

## VARIABLE ELECTRONIC EFFECT OF TRIMETHYLSILYL GROUP IN TRIMETHYLSILOXYALKANES\*

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Relative basicity of the oxygen in substituted trimethyl(alkoxy)silanes  $\text{XOSi}(\text{CH}_3)_3$ , measured from the IR spectra of hydrogen bonds of phenol interacting with  $\text{X—O—Si}(\text{CH}_3)_3$  in  $\text{CCl}_4$ , is shown to be controlled by variable electronic effect of  $(\text{CH}_3)_3\text{Si}$  group. Linear regression treatment of the  $\Delta\nu(\text{OH})$  data with parameter  $\sigma_{\text{X}}^*$  disclosed  $(\text{CH}_3)_3\text{Si}$  group to display polarizability effect higher than that of t-butyl group and comparable to that of other alkyl groups. Electronaccepting character of  $(\text{CH}_3)_3\text{Si}$  group in  $\text{X—O—Si}(\text{CH}_3)_3$  increases with increasing electron donating ability of group X.

Relative basicity of the oxygen in compounds  $\text{X—O—R}$  with substituents X inductive constants of which cover rather broad interval of values and with  $\text{R}=\text{H}$ , and variously substituted silyl or alkyl groups, measured as  $\Delta\nu(\text{OH})$  of phenol interacting with  $\text{X—O—R}$  in  $\text{CCl}_4$ , have been shown to reflect the electronic effect of the X and R groups (refs<sup>1-4</sup> and refs therein). The simple Taft equation<sup>5</sup> (Eq. 1), being quite sufficient and convenient to predict the total electronic effect of the X or R moieties

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

was, moreover, disclosed as simple and potent implement for the determination of relative polarizability effect of R moieties — this can be established from the  $\rho^*$  values of Eq. (1) written for individual sets  $\text{X—O—R}$  differing in R (refs<sup>1-3,6</sup>).

Guided by these results we present here additional support for and further comment on variable electronic effect of the trimethylsilyl group in the compounds  $\text{X—O—Si} \cdot (\text{CH}_3)_3$  based on linear regression analysis of the  $\Delta\nu(\text{OH})$  vs  $\sigma_{\text{X}}^*$  plots for the  $\text{XOSi} \cdot (\text{CH}_3)_3$  and XOR compounds.

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## EXPERIMENTAL

Trimethyl(2,2,2-trifluoroethoxy)silane was obtained by a treatment of 2,2,2-trifluoroethanol with hexamethyldisilazane. Equimolar amounts of both compounds were refluxed under nitrogen for 5 h and the mixture was then distilled. Trimethyl(2,2,2-trifluoroethoxy)silane ( $n_D^{20}$  1.3430) was isolated from fraction boiling at 72°C by preparative gas-liquid chromatography. Trimethyl(propargyloxy)silane (b.p. 111°C,  $n_D^{20}$  1.4090) was prepared according to the procedure described earlier<sup>7</sup>.

The oxygen relative basicity of both trimethyl(alkoxy)silanes was determined from the IR spectra of hydrogen bonds of phenol interacting with  $\text{XOSi}(\text{CH}_3)_3$  in  $\text{CCl}_4$  as described before<sup>4</sup>.

## RESULTS AND DISCUSSION

The trimethylsilyl group is generally assumed to be a strong electron supplying substituent whose  $\sigma^*$  is considered to be about  $-0.7$  (refs<sup>8,9</sup>). This value is, however, related to such systems in which  $(\text{CH}_3)_3\text{Si}$  is bonded to  $sp^3$  hybridized carbon. The oxygen relative basicity in trimethylsiloxyalkanes  $\text{X}-\text{O}-\text{Si}(\text{CH}_3)_3$  reported in our previous work<sup>4</sup> suggested the electronic effect of  $(\text{CH}_3)_3\text{Si}$  group to depend upon the nature of the group X. The electron donating effect of  $(\text{CH}_3)_3\text{Si}$  was estimated to decline with increasing electron supplying ability of X. Our, meanwhile carried out, analysis of the  $\Delta\nu(\text{OH})$  data on ethers<sup>2</sup> permitted us to distinguish the  $\rho^*$ 's for the individual sets XOR differing in R. The differences in the  $\rho^*$ 's have been explained by different polarizability effect of R.

