

THE ELECTRONIC EFFECT OF HYDROGEN IN ALKOXYSILANES $H_nSi(CH_3)_{3-n}(OCH_3)_m$ *

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The oxygen basicity of $[H(CH_3)_2Si]_2O$, $HSi(OC_2H_5)_n(CH_3)_{3-n}$ and $H_nSi(CH_3)_{3-n}OCH_3$ with $n = 1-3$ measured as $\Delta\nu(OH)$ of phenol due to its interaction with these compounds in CCl_4 is analysed by means of Taft equation. The electronic effect of the hydrogen attached to silicon has been revealed to depend on the nature of the silyl moiety and its variation is discussed in terms of the polarizability of the Si—H bond. The results are consonant with the Si—H bond polarity in Si—H compounds that have one moderately electronwithdrawing substituent and the Si—H bond polarity in di- or triethoxysilanes, the latter implying the reversal of the Si—H bond polarity during the reaction of Si—H compounds with nucleophiles.

There is evidence that the polar character of hydrogen relative to that of alkyl groups varies with the nature of the atom to which the substituents are attached¹. Also the variability of relative polar character of the hydrogen bonded to silicon can be attested from literature data. The direction of dipole moment for the Si—H bond in R_nSiH_{4-n} ($R = \text{alkyl}$ and $n = 1-3$) has been established as $\overset{+}{\text{Si}}-\overset{-}{\text{H}}$ (ref.²). This dipole bond moment orientation is consonant with the direction of the addition of Si—H compounds to multiple bonds and reactivity of Si—H compounds toward organometallic reagents, metals and protondonating nucleophiles^{3,4}. However, as it was shown many times, the nature of the hydrogen-silicon bond (dipole moment data⁵, IR data⁶⁻⁸) or that of the hydrogen itself (NMR data, refs⁹⁻¹¹ and refs therein) is strongly influenced by substituents on silicon. Moreover, it was deduced that hydrogen bonding of the type $SiH\dots L$ takes place between $(CH_3)HSi(OCH_3)_2$ and strong protonaccepting solvents L and the intermediate $(C_2H_5)_3N^+H\dots SiCl_3^-$ was suggested to arise from the interaction of tertiary amines with trichlorosilane^{12,13}. Thus, in some compounds the reversal of the Si—H bond polarity can occur either due to the electronic demand of substituents attached to the silicon, or due to an access of the reactant in reaction course.

We wish now to report what appears to be a new way to the quantitative appraisal of the variability of polar character of the hydrogen attached to silicon. With a view to assess the electronic effect of the hydrogen in $[H(CH_3)_2Si]_2O$, and in $HSi(OC_2H_5)_n(CH_3)_{3-n}$ and $H_n(CH_3)_{3-n}SiOCH_3$ with $n = 1-3$ this note reports analysis of the

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relative oxygen basicity in these compounds (measured as $\Delta\nu(\text{OH})$ of phenol due to interaction with these oxygen-containing silanes) by means of the Taft equation¹⁴.

RESULTS AND DISCUSSION

Information on the electronic effect of substituents bonded to oxygen was reported (refs¹⁵⁻¹⁷ and refs therein) to be easily acquired from the oxygen relative basicity measured from the IR spectra of hydrogen bonds of phenol interacting with oxygen-containing species in CCl_4 . In order to appraise the electronic effect of the hydrogen directly attached to silicon in oxygen-containing silanes we made use of correlation equation (1) for ethoxysilanes $\text{R}_{4-n}\text{Si}(\text{OC}_2\text{H}_5)_n$ interrelating the shift of $\nu(\text{OH})$ of phenol, $\Delta\nu(\text{OH})$, and parameter $\sum\sigma_{\text{R}_1\text{R}_2\text{R}_3}^*$ (Table I). The oxygen relative basicity for Si—H compounds and the assessed values of Taft σ^* parameter for the hydrogen

$$\Delta\nu(\text{OH}) = \Delta\nu(\text{OH})^\circ + \rho^* \cdot \sum\sigma_{\text{R}_1\text{R}_2\text{R}_3}^* \quad (1)$$

are given in Table II. Our results indicate that the lowest electronwithdrawing action is exerted by the hydrogen in siloxanes, and in passing from monoethoxy- (or diethoxy-) to triethoxysilane the electronwithdrawing ability of H increases. This may perhaps be explained in terms of the polarizability of the Si—H bond. It follows from our previous work¹⁶ that electronwithdrawing ability of $\text{C}_2\text{H}_5\text{O}$ group in $(\text{CH}_3)_{4-n} \cdot \text{Si}(\text{OC}_2\text{H}_5)_n$ is almost the same ($\sigma_{\text{C}_2\text{H}_5\text{O}}^* \sim 0.3$) for all n and is strongly reduced

