

VARIABLE POLAR EFFECT OF $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ GROUPS ATTACHED TO OXYGEN*

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Relative basicity of the oxygen in the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ with various electron donating and electron accepting groups R and $n = 1-3$ was measured by the IR spectroscopy and is discussed together with that for the above compounds with $n = 0$. $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups have been revealed to display strongly dichotomous behaviour as a consequence of their enormous polarizability.

Several organosilyl groups have been reported to change their polar effect on the substitution in the rest of the molecule, or to participate in anchimeric assistance. This concerns of the trimethylsilyl^{1,2} and poly(alkylsilyl)³ groups when attached to an aromatic system and trimethylsilylmethyl group in oxygen-containing α -carbofunctional compounds⁴. The electron accepting character of the trimethylsilyl group in the $(\text{CH}_3)_3\text{SiOR}$ compounds was also recently found to depend on the nature of the group R (ref.^{5,6}), and the anchimeric assistance of some silyl groups may be inferred from the observed dependence of the relative basicity of some silyl ethers on the strength of the interacting acid⁷.

The methylchlorosilyl groups were, up to now, considered to possess a significant electron withdrawing effect when attached, *e.g.* to an aromatic system⁸ or to an oxygen (see *e.g.* ref.⁹). The examination of the relative basicity of the oxygen in the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ with $n = 1-3$ and R = $(\text{CH}_3)_3\text{SiCH}_2$, $(\text{CH}_3)_2\text{CH}$, C_2H_5 , $(\text{CH}_2)_3\text{Cl}$, $(\text{CH}_2)_2\text{Cl}$, CH_2CHCl_2 , and CH_2CCl_3 presented in this work is being directed toward gaining an understanding of the electronic effect of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups.

EXPERIMENTAL

The preparation of the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ where $n = 0-3$ and R = $(\text{CH}_3)_3\text{SiCH}_2$, $(\text{CH}_3)_2\text{CH}$, C_2H_5 , $(\text{CH}_2)_2\text{Cl}$, $(\text{CH}_2)_3\text{Cl}$, CH_2CHCl_2 , and CH_2CCl_3 has been described elsewhere^{5,10}. The relative basicity of the oxygen atom was determined from hydrogen bond IR spectra of the $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ compounds interacting with phenol in CCl_4 as described before⁵.

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RESULTS AND DISCUSSION

The relative basicity of the oxygen atom in the compounds $(\text{CH}_3)_3\text{SiOR}$ defined as $\Delta\nu(\text{OH})$ of phenol due to its interaction with the oxygen of $\text{Si}-\text{O}-\text{C}$ grouping is not linearly dependent on the Taft σ^* constant of group R (ref.⁵). The deviation of the experimental data (Fig. 1, curve 1) from the line depicting the trend of the relative basicity calculated for $(\text{CH}_3)_3\text{Si}$ group having constant polar effect ($\sigma^* = -0.72$) increases with increasing electron donating ability of group R. The match of the experimental and calculated relative basicity of the above compounds for the groups R with $\sigma^* = 0.5-1$ proved the lack of back bonding in $\text{Si}-\text{O}$ bond of these compounds and progressively increasing deviation between experimental and calculated basicity, when going from $\sigma^* = 0.5$ to lower values, was interpreted^{5,6} by the variation of polar effect of $(\text{CH}_3)_3\text{Si}$ group, this being stronger electron acceptor with more electron donating groups R.

The examination of the oxygen relative basicity of the chloro(methyl)alkoxysilanes $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ (Table I) reveals its linear dependence on σ^* constant of group R (Fig. 1). The response of the oxygen relative basicity to the change of group R differs with n — the Taft ρ^* constant in the equation $\Delta\nu(\text{OH}) = \rho^* \cdot \sigma^* + C$ is -178.4 , -88.2 , and -39.5 when going from $n = 0$ to $n = 2$. We suppose dichotomous behaviour of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups to be responsible for very significant variance of the ρ^* constant with n . We presume the above groups to behave as progressively

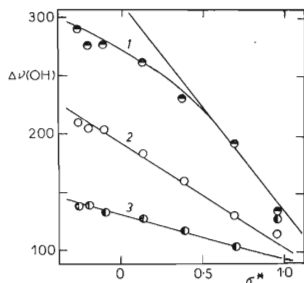


FIG. 1

The Dependence of the Quantity $\Delta\nu(\text{OH})$ on σ^* Constant of the Group R in the Systems $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ — Phenol — CCl_4 $n = 0$ (1, ref.⁵), $n = 1$ (2), $n = 2$ (3).