Results of the correlation with Eq.(1) for the sets XOR allow us to determine now the parameter  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  in  $\text{XOSi}(\text{CH}_3)_3$  (provided that  $\Delta\nu(\text{OH})$ 's for  $(\text{CH}_3)_3\text{SiOX}$  are known, Table I) and to answer the question whether  $(\text{CH}_3)_3\text{Si}$  group in different  $(\text{CH}_3)_3\text{SiOX}$  exerts variable electronic effect more reliably.

Table I shows that  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  in all the  $\text{X}-\text{O}-\text{Si}(\text{CH}_3)_3$  compounds but  $\text{ClCH}_2\text{OSi}(\text{CH}_3)_3$  is significantly lower than  $-0.7$ . This means that electron donating ability of  $(\text{CH}_3)_3\text{Si}$  in all  $\text{XOSi}(\text{CH}_3)_3$  is considerably reduced excepting  $\text{ClCH}_2\text{OSi}(\text{CH}_3)_3$  where it is increased. Moreover, the electron donating ability of  $(\text{CH}_3)_3\text{Si}$  declines roughly with increasing electron donating nature of X. In order to determine whether  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  and  $\sigma_X^*$  in  $(\text{CH}_3)_3\text{SiOX}$  are interrelated, both quantities were treated by linear regression analysis leading to Eq. (2) with correlation coefficient  $r = -0.764$ . Its significance inquired from comparison of  $r$  with critical value  $r_p$  for confidence

$$\sigma_{(\text{CH}_3)_3\text{Si}}^* = -0.676\sigma_X^* + 0.167 \quad (2)$$

level  $p = 0.01$  (T-test,  $r_p = 0.735$ ) speaks in favor of the existence of the above  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  vs  $\sigma_X^*$  relationship. However, the  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  vs  $\sigma_X^*$  plot is not very tight and we can speculate on probable reason for it using our preceding interpretation of the oxygen basicity in ethers XOR (ref.<sup>2</sup>). The different  $\rho^*$ 's of the  $\Delta\nu(\text{OH})$  vs  $\sigma_X^*$  for the sets XOR have been attributed to a different polarizability of R. Provided

that polarizability effect of R favors the electronically rich or deficient oxygen by either electronwithdrawing action (X is electrondonating, structure I) or by electron-donating action (X is electronwithdrawing, structure II), the overall electronic effect (being a blend of polar and polarizability effects) can be modified<sup>2</sup> by variation in X.



Naturally, the polarizability effect has to result in the decrease in  $\rho^*$  in Eq. (I). We have deduced<sup>2</sup> that the polarizability effect in ethers occurs *via* the C—H hyperconjugation of the X's C—H bond neighbouring to the oxygen, for the polarizability effect of R turned out to depend linearly on the polar effect of R and to operate in the opposite direction. Earlier suggested<sup>2</sup> relation between transmission of electronic effect of a substituent to a reaction site (a probe) and the polarizability of an interposing moiety together with the higher electronic effect transmission through oxygen relative to that through  $sp^3$  hybridized carbon<sup>11</sup> are to be now recalled in order that the following suggestion could be made. The  $\sigma_X^*$  parameter evaluated mostly for X attached to  $sp^3$  hybridized carbon should likely reflect chiefly pure

TABLE I

Results of Correlation with Equation (I) for XOR, Oxygen Basicity in  $(\text{CH}_3)_3\text{SiOR}$  and  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  Values in These Compounds