TABLE I

Parameters of Correlation According to Eq. (1)

Set	$-\rho^*$	h^a	r^b	$\Delta\nu(\text{OH})^\circ$	l^c	n^d
$(\text{R}_1\text{R}_2\text{R}_3\text{Si})_2\text{O}^e$	18.8	1.6	0.942	159.3	0.7	15
$\text{R}_1\text{R}_2\text{R}_3\text{SiOC}_2\text{H}_5^f$	62.0	3.0	0.988	273.1	1.2	13
$\text{R}_1\text{R}_2\text{Si}(\text{OC}_2\text{H}_5)_2^g$	63.0	4.1	0.992	257.9	1.8	6
$\text{R}_1\text{Si}(\text{OC}_2\text{H}_5)_3^g$	48.2	4.5	0.988	238.6	1.6	6

^a Standard error of ρ^* . ^b Correlation coefficient. ^c Standard error of $\Delta\nu(\text{OH})^\circ$. ^d Number of points in set. ^e Compounds considered in correlation: $[\text{CH}_3(\text{n-C}_4\text{H}_9)_2\text{Si}]_2\text{O}$, $[\text{CH}_3(\text{n-C}_3\text{H}_7)_2 \cdot \text{Si}]_2\text{O}$, $(\text{CH}_3)_3\text{SiOSiCH}_3(\text{i-C}_3\text{H}_7)_2$, $[\text{i-C}_3\text{H}_7(\text{CH}_3)_2\text{Si}]_2\text{O}$, $\text{n-C}_4\text{H}_9(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3$, $[\text{n-C}_4\text{H}_9(\text{CH}_3)_2\text{Si}]_2\text{O}$, $[\text{n-C}_3\text{H}_7(\text{CH}_3)_2\text{Si}]_2\text{O}$, $\text{n-C}_3\text{H}_7(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3$, $\text{i-C}_3\text{H}_7(\text{CH}_3)_2 \cdot \text{SiOSi}(\text{CH}_3)_3$, $\text{n-C}_4\text{H}_9(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3$, $\text{n-C}_3\text{H}_7(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3$ (all ref.¹⁸), $\text{F}_3\text{CCH}_2 \cdot \text{CH}_2(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3$, $\text{CH}_3(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiOSi}(\text{CH}_3)_3$, $[\text{F}_3\text{CCH}_2\text{CH}_2(\text{CH}_3)_2\text{Si}]_2\text{O}$ (all ref.¹⁹); ^f Ref.²⁰. ^g Ref.¹⁶.

when compared to other compounds ($\sigma_{\text{C}_2\text{H}_5\text{O}}^* \sim 1.5$, ref.²⁴). The electronwithdrawing ability of $\text{H}(\text{CH}_3)_2\text{SiO}$ group attached to silicon can be suggested to be reduced as well. However, there are reasons to assume that its electronwithdrawing effect is higher than that of $\text{C}_2\text{H}_5\text{O}$ group (ref.²⁵). This implicates that lower σ_{H}^* for $\text{H}(\text{CH}_3)_2 \cdot \text{SiOSi}(\text{CH}_3)_2\text{H}$ compared to σ_{H}^* for $\text{H}(\text{CH}_3)_2\text{SiOC}_2\text{H}_5$ indicates the hydrogen in the former compound to be more engaged in the compensation of electronic deficit on the silicon to which it is attached. Offering this explanation we can simultaneously suggest the $\overset{\delta+}{\text{Si}}-\overset{\delta-}{\text{H}}$ polarity in $\text{HSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{H}$ and $\text{HSi}(\text{CH}_3)_2\text{OC}_2\text{H}_5$ compounds since wavenumbers of $\nu(\text{Si}-\text{H})$ [$\text{HSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{H}$ 2127 cm^{-1} , (ref.²⁶), $\text{HSi}(\text{CH}_3)_2\text{OC}_2\text{H}_5$ 2114 cm^{-1}] are in accordance with the greater force constant in $\text{HSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{H}$. The (Si)H proton resonance of the siloxane ($\delta(\text{H}) = 4.73$, ref.²²) being at a lower field than the (Si)H resonance of $\text{HSi}(\text{CH}_3)_2 \cdot \text{OCH}_3$ ($\delta(\text{H}) = 4.60$, ref.²²) implies that the shielding of the (Si)H proton is smaller in the siloxane than in the CH_3O derivative.