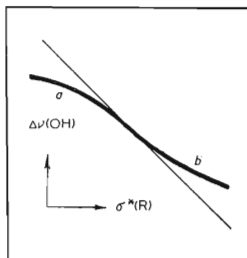


FIG. 2

The Dichotomous Effect of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ Groups Manifestation in the Relative Basicity of the Oxygen of the $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ Compounds

becoming greater electron acceptors when group R of the compounds $\text{Cl}_n(\text{CH}_3)_3\text{SiOR}$. SiOR becomes greater electron donor, and *vice versa*, to increase their electron donating effect when group R progressively changes for greater electron acceptor. The former ability of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups would result in similar deviation of the experimental basicities from calculated line (the constant polar effect of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups) as observed for the $(\text{CH}_3)_3\text{SiOR}$ compounds⁵ (Fig. 1). It can be depicted as in structure *I* and its consequence illustrated by the curve *a* in Fig. 2. The latter ability of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups, imagined as in structure *II*, would lead to the opposite deviation of the experimental relative basicity from the calculated line considering constant polar effect of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups and ought to yield the curve *b* in Fig. 2. Both the interactions illustrated in structures *I* and *II* can reasonably explain the decrease in the sensitivity of the oxygen relative basicity to the polar effect of group R in the $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ compounds when being brought together as the levelling effect of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups, that becomes more significant with increasing number of the chlorine atoms.



Fig. 3 gives a decrease of the relative oxygen basicity in the $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ compounds with $\text{R} = \text{C}_2\text{H}_5$ and CH_2CCl_3 with an increasing number of the chlorine atoms in the silyl group. From the data shown in Table I it appears that the slope

TABLE I

Relative Basicity, $\Delta\nu(\text{OH})$ in cm^{-1} , of the $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ Compounds in CCl_4

R	n			
	0 ^a	1	2	3
$(\text{CH}_3)_3\text{SiCH}_2$	293	212 ^b	141 ^b	121 ^b
$(\text{CH}_3)_2\text{CH}$	277	208	142	86
C_2H_5	280	207 ^b	136 ^b	84 ^b
$(\text{CH}_2)_3\text{Cl}$	264	186	130	^c
$(\text{CH}_2)_2\text{Cl}$	233	161	120	^c
CH_2CHCl_2	193	130	103	^c
CH_2CCl_3	135	115	120	130

^a Ref. 5; ^b ref. 14; ^c very flat absorption band $\nu(\text{OH})^{\text{assoc}}$ of low intensity.

of the linear dependence $\Delta\nu(\text{OH})$ vs n for the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOC}_2\text{H}_5$ is practically the same as for all the other compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ except those with $\text{R} = \text{CH}_2\text{CCl}_3$. The only point that deviates from the correlation line is that for compound $\text{Cl}_3\text{SiOCH}_2\text{Si}(\text{CH}_3)_3$. With regard to the correlation line higher value of $\Delta\nu(\text{OH})$ can be ascribed to a more extensive Si—C hyperconjugation¹¹⁻¹³ in this compound compared to that in the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOCH}_2\text{Si}(\text{CH}_3)_3$ with $n = 0-2$.

The linear character of the dependence $\Delta\nu(\text{OH})$ vs n is not observed for the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOCH}_2\text{CCl}_3$ (Fig. 3). Going from the point for $n = 0$ to the point for $n = 1$, the $\Delta\nu(\text{OH})$ value decreases much less than in the case of all the other $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ compounds, and going on further to higher n $\Delta\nu(\text{OH})$ value even increases. This type of the dependence serves as an additional support for the dichotomous behaviour of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups inferred from the above reported variance of ρ^* constant with n . The oxygen relative basicities are very alike for all the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOCH}_2\text{CCl}_3$ and they demonstrate almost the same polar effect of all the $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups ($n = 0-3$) in the compounds $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$, when R is very strong electron accepting substituent, and an enormous polarizability of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups.

More scrutinizing insight into never before reported variation of polar effect of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups attached to the oxygen, a study of the possibility of the polar effect variation of other silyl groups, and finally the development of a method for the group polarizability estimation are in progress.

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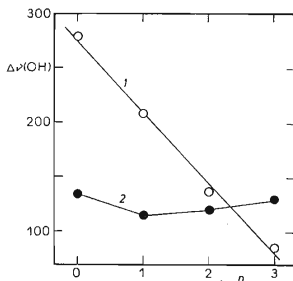


FIG. 3

The Dependence of the Quantity $\Delta\nu(\text{OH})$ in the Systems $\text{Cl}_n(\text{CH}_3)_{3-n}\text{SiOR}$ -Phenol- CCl_4 on the Number of Chlorine Atoms (n)
 $\text{R} = \text{C}_2\text{H}_5$ (1), $\text{R} = \text{CH}_2\text{CCl}_3$ (2)

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