1}(\text{CH}_3)_{4-n}\text{Si}-$ group when passing within $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ from $n = 1$ to $n = 4$. The linear regression analysis of the relationship $\Delta\nu(\text{OH})$ vs n (Eq. (1)) gives parameters (Table III) to be discussed further.

$$\Delta\nu(\text{OH}) = a - b \cdot n. \quad (1)$$

The value a reflects the ability of group R to supply or withdraw electrons – the higher the a parameter, the higher electron-supplying ability is exerted by group R. A perusal of Table III reveals that the parameters a and b follow in most instances the opposite order. It means that a steeper slope (higher b) for the $\Delta\nu(\text{OH})$ vs n plot is obtained with the more electronwithdrawing (lower a) group R. Such a situation is well understood, since the more electronwithdrawing the R group is, the deeper decrease in the $\Delta\nu(\text{OH})$ it has to bring about when the number of the OR groups at the silicon inclines. Passing thus with $(\text{RO})_n\text{Si}(\text{CH}_3)_{4-n}$ having $\text{R} = (\text{CH}_3)_3$. SiCH_2 in turn to those with $\text{R} = \text{Cl}_3\text{CCH}_2$ (down the column of Table III) the b parameter would increase. The deviations from the aforementioned order of a and b parameters seen with $\text{R} = (\text{CH}_3)_3\text{SiCH}_2$, $(\text{CH}_3)_3\text{Si}$, Cl_2CHCH_2 and Cl_3CCH_2 and in some of these instances even the linearity break of the $\Delta\nu(\text{OH}) - n$ plot for $n = 1-4$ can be explained as follows.

As far as the trimethylsilylmethyl and trimethylsilyl groups go, $[(\text{CH}_3)_3\text{SiCH}_2\text{O}]_n$. $\text{Si}(\text{CH}_3)_{4-n}$ and $[(\text{CH}_3)_3\text{SiO}]_n\text{Si}(\text{CH}_3)_{4-n}$ series are characterized by a linear $\Delta\nu(\text{OH}) - n$ plot. A relatively high b parameter for $[(\text{CH}_3)_3\text{SiCH}_2\text{O}]_n\text{Si}(\text{CH}_3)_{4-n}$ is likely caused by the so-called α -effect possibly decreasing electron-donating ability of $(\text{CH}_3)_3\text{SiCH}_2$ group with higher number of $(\text{CH}_3)_3\text{SiCH}_2\text{O}$ groups at the silicon. The unexpectedly flat relationship with $[(\text{CH}_3)_3\text{SiO}]_n\text{Si}(\text{CH}_3)_{4-n}$ (Fig. 1) has already been discussed¹⁷ in terms of the mutual polarizability effect of $(\text{CH}_3)_3\text{SiO}$ group; such an explanation found support in the recognition⁸ of the mutual polarizability effect of electronegative substituents bonded to silicon. This phenomenon also seems to be the most plausible explanation to use further. We suggest the mutual polarizability effect of OR groups to be responsible for nonlinear $\Delta\nu(\text{OH}) - n$ plot for

$n = 1-4$ with phenoxy(methyl)silanes, 2,2-dichloroethoxy(methyl)silanes, and with 2,2,2-trichloroethoxy(methyl)silanes. As far as the phenoxy derivatives are concerned, a relatively high b constant is obtained for $n = 1-3$ (Table III), but an unusually high oxygen basicity in $(C_6H_5O)_4Si$ (Fig. 1) indicates markedly reduced electron-withdrawing ability of C_6H_5O groups in this compound. Similarly is also manifested the reduced electronwithdrawing ability of Cl_3CCH_2O group in the $(Cl_3CCH_2O)_n \cdot Si(CH_3)_{4-n}$ compounds. In this case b parameter developed for $n = 1-2$ is lower than expected from the known electronaccepting ability of this group (or parameter a), and moreover, the oxygen basicity of $(Cl_3CCH_2O)_nSi(CH_3)_{4-n}$ with $n = 2-4$ is unusually high. A similar situation is also met with the $(Cl_2CHCH_2O)_n \cdot Si(CH_3)_{4-n}$ compounds – both the high b parameter for $n = 1-3$ and the high $\Delta\nu(OH)$ value for tetraalkoxysilane speak in favour of the operation of the mutual polarizability effect.

To summarize, the oxygen basicity in alkoxy silanes $(RO)_nSi(CH_3)_{4-n}$ turns out to be controlled chiefly by the electronic effect of OR groups. An unusually high oxygen basicity in some $(RO)_4Si$ (and even in some $(RO)_3SiCH_3$) and low b parameter of the $\Delta\nu(OH) - n$ plot for $(RO)_nSi(CH_3)_{4-n}$ having strongly electronwithdrawing groups R imply the operation of the mutual polarizability effect of OR groups. Silicon bonds with electronegative substituents X are⁸ very prone to the synergistic action $X \rightleftharpoons Si \leftrightarrow X$. This action is documented in this work to grow more significant with the increasing electronaccepting ability of X.

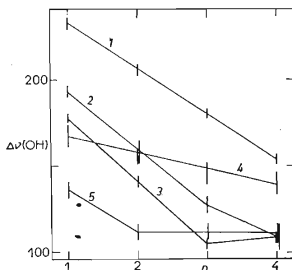


FIG. 1
The $\Delta\nu(OH) - n$ Dependence for $(RO)_n \cdot Si(CH_3)_{4-n}$
R = $ClCH_2CH_2$ (1), Cl_2CHCH_2 (2),
 C_6H_5 (3), $(CH_3)_3Si$ (4), Cl_3CCH_2 (5).

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