

THE OXYGEN BASICITY IN SILOXANES. VARIABLE ELECTRONIC EFFECT OF TRIMETHYLSILOXY GROUP*

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The oxygen relative basicity of some siloxanes $[X(CH_2)_nSi(CH_3)_2]_2O$, $XCH_2Si(CH_3)_2OSi(CH_3)_3$ and $XSi[OSi(CH_3)_3]_3$ was measured as $\Delta\nu(OH)$ of phenol due to interaction with these compounds in CCl_4 . The earlier reported data on $(CH_3)_{4-n}Si[OSi(CH_3)_3]_n$ are accounted for by mutual polarizability effect of $(CH_3)_3SiO$ groups. The oxygen basicity in $XSi[OSi(CH_3)_3]_3$ has been found to be insensitive to the substituent X variation. It is suggested to have an electronic rather than steric origin and demonstrated to be consonant with the electronic effect variation of $(CH_3)_3SiO$ groups.

Recent years have seen a continuous interest¹⁻⁵ in siloxanes aiming at the inspection and elucidation of their earlier determined properties^{6,7}. Low basicity of the oxygen interposed between two silicon atoms can be suggested to result from the so-called $O \Rightarrow Si$ back bonding⁸ and from a lack of conjugation between the two $(p-d)_\pi$ bonds of the $Si-O-Si$ system¹. Despite that much work has gone into getting deeper insight into structure of siloxanes, the electronic effect of $(CH_3)_3SiO$ group in siloxanes has not yet been investigated.

Published results on similar systems, alkoxysilanes $XYZSi-OR$ (refs^{9,10}), indicate the $XYZSi$ groups to have their electronic effect influenced by the nature of the molecular rest R and revealed¹¹ the synergistic action of X, Y, Z substituents: their electro-donating ability in alkoxysilanes is higher than that exerted in organic compounds, presumably due to their mutual polarizability effect. Guided by our previous studies⁹⁻¹¹ we have attempted in this work to answer the question whether the trimethyl-siloxy group bonded to silicon is, responding the electronic demand of the molecular rest, capable to vary its electronic effect as well.

EXPERIMENTAL

Model compounds. All the siloxanes the relative oxygen basicity of which was measured *i.e.* $[C_6H_5CH_2Si(CH_3)_2]_2O$, $[X(CH_2)_nSi(CH_3)_2]_2O$ with $n = 1, 3$ and $X = Cl, Br, I$ and XSi .

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$[\text{OSi}(\text{CH}_3)_3]_3$ with $\text{X} = \text{H}, \text{Cl}(\text{CH}_2)_3, \text{ClCH}_2, \text{CH}_3, \text{C}_6\text{H}_5, \text{CH}_2=\text{CH}$ and Cl and $\text{XCH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$ have been synthesized by the procedures reported^{12,13}. In order to prepare siloxanes $\text{XSi}[\text{OSi}(\text{CH}_3)_3]_3$ with $\text{X} = \text{Cl}(\text{CH}_2)_2, \text{Cl}_2\text{CHCH}_2$ and $\text{cyclo-C}_6\text{H}_{11}$ the method of Haluska¹⁴ was used. 3,3,3-Trichloropropyl[tris(trimethylsiloxy)]silane was obtained by the addition of chloroform to vinyl[tris(trimethylsiloxy)]silane in such a way that vinyl[tris(trimethylsiloxy)]silane (11.4 g, 0.035 mol) was treated with an excess of chloroform (60 ml) in the presence of dibenzoyl peroxide (2 g) for 20 h at 67°C. The excess chloroform was removed at room temperature in a rotatory evaporator and the rest was dissolved in acetone. Thereafter, sodium iodide was added and sodium benzoate precipitated was filtered off. A minute amount of iodine was destroyed with sodium thiosulfate and 3,3,3-trichloropropyl[tris(trimethylsiloxy)]silane was obtained by rectification. Bis(3-iodopropyl)tetramethyldisiloxane was prepared by a treatment of bis(3-chloropropyl)tetramethyldisiloxane with sodium iodide in acetone. The products purity was checked by gas-liquid chromatography and their identity confirmed by NMR spectroscopy or by elemental analysis. Physical constants of those compounds reported previously were in agreement with literature data^{12,13}. Those of new compounds are recorded in Table I along with reaction yields.