In an effort to reconcile the order of σ_{H}^* parameters for $\text{HSi}(\text{OC}_2\text{H}_5)_n(\text{CH}_3)_{3-n}$ (Table II) with the IR data on $\text{HSi}(\text{OR})_n(\text{CH}_3)_{3-n}$ (refs.^{7,27}) (the wavenumber of $\nu(\text{SiH})$ increases and the intensity of the $\nu(\text{SiH})$ band diminishes with increasing n) we have to admit either homopolar binding in the Si—H bond or the $\overset{\delta-}{\text{Si}}-\overset{\delta+}{\text{H}}$ bond polarity in $\text{HSi}(\text{OC}_2\text{H}_5)_n(\text{CH}_3)_{3-n}$ with $n \geq 1$ or at least $n \geq 2$, and moreover to suggest the operation of mutual polarizability effect of the ethoxy groups. This effect¹⁶ is responsible for the reduction of electronwithdrawing ability of $\text{C}_2\text{H}_5\text{O}$ group when attached to silicon and appears to develop an increase in electron density on silicon. In a view of this consideration the increasing number of ethoxy groups (n) resulting in an increase of electron density on the silicon can then facilitate electron transfer from the silicon to the hydrogen and make the hydrogen more electron-

TABLE II

Wavenumber Shift, $\Delta\nu(\text{OH})$ in cm^{-1} , of Phenol Due to Interaction with Oxygen-Containing Silanes and Values of σ_{H}^* for Hydrogen in These Compounds

Silane	$\Delta\nu(\text{OH})$	σ_{H}^*	Silane	$\Delta\nu(\text{OH})$	σ_{H}^*
$[\text{HSi}(\text{CH}_3)_2]_2\text{O}$	156 ^a	0.09 ± 0.05	$\text{H}(\text{CH}_3)_2\text{SiOCH}_3$	251 ^b	0.29 ± 0.09
$\text{HSi}(\text{CH}_3)_2\text{OC}_2\text{H}_5$	253	0.32 ± 0.04	$\text{H}_2(\text{CH}_3)\text{SiOCH}_3$	221 ^c	0.40 ± 0.09
$\text{HSi}(\text{OC}_2\text{H}_5)\text{CH}_3$	233	0.40 ± 0.05	H_3SiOCH_3	185 ^c	0.46 ± 0.08
$\text{HSi}(\text{OC}_2\text{H}_5)_3$	206	0.68 ± 0.10			

^a Ref.²¹. ^b Ref.²². ^c Ref.²³.

withdrawing. This conclusion, being consistent with the above changes in the position and intensity of the $\nu(\text{Si—H})$ bond, is also supported by the fact that the shielding of the $\text{H}(\text{Si})$ proton increases with increasing number of alkoxy groups on silicon [$\text{HSi}(\text{OCH}_3)(\text{CH}_3)_2$, $\delta(\text{H})$ 4.60 ppm in cyclohexane ref.²²], $\text{HSi}(\text{OC}_2\text{H}_5)_2\text{CH}_3$ $\delta(\text{H})$ 4.50 ppm and $\text{HSi}(\text{OC}_2\text{H}_5)_3$ $\delta(\text{H})$ 4.15 ppm (both in CCl_4 ref.²⁸).