R <sup>a</sup>	$\Delta\nu(\text{OH})^\circ$	$k^b$	$-\rho^*$	$l^c$	$r^d$	$n^e$	$\Delta\nu(\text{OH})^f$	$\sigma_{(\text{CH}_3)_3\text{Si}}^*$
C(CH <sub>3</sub> ) <sub>3</sub>	290.1	5.5	127.7	12.9	0.953	12	265	0.21 ± 0.09
CH(CH <sub>3</sub> ) <sub>2</sub>	277.3	3.5	104.4	7.9	0.978	10	277	0.01 ± 0.07
C <sub>2</sub> H <sub>5</sub>	265.0	3.0	102.5	6.7	0.983	10	280	-0.14 ± 0.05
CH <sub>3</sub>	256.7	3.5	110.0	7.9	0.980	10	274	-0.16 ± 0.04
CH <sub>2</sub> CH=CH <sub>2</sub>	248.4	2.6	99.6	5.9	0.985	10	256	-0.08 ± 0.06
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	245.0	2.9	76.5	9.3	0.951	10	238	0.09 ± 0.10
(CH <sub>2</sub> ) <sub>2</sub> Cl	221.2	3.3	99.0	6.5	0.982	12	233	-0.12 ± 0.06
H	220.8	2.2	91.7	5.3	0.982	11	216 <sup>g</sup>	0.05 ± 0.05
CH <sub>2</sub> C≡CH	208.0	2.3	76.9	7.7	0.962	10	222	-0.18 ± 0.05
C <sub>6</sub> H <sub>5</sub>	158.2	1.2	61.5	3.9	0.986	8	177	-0.30 ± 0.05
CH <sub>2</sub> Cl	139.0	3.5	33.2	7.5	0.912	6	176	-1.13 ± 0.06

<sup>a</sup> Ref.<sup>2</sup>. <sup>b</sup> Standard error of the  $\Delta\nu(\text{OH})^\circ$ . <sup>c</sup> Standard error of the  $\rho^*$ . <sup>d</sup> Correlation coefficient. <sup>e</sup> Number of X. <sup>f</sup> For  $(\text{CH}_3)_3\text{SiOR}$ , in  $\text{cm}^{-1}$ , ref.<sup>4</sup>. <sup>g</sup> Ref.<sup>10</sup>.

polar effect of a substituent X, and the polar effect of X attached to oxygen should likely be compounded by the polarizability effect. If the polarizability effect in ethers or in trimethyl(alkoxy)silanes operates under conditions of the oxygen basicity measurement (that is it takes place in complexes XOR...PhOH or XOSi(CH<sub>3</sub>)<sub>3</sub>...PhOH in CCl<sub>4</sub> and possibly even in the ground state of XOR or XOSi(CH<sub>3</sub>)<sub>3</sub>) (ref.<sup>2</sup>), parameter  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  found ought to reflect the total electronic effect of (CH<sub>3</sub>)<sub>3</sub>Si group (total electronic effect parameter can be referred to as  $\sigma^{\text{electronic}}$ ). Provided that the parameter  $\sigma_X^*$  reflects also the overall electronic effect of X group, the above  $\sigma_{(\text{CH}_3)_3\text{Si}}^* - \sigma_X^*$  interrelation can be described by Eq. (3).

$$\sigma_{(\text{CH}_3)_3\text{Si}}^{\text{electronic}} = -\sigma_X^{\text{electronic}} \cdot k + C \quad (3)$$

On the other hand, should the  $\sigma_X^*$  reflect chiefly the polar effect of X (which can be represented by  $\sigma_X^{\text{polar}}$ ), the mutual relation between  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  and  $\sigma_X^*$  can be written as Eq. (4),

$$\sigma_{(\text{CH}_3)_3\text{Si}}^{\text{electronic}} = -\sigma_X^{\text{polar}} \cdot (k - k' \cdot k') + C, \quad (4)$$

where

$$\sigma_X^{\text{electronic}} = \sigma_X^{\text{polar}} + \sigma_X^{\text{polarizability}} = \sigma_X^{\text{polar}} - k' \cdot \sigma_X^{\text{polar}},$$

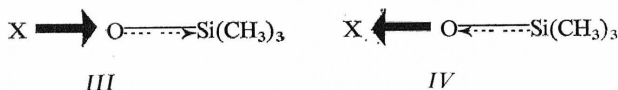
$\sigma^{\text{polarizability}}$  is parameter of polarizability effect and  $k' > 0$ .