The IR spectra of hydrogen bonds of phenol were recorded on a double-beam Zeiss (Jena) spectrometer, Model UR 20, in 3700–3200 cm^{-1} region (LiF prism) using 0.1 cm thick NaCl cells. The concentration of proton donating phenol in CCl_4 (spectral grade) was 0.02M, that of proton accepting siloxane was 0.2–0.5M. The wavenumbers of the absorption bands represent averages from three measurements. Due to a considerable half-width of the associated band $\nu_{\text{OH}\cdots\text{O}}$ the position of this maximum can be determined with the accuracy of $\pm 8 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The three earlier papers dealing with the oxygen basicity in siloxanes are to be started from. They have come from West and his associates¹⁵ and from our laboratory^{16,17} and reported the $\Delta\nu(\text{OH})$ values for siloxanes $(\text{CH}_3)_{4-n}\text{Si}[\text{OSi}(\text{CH}_3)_3]_n$ ($n = 1-4$, $(\text{CH}_3)_3\text{Si}$ will be referred to hereafter as M) to be always lower than that of analogous ethers. In the years since, much evidence accumulated in support of that essential validity incited Milechkevich¹⁸ to correlate $\Delta\nu(\text{OH})$ values of phenol

TABLE I
Physical Properties and Yields of New Siloxanes

Compound	B.p. °C/Torr	n_D^{20}	Yield, %
$\text{Cl}(\text{CH}_2)_2\text{Si}[\text{OSi}(\text{CH}_3)_3]_3$	157/72	1.4101	75
$\text{Cl}_2\text{CHCH}_2\text{Si}[\text{OSi}(\text{CH}_3)_3]_3$	175/80	1.4194	16
$\text{Cl}_3\text{C}(\text{CH}_2)_2\text{Si}[\text{OSi}(\text{CH}_3)_3]_3$	150/10	1.4264	84
$\text{cyclo-C}_6\text{H}_{11}\text{Si}[\text{OSi}(\text{CH}_3)_3]_3$	86/12	1.4222	66
$[\text{I}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{O}]_3$	134/1	1.5314	81

for various disiloxanes with the substituent parameter $\sum\sigma^*$ of groups attached to the Si—O—Si grouping. The flatter slope obtained for the plot $\Delta\nu(\text{OH})$ vs $\sum\sigma^*$ with disiloxanes compared to that with ethoxysilanes was explained¹⁸ by lower transmission of the electronic effect through silicon in disiloxanes. The closer inspection of the plot for disiloxanes reveals, however, that conclusion somewhat deceptive, for the data gathered for alkylsiloxanes from two laboratories differ considerably and the points falling into the range of $\sum\sigma^* = 1.7-2.1$ referring to $[\text{XCH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ with X = Cl, Br, I don't reflect the basicity of the oxygen (as was suggested in ref.¹⁹) but the basicity of the halogens (refs^{20,21}).

To establish the true $\Delta\nu(\text{OH})$ vs $\sum\sigma^*$ relationship we measured $\Delta\nu(\text{OH})$ value of disiloxanes having electronwithdrawing group(s) on silicon(s). All the $[\text{X}(\text{CH}_2)_n \cdot \text{Si}(\text{CH}_3)_2]_2\text{O}$ and $\text{XCH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$ with C_6H_5 group in α -position or with halogen X (Cl, Br, I) in α - or γ -position gave $\Delta\nu(\text{OH})$ within range $57-70 \text{ cm}^{-1}$, which corresponds to the $\text{OH}\cdots\text{C}_6\text{H}_5$ or $\text{OH}\cdots\text{X}$ interaction (refs^{15,20,21}). As for the maximum of the $\nu(\text{OH}\cdots\text{O})$ absorption band is concerned, its exact determination is difficult because of low intensity of the $\nu(\text{OH}\cdots\text{O})$ band. To overcome this drawback with alkylsubstituted siloxanes, their concentration in CCl_4 was increased up to 1M (ref.¹³). This however cannot be applied when phenyl- or halogenosubstituted siloxanes are treated with phenol since the $\nu(\text{OH}\cdots\text{X})$ or $\nu(\text{OH}\cdots\text{C}_6\text{H}_5)$ absorption bands mount over that of $\nu(\text{OH}\cdots\text{O})$ and tend to overlap it. The oxygen basicity of these disiloxanes can be therefore established only as falling into the range of 120 to 140 cm^{-1} .

