

THE EXTENT OF SOME INTRAMOLECULAR EFFECTS IN TRIETHOXY- AND TRIMETHOXYSILANES*

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Relative basicity of the oxygen in some trialkoxysilanes $\text{XSi}(\text{OR})_3$ having X electron-donating and electron-withdrawing substituents and R methyl and ethyl group was measured from the IR spectra of hydrogen bonds of phenol interacting with the trialkoxysilanes in CCl_4 . The measurements indicate the reduced electron-withdrawing ability of $\text{Cl}_n\text{H}_{3-n}\text{C}$ -groups with $n > 1$ in both series of alkoxy-silanes. The extent of the reduction of $-I$ effect of some X substituents involved in the so-called α -effect and mutual polarizability effect is shown to depend on the nature of R group.

Previous results on the oxygen basicity of ethers¹, alkoxy-silanes²⁻⁴ and siloxanes⁵ suggest that the polarizability effect of substituents plays an important role in these compounds. The polarizability effect was argued^{4,5} to be much responsible for the transmission of the electronic effect of a substituent X through the silicon atom in $\text{XSiY}_n(\text{OZ})_{3-n}$ where Y is alkyl or halogen and Z is alkyl, substituted alkyl or trimethylsilyl group. Moreover, its operation in these compounds has been established^{2,3,5} to reduce electron-withdrawing action of electronegative or unsaturated groups directly bonded to the silicon. The electronic effect of a substituent is now supposed⁶ to be a blend of polar and polarizability effect and our results, placing some limit on the importance of polar effect in affecting the electron distribution in the above compounds, suggested^{1,3} the resultant electron density on the ethereal-like oxygen to be controlled by a mutual operation of the polar effect of one and the polarizability effect of the second substituent, both effects being directed against each other.

The present note is a continuation of our previous studies¹⁻⁵ as well as of our examination^{7,8} on intramolecular interaction called the α -effect (refs⁷⁻⁹). This interaction taking place between silicon and halogen in halogenomethylsilanes results in the decrease in the electron-accepting action of halogen⁸. In this work the attempt is made to determine whether the intramolecular interaction in $\text{XCH}_2\text{Si}(\text{OR})_3$ (X=Cl, Br and I) and $\text{Cl}_n\text{H}_{3-n}\text{CSi}(\text{OR})_3$ as well as the electron-accepting ability of electronegative or unsaturated substituents X (C_6H_5 , Cl, CH_3O) in $\text{XSi}(\text{OR})_3$ is dependent on the nature of R (R= CH_3 , C_2H_5). Additionally, we hope to contribute to the knowledge of electron-acceptive action of $\text{Cl}_n\text{H}_{3-n}\text{C}$ groups with $n > 1$

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attached to silicon. With this view a reexamination of the transmission of the electro-
nic effect of X in the $\text{XSi}(\text{OR})_3$ compounds is also presented, based on the oxygen
basicity measured from the IR spectra of hydrogen bonds of phenol interacting with
 $\text{XSi}(\text{OR})_3$.

EXPERIMENTAL

All the compounds studied, $\text{XSi}(\text{OCH}_3)_3$ with $\text{X} = \text{cyclo-C}_6\text{H}_{11}$, $\text{CH}_2=\text{CHCH}_2$, CH_3 ,
 $\text{Cl}(\text{CH}_2)_3$, $\text{Cl}(\text{CH}_2)_2$, Cl_2CHCH_2 , ClCH_2 , Cl_2CH , Cl , C_6H_5 , CH_3O and $\text{XSi}(\text{OC}_2\text{H}_5)_3$ with
 $\text{X} = \text{Cl}_2\text{CH}$ and Cl_3C were prepared by treating either corresponding trichlorosilanes with equi-
molar amounts of dry pyridine and methanol in dry diethyl ether (method *A*), or trichlorosilanes
with methanol or ethanol in dry pentane (method *B*). These procedures are customary and
deserve no particular comment. All the operations were carried out under nitrogen and the
trialkoxysilanes were obtained by rectification or by preparative gas-liquid chromatography.
The products purity was checked by chromatographically. Physical constants of the compounds
described previously were in agreement with reported data^{10,11}. Physical constants and yields
of the unreported or insufficiently characterized trialkoxysilanes are given in Table I.

