

**BASE-CATALYSED METHANOLYSIS
OF TRIMETHYLSILOXYALKANES $R(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$
AND THE α -EFFECT***

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The relative rate constants of the ethylamine catalysed methanolysis of trimethylsiloxyalkanes $R(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($R = (\text{CH}_3)_3\text{Si}; (\text{CH}_3)_3\text{Ge}; \text{OCH}_3; \text{Cl}; \text{alkyl}$) were measured. The logarithms of the relative rate constants follow the extended Taft equation and correlate with the σ^* and E_s constants of the substituents. The results are consistent with the absence of intramolecular ($p-d$)_o interactions in the above compounds with $R = (\text{CH}_3)_3\text{M}$, OCH_3 , Cl and $n > 2$. The relative rate constants of the $(\text{CH}_3)_3\text{MCH}_2\text{OSi}(\text{CH}_3)_3$ compounds are discussed in terms of the α -effect.

The base-catalysed solvolysis of organosilicon compounds with Si—O—C bonding has been studied for aryloxysilanes $R_nR'_{3-n}\text{SiOAr}$ ($R = \text{alkyls}$, $R' = \text{aryl}$)¹⁻⁶. The reactions were described by the kinetic equation (I); the rate-determining step included synchronous bond-making and bond-breaking in the transition state I.

$$k = k' + k^B(\text{B}), \quad \text{B} = \text{base} \quad (I)$$

The rate constant k^B was correlated with various σ constants and the sensitivity of the reaction towards a change in the polar effect of substituents either on silicon or in the phenoxy group is well-known. Nevertheless, the influence of the steric effect of substituents on the solvolysis rate has been examined only qualitatively, and then only for groups bonded to silicon^{1,2}. Until now, no separation of the electronic and the steric effects of the substituent on the reaction rate has been carried out.

Thus, the object of this work was to obtain kinetic data for the base-catalysed methanolysis of trimethylsiloxyalkanes $R(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($R = \text{alkyl}, (\text{CH}_3)_3\text{Si}, (\text{CH}_3)_3\text{Ge}, \text{Cl}, \text{OCH}_3$). It was hoped that such a study would provide not only a separation of the two effects (electronic and steric) mentioned above, but also

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information about the importance of the intramolecular interactions (α -effect^{7,8} and $(p-d)_\sigma$ coordinate bonding^{9,10}) which have been proposed in similar compounds.

EXPERIMENTAL

All compounds $R(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($R = \text{alkyl}, (\text{CH}_3)_3\text{Si}, (\text{CH}_3)_3\text{Ge}, \text{Cl}, \text{OCH}_3$) were prepared by reactions of the appropriate alcohols with either hexamethyldisilazane or trimethylchlorosilane in the presence of stoichiometric amounts of pyridine in diethyl ether. Yields were 80–95%. The purity of compounds was checked by gas-liquid chromatography, and the identity was confirmed by NMR spectroscopy. The physical constants of those compounds described previously are in agreement with literature data^{11,12}.

$\text{ROSi}(\text{CH}_3)_3$ [R, b.p. ($^\circ\text{C}/\text{Torr}$), n_D^{20}]: C_2H_5 , 76, 1.3731; $n\text{-C}_3\text{H}_7$, 102, 1.3819; $i\text{-C}_3\text{H}_7$, 87, 1.3762; $n\text{-C}_4\text{H}_9$, 125, 1.3920; $i\text{-C}_4\text{H}_9$, 102, 1.3856; $n\text{-C}_5\text{H}_{11}$, 152, 1.3984; $n\text{-C}_6\text{H}_{13}$, 171, 1.4042; $n\text{-C}_7\text{H}_{15}$, 190, 1.4098; $n\text{-C}_8\text{H}_{17}$, 214, 1.4134; $n\text{-C}_9\text{H}_{19}$, 231, 1.4179; $\text{CH}_2=\text{CHCH}_2$, 100, 1.3936; $\text{C}_6\text{H}_5\text{CH}_2$, 90/20, 1.4749. $\text{Cl}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ [n, b.p. ($^\circ\text{C}/\text{Torr}$), n_D^{20}]: 2, 132, 1.4119; 3, 154, 1.4166; 4, 173, 1.4229; 5, 196, 1.4282; 6, 127/30, 1.4324.

$(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ [n, b.p. ($^\circ\text{C}/\text{Torr}$), n_D^{20}]: 1, 126, 1.3893; 2, 78/44, 1.4010; 3, 96/38, 1.4064; 4, 88/20, 1.4120. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ [n, b.p. ($^\circ\text{C}/\text{Torr}$), n_D^{20}]: 1–4 (see¹³), 5, 120/20, 1.4200; 6, 144/45, 1.4231. $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ [n, b.p. ($^\circ\text{C}/\text{Torr}$), n_D^{20}]: 1, 94/145, 1.4152; 2, 89/72, 1.4245; 3, 116/67, 1.4272; 4, 122/45, 1.4305. $\text{CH}_3\text{O}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ [n, b.p. ($^\circ\text{C}/\text{Torr}$), n_D^{20}]: 2, 131, 1.3945; 3, 80/115, 1.3992; 4, 102/115, 1.4061; 5, 107/70, 1.4116; 6, 122/50, 1.4158.