Fortunately enough, a bit more intense $\nu(\text{OH}\cdots\text{O})$ absorption band is observed with tris(trimethylsiloxy)silanes. The $\Delta\nu(\text{OH})$ values for the $\text{XSi}(\text{OM})_3$ were read as follows (X, $\Delta\nu(\text{OH})$ in cm^{-1}): cyclo- C_6H_{11} , 123; CH_3 , 136; H, 127; $\text{Cl}(\text{CH}_2)_3$, 120; $\text{Cl}(\text{CH}_2)_2$, 117; ClCH_2 , 118; $\text{Cl}_3\text{CCH}_2\text{CH}_2$, 127; $\text{CH}_2=\text{CH}$, 131; Cl_2HCCH_2 , 125; C_6H_5 , 123 and Cl, 120. A perusal of Fig. 1 that depicts the $\Delta\nu(\text{OH})$ vs σ_X^* plot for $\text{X-Si}(\text{OM})_3$ and for $\text{X-Si}(\text{OC}_2\text{H}_5)_3$ (ref.²²) reveals that the oxygen basicity for tris(trimethylsiloxy)silanes, contrary to that for triethoxysilanes, does not reflect the change in the electronic effect of X and is about the same irrespective of the nature of X. One could presume steric effect of X groups to be responsible for it. However, a treatment of the $\Delta\nu(\text{OH})$ data by means of the two parameter equation with Taft's σ^* (ref.²⁴) and Charton's ν (ref.^{25,26}) constants shows that it is not so. The explanation including low transmission of the electronic effect through the silicon does not sound probable as well, since the halogen basicity in siloxanes such as $[\text{Br}(\text{CH}_2)_3\text{Si} \cdot (\text{CH}_3)_2]_2\text{O}$ ($\Delta\nu(\text{OH}) = 71 \text{ cm}^{-1}$), $[\text{BrCH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$, $\Delta\nu(\text{OH}) = 57 \text{ cm}^{-1}$ and $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{OM}$ ($\Delta\nu(\text{OH}) = 67 \text{ cm}^{-1}$) differs and suggests the electronic effect transmission through the Si—O—Si system not to be small. Similarly, rather good transmission of the electronic effect through the SiOSi linkage was assumed⁵ even for $\text{H}(\text{CH}_3)_2\text{SiOSiR}_1\text{R}_2\text{R}_3$ system.

In an effort to reconcile these data with our interpretation of the oxygen basicity in alkoxy-silanes and ethers advanced in earlier studies^{9-11,27}, we prefer to explain the difference in slopes of the $\Delta\nu(\text{OH})$ vs σ_X^* plot for $\text{XSi}(\text{OM})_3$ and $\text{XSi}(\text{OC}_2\text{H}_5)_3$ (Fig. 1) by different polarizability of $(\text{Si})-\text{O}-\text{M}$ and $(\text{Si})-\text{O}-\text{C}_2\text{H}_5$ groupings. Similar explanation was put forward to explain different slopes of the $\Delta\nu(\text{OH})$ vs σ_X^* plots for several sets of ethers $\text{X}-\text{O}-\text{R}$ (ref.²⁷) and alkoxy-silanes $\text{X}-\text{O}-\text{SiR}_1\text{R}_2\text{R}_3$ (refs⁹⁻¹¹) in which cases the R and the $\text{SiR}_1\text{R}_2\text{R}_3$ groups have been demonstrated to respond the electronic demand of the neighbouring oxygen by their polarizability effect. This polarizability effect diminishes the electronic excess or lack on the oxygen, compensates thus, in part, the electronic effect of the X group and makes the slope of the $\Delta\nu(\text{OH})$ vs σ_X^* plot flatter. The polarizability effect in tris(trimethylsiloxy)-silanes can be then envisaged as follows:



Regarding the mechanism of polarizability effect, the greater effect of OM group with respect to that of OC_2H_5 group inferred from Fig. 1, together with a lack of conjugation between the two $(p-d)_\pi$ bonds of the $\text{Si}-\text{O}-\text{Si}$ system¹ is consonant with a view that high polarizability effect of the OM group realizes itself, in major, by means of $\sigma \text{O}-\text{Si}_M$ bonds.