Proton acceptor ability (basicity) of the oxygen in trimethoxy- and triethoxysilanes was
determined from the IR spectra of hydrogen bonds of phenol due to interaction with these
compounds in CCl_4 by usual way¹².

RESULTS AND DISCUSSION

An easy attack on the problem of determining the way of the control of the oxygen
basicity in trimethoxysilanes $\text{XSi}(\text{OCH}_3)_3$ by the substituent effect of X can be made
by means of Taft equation (Eq. (I)). Results of the correlation with Eq. (I) for the
set $\text{XSi}(\text{OCH}_3)_3[\text{X}, \sigma_{\text{X}}^*, \Delta\nu(\text{OH})$ in cm^{-1} : cyclo- C_6H_{11} , -0.18 , 230; CH_3 , 0, 226;

TABLE I
Yields and Physical Constants of $\text{XSi}(\text{OR})_3$

Compound	B.p. °C/Torr	n_D^{20}	Yield, %	Method
cyclo- $\text{C}_6\text{H}_{11}\text{Si}(\text{OCH}_3)_3$	208	1.4367	73	<i>A</i>
$\text{CH}_2=\text{CHCH}_2\text{Si}(\text{OCH}_3)_3$	136	1.4084	57	<i>A</i>
$\text{Cl}_2\text{CHCH}_2\text{Si}(\text{OCH}_3)_3$	100/30	1.4376	26	<i>A</i>
$\text{Cl}_2\text{CHSi}(\text{OC}_2\text{H}_5)_3$	102/22	1.4252	35	<i>B</i>

$\text{Cl}(\text{CH}_2)_3$, 0.14, 220; $\text{CH}_2=\text{CHCH}_2$, 0.21, 218; $\text{Cl}(\text{CH}_2)_2$, 0.39, 204; Cl_2CHCH_2 , 0.69, 197] are given

$$\Delta\nu(\text{OH}) = \Delta\nu(\text{OH})^\circ + \rho^* \cdot \sigma_{(\text{X})}^* \quad (1)$$

as parameters $\Delta\nu(\text{OH})^\circ = 224.4 \pm 0.5$ and $-\rho^* = 41.2 \pm 3.1$. Earlier reported² parameters of a similar correlation for triethoxysilanes $\text{XSi}(\text{OC}_2\text{H}_5)_3$ are following: $\Delta\nu(\text{OH})^\circ = 238.6 \pm 1.6$ and $-\rho^* = 48.2 \pm 4.5$; the ρ^* 's are thus very similar, even though the $-\rho^*$ for $\text{XSi}(\text{OCH}_3)_3$ might be slightly lower. The transmission of the electronic effect of X *via* the silicon to the oxygen appears therefore comparable in both series of trialkoxysilanes. This observation, along with our earlier advanced interpretation of the ρ^* values in similar sets further suggest similar polarizability action of OCH_3 and OC_2H_5 groups in the trialkoxysilanes. Here, a remark concerning the choice of $\text{XSi}(\text{OCH}_3)_3$ and $\text{XSi}(\text{OC}_2\text{H}_5)_3$ (ref.²) set members is to be made. No compounds having X capable of the α -effect or the back-bonding have been used. The ρ^* 's so obtained should therefore correctly reflect the relative electronic effect transmission and hence the relative polarizability effect of both alkoxy groups.* The electronic effect of substituents X capable of back-bonding and of the α -effect is now easily estimated from the deviations of the $\Delta\nu(\text{OH})$ values of the compounds incorporating these X's from the correlation lines. A perusal of Table II reveals that following inferences can be drawn.

1) As for the α -effect, ClCH_2 , BrCH_2 and ICH_2 groups show reduced electronwithdrawing ability when attached to the $\text{Si}(\text{OC}_2\text{H}_5)_3$ moiety^{9,14}. The reduction of $-\text{I}$ effect in trimethoxysilanes is less noticeable for ClCH_2 and BrCH_2 , but about the same for ICH_2 group.

