

## RELATIVE BASICITY OF ORGANOTRIALKOXY-SILANES AND ELECTRONIC EFFECTS OF SUBSTITUENTS\*

N.I.ŠERGINA<sup>a</sup>, M.G.VORONKOV<sup>a</sup>, M.JAKOUBKOVÁ<sup>b</sup> and V.CHVALOVSKÝ<sup>b</sup>

<sup>a</sup> Institute of Organic Chemistry, Academy of Sciences U.S.S.R, 664033 Irkutsk,

<sup>b</sup> Institute of Chemical Process Fundamentals,

Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát

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Relative basicity of organotrialkoxysilanes  $R^1Si(OR^2)_3$ , where  $R^1$  is an organic substituent and  $R^2$  is a methyl or ethyl group, was determined by IR spectroscopy. It was found that the relative basicity,  $\Delta\nu(OH)$ , is linearly dependent on Taft  $\sigma^*$  inductive constant of substituent  $R^1$ .

The relative basicity,  $\Delta\nu(OH)$ , is a parameter which is sensitive to electronic effects of substituents. In studies of alkoxy-silanes<sup>1,2</sup>, alkoxygermanes<sup>2</sup>, ethynylalkoxy-silanes<sup>3</sup>, and phenoxy-silanes<sup>4</sup> of the type  $R^1_{4-n}Si(OR^2)_n$  it was shown that the basicity of oxygen decreases nonlinearly with increasing number of alkoxy groups  $OR^2$  ( $n = 1-4$ ). With disubstituted aryloxy-silanes<sup>4</sup>,  $\Delta\nu(OH)$  is linearly dependent on  $\sigma$  substituent constants characterizing electronic effects of substituents attached to aromatic ring.

As known<sup>5-8</sup>, the basicity of oxygen in organic compounds of Group IVb elements (M) containing M—O linkage depends strongly on electronic effects of substituents on atom M (M = Si, Sn, and Ge). The extent of back donation in Si ← O bond is also affected by the nature of substituents on silicon<sup>9</sup>.

In the present communication the effect of substituents on silicon on the basicity of oxygen in organotrialkoxy-silanes was studied. For this purpose the formation of hydrogen bond between organotrialkoxy-silanes as proton acceptors and standard proton donors, phenol and pyrrole, was investigated. The shifts  $\Delta\nu(OH)$  of phenol and  $\Delta\nu(N-H)$  of pyrrole were taken as a measure of basicity. Energy of hydrogen bond was calculated on the basis of temperature dependence of equilibrium constants<sup>10</sup>.

### EXPERIMENTAL

Preparation and physico-chemical constants of starting compounds were reported earlier: n-propyltriethoxy-silane<sup>2</sup>, benzyltriethoxy-silane<sup>11</sup>, vinyl- and phenyltriethoxy-silane<sup>12</sup>, (chloromethyl)triethoxy-silane<sup>13</sup>, (2-thio-1-butyl)trimethoxy-silane and (3-phenyl-2-thio-1-propyl)trimethoxy-silane<sup>14</sup>, iodomethyl-, bromomethyl-, and (trichloromethyl)trimethoxy-silane<sup>15</sup>.

IR spectra were recorded with a Zeiss, Model UR-20, spectrophotometer (Jena, GDR) in the 3700–3200  $cm^{-1}$  region (LiF prism). For each compound  $\Delta\nu$  value was taken as an average

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of three measurements. Wavenumbers were read with an accuracy of  $\pm 2 \text{ cm}^{-1}$ . Concentrations of proton acceptors are given in the table; phenol and pyrrole concentrations were 0.02 M and 0.015 M, respectively (for  $\Delta\nu$ 's determinations). Spectrograde  $\text{CCl}_4$  was used as a solvent. Infrasil cell was 1 cm thick. Temperature measurements in the 6–48°C region were made with special temperature controlled blocks.

## RESULTS AND DISCUSSION

The values of  $\Delta\nu$  of stretching OH and NH frequencies of phenol and pyrrole, respectively, as well as Taft  $\sigma^*$  inductive constants of substituents, which were used as a quantitative measure of inductive effect, for all the organotrialkoxysilanes investigated are summarized in Table I. As follows from the table, with both proton donors, phenol and pyrrole, the basicity changes parallel changes in inductive effect of substituents. The greatest basicity was observed with alkylsubstituted compounds (1, 2) in which substituent  $\text{R}^1$  is electron donating. As substituents on silicon become stronger electron acceptors, the positive charge on silicon increases. This results in an extension of  $\text{Si} \leftarrow \text{O}$  back donation which brings about a decrease in basicity of oxygen (Table I).

The lowest basicity is exhibited by compound 11 in which strongly electron-attracting  $\text{CCl}_3$  group is attached to silicon. According to the earlier reported data<sup>4</sup>, the presence of phenyl and vinyl groups (compounds 4 and 5) should lead to the lower basicity, compared to the values predicted on the basis of Taft  $\sigma^*$  constants. However, the data for these compounds lie on the  $\Delta\nu(\text{OH})$  vs  $\sigma^*$  plot (Fig. 1). Therefore, substituent  $\text{R}^1$  affects the basicity of the oxygen in compounds 4 and 5 predominantly by its inductive effect. A linear dependence of  $\Delta\nu(\text{OH})$  on  $\sigma^*$  (Fig. 1) and the values of correlation coefficients (0.992 for  $\text{R}^1\text{Si}(\text{OC}_2\text{H}_5)_3$ ; 0.965 for  $\text{R}^1\text{Si}(\text{OCH}_3)_3$ ) further indicate that the electronic effects are transferred through silicon by inductive mechanism.