This explanation assuming the polarizability effect of the $\text{O}-\text{M}$ groups to be responsible for equalizing the oxygen basicity in $\text{XSi}(\text{OM})_3$ gets additional support from the earlier reported oxygen basicity in $(\text{CH}_3)_{4-n}\text{Si}(\text{OM})_n$ with $n = 1-4$ (ref.¹⁷). In Fig. 2 the oxygen basicity for $(\text{CH}_3)_{4-n}\text{Si}(\text{OM})_n$ (ref.¹⁷), $(\text{CH}_3)_{4-n}\text{Si} \cdot (\text{OC}_2\text{H}_5)_n$ (ref.¹⁵) and $(\text{CH}_3)_{4-n}\text{Si}(\text{OCH}_2\text{CH}_2\text{Cl})_n$ (ref.²¹) is plotted against the number of the oxygen containing groups n . The electronic effect of $\text{C}_2\text{H}_5\text{O}$ groups in $(\text{CH}_3)_{4-n}\text{Si}(\text{OC}_2\text{H}_5)_n$ having $n = 2-4$ has been demonstrated to be about the same ($\sigma^*\text{C}_2\text{H}_5\text{O} = 0.26-0.41$) for all n (ref.¹¹). The $\Delta\nu(\text{OH})$ vs n plot for $(\text{CH}_3)_{4-n} \cdot \text{Si}(\text{OC}_2\text{H}_5)_n$ thus proves to be very helpful for the estimation of the electronic effect of OM and $\text{OCH}_2\text{CH}_2\text{Cl}$ groups in $(\text{CH}_3)_{4-n}\text{Si}(\text{OM})_n$ and $(\text{CH}_3)_{4-n}\text{Si}(\text{OCH}_2\text{CH}_2 \cdot \text{Cl})_n$ respectively. It can be seen from Fig. 2 that the first values ($n = 1$) of the $\Delta\nu(\text{OH})$ vs n plots decrease in turn $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5 > (\text{CH}_3)_3\text{SiOCH}_2\text{CH}_2\text{Cl} > (\text{CH}_3)_3 \cdot \text{SiOM}$, which corresponds to the following order for group electronwithdrawing action: $\text{M} > \text{CH}_2\text{CH}_2\text{Cl} > \text{C}_2\text{H}_5$. Proceeding then to the higher n , the difference between the $\Delta\nu(\text{OH})$ of $(\text{CH}_3)_{4-n}\text{Si}(\text{OC}_2\text{H}_5)_n$ and that of $(\text{CH}_3)_{4-n}\text{Si}(\text{OCH}_2\text{CH}_2\text{Cl})_n$ increases due to a steeper slope of the plot for the latter compounds. This can be accounted for by a higher electronwithdrawing ability of the 2-chloroethyl group. The opposite situation is however seen when proceeding along the slope for $(\text{CH}_3)_{4-n} \cdot \text{Si}(\text{OM})_n$. In this case the difference in the $\Delta\nu(\text{OH})$ for $(\text{CH}_3)_{4-n}\text{Si}(\text{OM})_n$ and that

for $(\text{CH}_3)_{4-n}\text{Si}(\text{OC}_2\text{H}_5)_n$ decreases. Very flat slope of the plot for $(\text{CH}_3)_{4-n}\text{Si}(\text{OM})_n$ is responsible for it and reveals that electronwithdrawing effect of the trimethylsiloxy group in $(\text{CH}_3)_{4-n}\text{Si}(\text{OM})_n$ has to decline with increasing number of OM groups in the siloxane system very considerably. We can suppose mutual polarizability effect of OM groups to bring about the reduction of their electronwithdrawing effect. Such action has been shown¹¹ to result in saturation effect with $\text{X}_n\text{SiR}_{4-n}$ having alkyl group R, easily polarizable substituent X and $n \geq 2$, and to promote the electronic effect variation of silyl $\text{X}_n\text{R}_{3-n}\text{Si}$ group with $\text{X}_n\text{R}_{3-n}\text{SiY}$ compounds having strongly electronwithdrawing and hardly polarizable group Y. As far as the $(\text{CH}_3)_{4-n}\text{Si}(\text{OM})_n$ and $\text{XSi}(\text{OM})_3$ are concerned, the polarizability effect of OM groups found for the former compounds then makes the electronic effect variation of these groups in the latter compounds probable and easier under the influence of the electronwithdrawing group X.