2) As for the electronic effect of Cl_3C and Cl_2CH groups attached to silicon, it has only been, as far as we are aware, examined by ^{35}Cl -NQR spectroscopy, which indicated the involvement of these groups in the α -effect¹⁶. The oxygen basicity data show these groups to possess reduced $-\text{I}$ effect when attached to $\text{Si}(\text{OCH}_3)_3$ and $\text{Si}(\text{OC}_2\text{H}_5)_3$ moieties in about the same extent.

3) As to the substituents capable of back-bonding, phenyl, chlorine and methoxy substituents exert reduced $-\text{I}$ effect in triethoxysilanes due to the mutual polarizability effect². Passing from triethoxysilanes to trimethoxysilanes chlorine seems to modify (to increase) its electronwithdrawing ability, but phenyl and methoxy groups do not.

No simple reason can likely be offered as responsible for these observations. The polarizability effects of methyl, ethyl and trimethylsilyls groups attached to the OR

* Recently reported¹³ difference in ρ^* for both sets is obviously brought about by improper choice of set members and by the fact that $\Delta\nu(\text{OH})$ reported for sulphur-containing trialkoxysilanes reflects also the $\text{C}_6\text{H}_5\text{O}\dots\text{H}\dots\text{S}$ interaction.

TABLE II

Wavenumber Shift, $\Delta\nu(\text{OH})$ in cm^{-1} , of Phenol Due to Interaction with $\text{XSi}(\text{OR})_3$ in CCl_4 and σ^* of Substituent X in $\text{XSi}(\text{OR})_3$

X	R = CH_3		R = C_2H_5^a		$\sigma^{*,c}$
	$\Delta\nu(\text{OH})$	$\sigma^{*,b}$	$\Delta\nu(\text{OH})$	$\sigma^{*,b}$	
Cl	156	1.67 ± 0.13	179	1.24 ± 0.14	2.9
C_6H_5	210	0.35 ± 0.04	221 ^d	0.37 ± 0.07	0.6
RO	206	0.45 ± 0.05	219 ^e	0.41 ± 0.07	1.5
ClCH_2	192	0.79 ± 0.07	210	0.59 ± 0.09	1.05
BrCH_2	191	0.81 ± 0.07	210	0.59 ± 0.09	1.0
ICH_2	202 ^e	0.55 ± 0.05	213	0.53 ± 0.09	0.85
Cl_2CH	172 ^e	1.28 ± 0.09	181	1.21 ± 0.14	1.94
Cl_3C	144 ^e	1.96 ± 0.16	152	1.82 ± 0.20	2.65

^a With the exclusion of the last two data refs^{2,14}. ^b Derived from the $\Delta\nu(\text{OH})$ of $\text{XSi}(\text{OR})_3$ and the $\Delta\nu(\text{OH})$ vs $\sigma^*_{(\text{X})}$ plot for $\text{XSi}(\text{OR})_3$ having X incapable of back-bonding and α -effect. ^c Assumed in organic compounds¹⁵. ^d See also ref.¹⁹. ^e See also ref.¹³.

moiety can be regarded^{1,17} as very similar. However, the $\Delta\nu(\text{OH})$ vs $\sigma^*_{(\text{X})}$ plot for $\text{XSi}[\text{OSi}(\text{CH}_3)_3]_3$ (the q^* is close to zero, ref.⁵) doesn't resemble that for $\text{XSi}(\text{OCH}_3)_3$ or $\text{XSi}(\text{OC}_2\text{H}_5)_3$ (the q^* 's see above). Our study¹⁸ on the polarizability effect of OR groups attached to silicon clearly demonstrates the following order of the group polarizability: $(\text{CH}_3)_3\text{SiO} > \text{CH}_3\text{O} \sim \text{C}_2\text{H}_5\text{O}$. However, the polarizability effect of $(\text{CH}_3)_3\text{Si}$, CH_3 and C_2H_5 groups attached to oxygen is $(\text{CH}_3)_3\text{Si} \cong \text{CH}_3 \cong \text{C}_2\text{H}_5$ (refs^{1,18}). It appears that final elucidation of relations between polarizability effect of group R bonded to oxygen and that of OR group attached to silicon as well as of the nature of intramolecular effects in alkoxysilanes still awaits further data.

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