Proceeding now to the values σ_{H}^* for $\text{H}_n\text{Si}(\text{CH}_3)_{3-n}\text{OCH}_3$ with $n = 1-3$ (Table II) we will comment upon their deriving. The methyl and the ethyl groups bonded to the oxygen in ethers exert about the same polarizability effect – comparable ρ^* 's in the $\Delta\nu(\text{OH})$ vs σ_{X}^* plot for X—O—CH_3 and $\text{X—O—C}_2\text{H}_5$ have been established¹⁵. The $\Delta\nu(\text{OH})$ data for the ethers X—O—CH_3 and $\text{X—O—C}_2\text{H}_5$ are well fitted¹⁵ with correlation equation (2) and (3) respectively.

$$\Delta\nu(\text{OH}) = (256.7 \pm 3.5) - (110.0 \pm 7.9) \cdot \sigma_{\text{X}}^* \quad (2)$$

$$\Delta\nu(\text{OH}) = (265.0 \pm 3.0) - (102.5 \pm 6.7) \cdot \sigma_{\text{X}}^* \quad (3)$$

Therefore, the $\Delta\nu(\text{OH})$ vs σ_{X}^* plot for $\text{R}_1\text{R}_2\text{R}_3\text{SiOCH}_3$ can be constructed from the plot for $\text{R}_1\text{R}_2\text{R}_3\text{SiOC}_2\text{H}_5$ (Table I) by subtracting increment 8 from the $\Delta\nu(\text{OH})^\circ$ value. The $\Delta\nu(\text{OH})$ vs $\sum\sigma_{\text{R}_1\text{R}_2\text{R}_3}^*$ plot for $\text{R}_1\text{R}_2\text{R}_3\text{SiOCH}_3$ is then obtained as equation (4). σ_{H}^* for $\text{H}_n\text{Si}(\text{CH}_3)_{3-n}\text{OCH}_3$ derived from this equation are presented in Table II. The procedure is seen to be justified by the match of σ_{H}^* 's for $\text{HSi}(\text{CH}_3)_2\text{OCH}_3$ and $\text{HSi}(\text{CH}_3)_2\text{OC}_2\text{H}_5$ (Table II). The σ_{H}^* for $\text{H}_n\text{Si}(\text{CH}_3)_{3-n}\text{OCH}_3$ are comparable,

$$\Delta\nu(\text{OH}) = (268 \pm 3.5) - (61.3 \pm 7.9) \cdot \sum\sigma_{\text{R}_1\text{R}_2\text{R}_3}^* \quad (4)$$

however one might admit their increasing value with increasing n .

To interpret the increase in σ_{H}^* for $\text{H}_n\text{Si}(\text{CH}_3)_{3-n}\text{OCH}_3$ when passing from $n = 1$ to $n = 3$ the suggestion of the operation of mutual polarizability effect assumed in $\text{HSi}(\text{OC}_2\text{H}_5)_n(\text{CH}_3)_{3-n}$ appears to be fruitful also with $\text{H}_n\text{Si}(\text{CH}_3)_{3-n}\text{OCH}_3$. Thus the increasing electronwithdrawing ability of H in $\text{H}_n\text{Si}(\text{CH}_3)_{3-n}\text{OCH}_3$ could be best explained of all by mutual polarizability effect of OCH_3 and H substituents provided that the polarity Si—H is assumed. The ordering of the σ_{H}^* is in agreement with the NMR spectral data on these compounds (ref.²²) which show the $\text{H}(\text{Si})$ hydrogen to become more shielded with increasing n .

We can therefore conclude that the results presented here are in accordance with Si—H bond polarity in monoalkoxysilanes and speak in favor of Si—H bond polarity in di- or triethoxysilanes. The Si—H bond polarity in di- and triethoxysilanes emphasizes the importance of the additional Si—H bond polarizability during the reaction of the Si—H compounds having only one moderately electronwithdrawing

group with nucleophiles. In introduction presented chemical evidence for Si—H bond polarity for these compounds together with the present results suggest that the Si—H bond polarity is perhaps created as a consequence of the access of a nucleophile to the silicon of the Si—H bond.

EXPERIMENTAL

Ethoxysilanes $\text{HSi}(\text{OC}_2\text{H}_5)_n(\text{CH}_3)_{3-n}$ with $n = 1-3$ were prepared²⁹ by reaction of $\text{HSiCl}_n \cdot (\text{CH}_3)_{3-n}$ with ethanol in the presence of stoichiometric amount of pyridine in ether. Their purity was checked by gas-liquid chromatography and their identity was confirmed by NMR spectroscopy. Relative basicity of the oxygen was determined from the IR spectra of hydrogen bonds of phenol interacting with ethoxysilanes in CCl_4 as described³⁰.

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