Two conclusions can be drawn. First, the term electronic effect, being a blend of the polar and the polarizability effects, has been successfully used to account for acid-base equilibria in the gas phase^{28,29}. The polarizability effect is known to be very strongly attenuated^{30,31} in solution leading thus to many of the reversals that

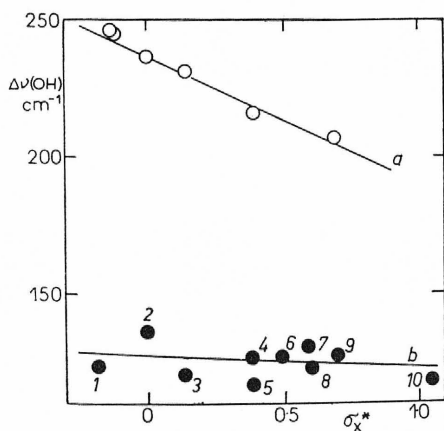


FIG. 1

The $\Delta\nu(\text{OH})$ vs σ_X^* Plot for $\text{XSi}(\text{OC}_2\text{H}_5)_3$ and $\text{XSi}(\text{OSi}(\text{CH}_3)_3)_3$

Line *a* and *b* refer to $\text{XSi}(\text{OC}_2\text{H}_5)_3$ (ref.²², see also ref.²³) and $\text{XSi}(\text{OSi}(\text{CH}_3)_3)_3$ respectively. Points 1 to 10 relate to X = $\text{c-C}_6\text{H}_{11}$, CH_3 , $\text{Cl}(\text{CH}_2)_3$, $\text{Cl}_3\text{C}(\text{CH}_2)_2$, $\text{Cl}(\text{CH}_2)_2$, H, $\text{CH}_2=\text{CH}$, C_6H_5 , Cl_2HCCH_2 and ClCH_2 in given order.

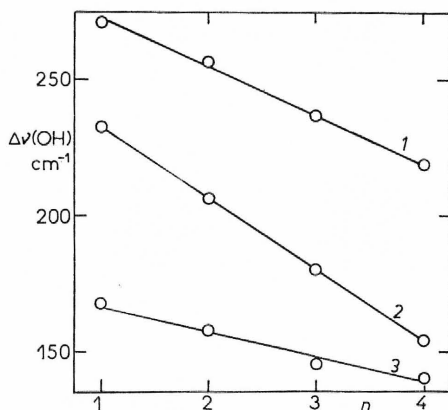


FIG. 2

Dependence of $\Delta\nu(\text{OH})$ on the Number of Oxygen-Containing Groups, n

- 1 $(\text{CH}_3)_{4-n}\text{Si}(\text{OC}_2\text{H}_5)_n$ (ref.¹⁵), 2
 $(\text{CH}_3)_{4-n}\text{Si}(\text{OCH}_2\text{CH}_2\text{Cl})_n$ (ref.²¹), 3
 $(\text{CH}_3)_{4-n}\text{Si}(\text{OSi}(\text{CH}_3)_3)_n$ (ref.¹⁷).

make gas-phase and solution basicities so different^{32,33}. However, our previous data on the oxygen basicity in ethers²⁷ and alkoxy silanes^{9,10} and those for siloxanes presented in this paper measured in tetrachloromethane detect the polarizability effect rather well and demonstrate that it operates also in solvents of low polarity.

Second, in spite of the growing number of papers reporting the applicability of linear free energy relationship (LFER), practically none effort is made to reveal systems in which LFER is invalid. This likely stems from difficulty to find such systems. Our earlier data on 3,3,3-trichloroethoxysilanes^{9,10} and here presented data for tris(trimethylsiloxy)silanes show the oxygen basicity in both series to be very little, if at all sensitive to the variation of the polar effect of substituents bonded to silicon as a result of an enormous polarizability of the —Si—O—moieties. On the basis of an enormous role of the polarizability component to the total electronic effect of the groups with Si—O bond it is reasonable to deduce that similar equalization or even reversal of properties can take place in compounds having other easily polarizable groups.