Therefore, in such a case a lower sensitivity of  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  to  $\sigma_X^*$  variation is to be observed. Nevertheless, the low tightness of the  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  vs  $\sigma_X^*$  plot is obviously due to the fact that the mechanism of the polarizability effect of X can be at least for some X different and then also the extent of compensation of the polar effect by the polarizability effect can be at least for some X not in linear relation to the polar effect of X ( $\sigma^{\text{polarizability}} \neq \sigma^{\text{polar}} - k' \cdot \sigma^{\text{polar}}$ ).

Published results indicate that the electron-donating ability of (CH<sub>3</sub>)<sub>3</sub>Si in X—O—Si(CH<sub>3</sub>)<sub>3</sub> declines with increasing electron-donating nature of X which was arrived at also previously<sup>4</sup>. However, the electronic effect of (CH<sub>3</sub>)<sub>3</sub>Si in (CH<sub>3</sub>)<sub>3</sub>SiOX having X's the  $\sigma_X^*$ 's of those fall within interval 0.5–1.0 was, at that time, considered as constant. We can now suppose steric effect of X = Cl<sub>3</sub>CCH<sub>2</sub> and Cl<sub>2</sub>CHCH<sub>2</sub> to be reason for it. Having now at our disposal  $\Delta\nu(\text{OH})$  for other XOSi(CH<sub>3</sub>)<sub>3</sub> with strongly electron-withdrawing X exerting insignificant steric effect (X,  $\Delta\nu(\text{OH})$  in cm<sup>-1</sup>: HC≡CCH<sub>2</sub>, 222, F<sub>3</sub>CCH<sub>2</sub>, 167) the  $\Delta\nu(\text{OH})$  vs  $\sigma_X^*$  plot for XOSi(CH<sub>3</sub>)<sub>3</sub>/X = (CH<sub>3</sub>)<sub>3</sub>·SiCH<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>, n-C<sub>3</sub>H<sub>7</sub>, C<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>, Cl(CH<sub>2</sub>)<sub>3</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, Cl(CH<sub>2</sub>)<sub>2</sub>, (all ref.<sup>4</sup>), H (ref.<sup>10</sup>), HC≡CCH<sub>2</sub> and F<sub>3</sub>CCH<sub>2</sub> (this work) turns out to obey linear free energy relationship (Eq. (5),  $r = 0.985$ ). The  $\rho^*$  constant therein is almost comparable with those relating to the  $\Delta\nu(\text{OH})$  vs  $\sigma_X^*$  plot for X—O-alkyl (Table I). A similar action and extent of the polarizability effect for (CH<sub>3</sub>)<sub>3</sub>Si

$$\Delta\nu(\text{OH}) = (-97.11 \pm 5.06) \sigma_X^* + (268.75 \pm 2.37) \quad (5)$$

and alkyl groups attached to OX moiety can be thus deduced. However, it seems fair to state that the polarizability effect of the trimethylsilyl group is higher than that of t-butyl group, since the  $\rho^*$  in Eq. (5) is lower than that in Eq. (1) with X—OC<sub>4</sub>H<sub>9</sub>. (CH<sub>3</sub>)<sub>3</sub>Si (Table I). Electron donating X increases electron accepting character of (CH<sub>3</sub>)<sub>3</sub>Si (the increase in  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$ , structure III) and *vice versa* electron withdrawing X decreases electron accepting nature of (CH<sub>3</sub>)<sub>3</sub>Si (the decrease in  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$ , structure IV).



This conclusion, being in accordance with the operation of the polarizability effect in X—O—R (ref.<sup>2</sup>), is also consonant with the character of the relationship between  $\sigma_{(\text{CH}_3)_3\text{Si}}^*$  and  $\sigma_{\text{X}}^*$ .

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