As indicated by the slopes of the above plot, calculated by the least squares method<sup>17</sup>, for series of triorganoethoxysilanes<sup>8</sup> (–61.3), organotriethoxysilanes

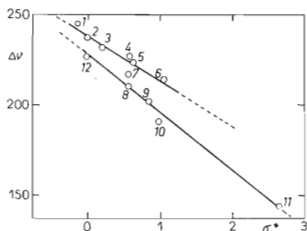


FIG. 1

The  $\Delta\nu(\text{OH})$  (in  $\text{cm}^{-1}$ ) vs  $\sigma_{\text{R}^1}^*$  Plot for  $\text{R}^1\text{Si}(\text{OC}_2\text{H}_5)_3$  (1–6,  $r$  0.992) and  $\text{R}^1\text{Si}(\text{OCH}_3)_3$  (7–12,  $r$  0.965)

TABLE I  
Wavenumber Shifts,  $\Delta\nu$  ( $\text{cm}^{-1}$ ), of Organoalkoxysilanes  $\text{R}^1\text{Si}(\text{OR}^2)_3$  and  $\sigma^*$  Constants of Substituents  $\text{R}^1$

No	$\text{R}^1$	$\text{R}^2$	Conc., M	$\Delta\nu$		$\sigma^*$
				phenol	pyrrole	
1	$n\text{-C}_3\text{H}_7$	$\text{C}_2\text{H}_5$	—	245 <sup>a</sup>	119 <sup>a</sup>	-0.12
2	$\text{CH}_3$	$\text{C}_2\text{H}_5$	—	237 <sup>b</sup>	114 <sup>b</sup>	0.00
3	$\text{C}_6\text{H}_5\text{CH}_2$	$\text{C}_2\text{H}_5$	0.19	232	112	0.23
4	$\text{CH}_2=\text{CH}$	$\text{C}_2\text{H}_5$	0.16	227	113	0.59
5	$\text{C}_6\text{H}_5$	$\text{C}_2\text{H}_5$	0.54	224	110	0.62
6	$\text{ClCH}_2$	$\text{C}_2\text{H}_5$	0.98	214	92	1.05
7	$\text{C}_2\text{H}_5\text{SCH}_2$	$\text{CH}_3$	0.36	216	98	0.57 <sup>c</sup>
8	$\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2$	$\text{CH}_3$	0.52	211	94	0.57 <sup>c</sup>
9	$\text{ICH}_2$	$\text{CH}_3$	1.37	202	85	0.85
10	$\text{BrCH}_2$	$\text{CH}_3$	1.63	191	80	1.00
11	$\text{CCl}_3$	$\text{CH}_3$	1.35	144	53	2.65
12	$\text{CH}_3$	$\text{CH}_3$	—	226 <sup>d</sup>	—	0.00

<sup>a</sup> Taken from ref.<sup>2</sup>, <sup>b</sup> Taken from ref.<sup>1</sup>, <sup>c</sup> Calculated according to the relation  $\sigma_1 = \sigma^*/6.23$ ;  $\sigma_1$  was determined from  $\text{p}K_a$  of aliphatic acids<sup>16</sup>. <sup>d</sup> Taken from ref.<sup>3</sup>.

(-24.7), and organotrimethoxysilanes (-31.8), the transmission of electronic effects through silicon depends strongly on the structure of the compounds. For the results of previous study<sup>2</sup> of series  $\text{R}_{4-n}\text{M}(\text{OC}_2\text{H}_5)_n$  ( $\text{M} = \text{C}, \text{Si}, \text{Ge}; n = 1-4$ ) the interpretation was used that due to the ( $p \rightarrow d$ )  $\pi$  interaction in silicon derivatives the slope of the  $\Delta\nu$  vs  $n$  plot is lower than in the case of carbon and germanium analogues in which the interaction between atom M and oxygen is absent or very weak. The fact that the extent to which inductive effects of substituents are transferred through silicon decreases with increasing number of alkoxy groups was established also in a <sup>1</sup>HNMR study of series<sup>18</sup>  $\text{R}_n\text{Si}(\text{OC}_2\text{H}_5)_{4-n}$ .

The difference between the slopes for organotrimethoxysilanes and organotriethoxysilane is probably due to the stronger electron-donating effect of ethyl group. The effect of substituents in both series can be described by the following regression equations:

$$\Delta\nu(\text{OH}) = 237 - 24.7\sigma^* \quad \text{for } \text{R}^1\text{Si}(\text{OC}_2\text{H}_5)_3, \text{ and}$$

$$\Delta\nu(\text{OH}) = 226 - 31.8\sigma^* \quad \text{for } \text{R}^1\text{Si}(\text{OCH}_3)_3.$$

As in our case substituent  $R^1$  affects the hydrogen bond energy very little, an attempt was made to estimate this energy only for compound 4. From temperature measurements and calculations of thermodynamics parameters according to the known method<sup>10</sup>, the hydrogen bond energy was found to be approximately 3.6 kcal/mol.

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