REFERENCES

1. Bordeau M., Dédier J., Frainnet E., Bothorel P.: *J. Organometal. Chem.* **61**, 103 (1973).
2. Mollère P., Bock H., Becker G., Fritz G.: *J. Organometal. Chem.* **61**, 113 (1973).
3. Pitt C. G., Bursey M. M., Chatfield D. A.: *J. Chem. Soc., Perkin Trans 1*, 1976, 434.
4. Glidewell C., Liles D. C.: *Chem. Commun.* 1977, 632.
5. Mileshkevich V. P., Reikhsfeld V. O., Suprunenko A. I., Pestunovich V. A., Larin M. F., Voronkov M. G.: *Dokl. Akad. Nauk SSSR* **231**, 1134 (1976).
6. Voronkov M. G., Mileshkevich V. P., Yuzhelevskii Y. A.: *Usp. Khim.* **45**, 2252 (1976).
7. Bažant V., Chvalovský V., Rathouský J.: *Organosilicon Compounds*, Vol. 1. Academia, Prague 1965.
8. Chvalovský V. in the book: *Organosilicon Compounds* (V. Bažant, V. Chvalovský, J. Rathouský, Eds), Vol. 3, p. 80. Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 1973.
9. Pola J., Chvalovský V.: *This Journal* **42**, 484 (1977).
10. Pola J., Chvalovský V.: *This Journal* **43**, 746 (1978).
11. Pola J., Jakoubková M., Chvalovský V.: *This Journal* **43**, 753 (1978).
12. Bažant V., Chvalovský V., Rathouský J.: *Organosilicon Compounds*, Vol. 2. Academia, Prague 1965.
13. Bažant V., Chvalovský V., Rathouský J.: *Organosilicon Compounds*, Vol. 4. Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 1973.
14. Haluska L. A.: Unpublished results.
15. West R., Whatley L. S., Lake K. J.: *J. Amer. Chem. Soc.* **83**, 761 (1961).
16. Horák M., Bažant V., Chvalovský V.: *This Journal* **25**, 2822 (1960).
17. Ulbricht K., Jakoubková M., Chvalovský V.: *This Journal* **33**, 1693 (1968).
18. Mileshkevich V. P., Nikolaev G. A., Karlin A. V., Parshina L. G.: *Org. Reactiv.* **9**, 805 (1972).
19. Engelhardt G., Kriegsmann H.: *Z. Anorg. Chem.* **336**, 286 (1965).
20. Schleyer P. R., West R.: *J. Amer. Chem. Soc.* **81**, 3164 (1959).
21. Jakoubková M., Papoušková Z., Chvalovský V.: *This Journal* **41**, 2701 (1976).
22. Pola J., Chvalovský V.: *This Journal* **42**, 358 (1977).

23. Shergina N. I., Voronkov M. G., Jakoubková M., Chvalovský V.: *This Journal* 39, 1740 (1974).
24. Zhdanov Yu. A., Minkin V. I.: *Korreliaconnyii Analiz v Organicheskoi Khimii*. Rostovskii Universitet, Rostov 1966.
25. Charton M.: *J. Amer. Chem. Soc.* 97, 1552 (1975).
26. Charton M.: *J. Org. Chem.* 41, 2217 (1976).
27. Pola J., Jakoubková M., Chvalovský V.: *This Journal* 43, 760 (1978).
28. Taft R. V. in the book: *Proton Transfer Reactions* (E. F. Caldin, V. Gold, Ed.), Chap. 2. Chapman and Hall, London 1975.
29. Taagepera M., Hehre W. J., Topsom R. D., Taft R. W.: *J. Amer. Chem. Soc.* 98, 7438 (1976).
30. Aue D. H., Webb H. M., Bowers M. T.: *J. Amer. Chem. Soc.* 98, 318 (1976).
31. Wolf J. E., Harch P. G., Taft R. W.: *J. Amer. Chem. Soc.* 97, 2904 (1975).
32. Arnett E. M.: *Accounts Chem. Res.* 6, 404 (1973).
33. Jones F. M., Arnett E. M.: *Progr. Phys. Org. Chem.* 11, 263 (1974).

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