The following new compounds were first prepared in this study: $(\text{CH}_3)_3\text{GeCH}_2\text{OSi}(\text{CH}_3)_3$, for $\text{C}_7\text{H}_{20}\text{GeOSi}$ (220.9) calculated: 38.17% C, 9.15% H; found: 38.00% C, 9.11% H. $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_2\text{OSi}(\text{CH}_3)_3$, for $\text{C}_8\text{H}_{22}\text{GeOSi}$ (235.0) calculated: 41.01% C, 9.47% H; found: 39.61% C, 9.20% H. $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_3\text{OSi}(\text{CH}_3)_3$, for $\text{C}_9\text{H}_{24}\text{GeOSi}$ (249.0) calculated: 43.53% C, 9.74% H; found: 43.49% C, 9.78% H. $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3$, for $\text{C}_{10}\text{H}_{26}\text{OSiGe}$ (263.0) calculated: 45.78% C, 9.99% H; found: 45.61% C, 9.96% H. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_5\text{OSi}(\text{CH}_3)_3$, for $\text{C}_{11}\text{H}_{28}\text{OSi}_2$ (232.5) calculated: 56.82% C, 12.14% H; found: 56.60% C, 12.08% H. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_6\text{OSi}(\text{CH}_3)_3$, for $\text{C}_{12}\text{H}_{30}\text{OSi}_2$ (246.6) calculated: 58.46% C, 12.27% H; found: 58.15% C, 12.14% H. $(\text{CH}_3)_3\text{C}(\text{CH}_2)_2\text{OSi}(\text{CH}_3)_3$, for $\text{C}_9\text{H}_{22}\text{OSi}$ (174.4) calculated: 61.99% C, 12.71% H; found: 61.99% C, 12.66% H. $(\text{CH}_3)_3\text{C}(\text{CH}_2)_3\text{OSi}(\text{CH}_3)_3$, for $\text{C}_{10}\text{H}_{24}\text{OSi}$ (188.4) calculated: 63.76% C, 12.84% H; found: 64.02% C, 13.00% H. $\text{Cl}(\text{CH}_2)_6\text{OSi}(\text{CH}_3)_3$, for $\text{C}_9\text{H}_{21}\text{ClOSi}$ (208.8) calculated: 51.77% C, 10.14% H; found: 51.80% C, 10.21% H. $\text{CH}_3\text{O}(\text{CH}_2)_3\text{OSi}(\text{CH}_3)_3$, for $\text{C}_7\text{H}_{18}\text{O}_2\text{Si}$ (162.3) calculated: 51.80% C, 11.18% H; found: 51.67% C, 11.03% H. $\text{CH}_3\text{O}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3$, for $\text{C}_8\text{H}_{20}\text{O}_2\text{Si}$ (176.3) calculated: 54.49% C, 11.43% H; found: 54.63% C, 11.47% H. $\text{CH}_3\text{O}(\text{CH}_2)_5\text{OSi}(\text{CH}_3)_3$, for $\text{C}_9\text{H}_{22}\text{O}_2\text{Si}$ (190.4) calculated: 56.79% C, 11.65% H; found: 56.80% C, 11.54% H. $\text{CH}_3\text{O}(\text{CH}_2)_6\text{OSi}(\text{CH}_3)_3$, for $\text{C}_{10}\text{H}_{24}\text{O}_2\text{Si}$ (204.4) calculated: 58.76% C, 11.84% H; found: 58.53% C, 11.70% H.

Methanol was refluxed with calcium oxide and rectified. Hydrocarbons (cyclohexane, n-nonane, n-decane, n-dodecane, *trans*-decalin, n-tridecane and n-tetradecane) used in kinetic measurements as standards were distilled, dried, and stored over molecular sieve.

Kinetic measurements. Approximately equimolar amounts of two trimethylsiloxyalkanes $R(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($\sim 10^{-3}$ mol) and a standard (hydrocarbon, $\sim 5 \cdot 10^{-4}$ mol) were weighted into a 10 ml reaction vessel. The reaction was started by addition of 5 ml of a 0.0016M solution of $\text{C}_2\text{H}_5\text{NH}_2$ in absolute methanol. (At this concentration of catalyst, the reaction reached 50%

conversion after a time of not less than 10 hours. The reaction mixture was then analysed several times by gas-liquid chromatography and the decrease of the area below the elution curve of each of the two trimethylsiloxyalkanes was compared to the area below the elution curve of the standard. The analyses were made on chromatograph equipped with thermal conductivity detector on a column filled with 8.8% silicon elastomer Sil E on Chromaton N (carrier gas was hydrogen, column temperature was programmed).

The reaction conditions chosen enabled the relative reaction constants, k_{rel} , to be determined from equation (2)

$$k_{rel} = \frac{k_1}{k_2} = \frac{\log A/A_t}{\log B/B_t}, \quad (2)$$

in which A , B , and A_t , B_t , respectively, are the areas of the elution curves of the trimethylsiloxyalkane above that of the standard at the beginning of the reaction and at time t during the course of the reaction. The relative rate constants were determined as the average of at least 10 values, the relative confidence interval¹⁴ of which did not exceed 5%. The relative rate constants with respect to trimethylsiloxyethane are summarized in Table I.

RESULTS AND DISCUSSION

The relative rate constants of the ethylamine catalysed methanolysis of trimethylsiloxyalkanes $R(CH_2)_nOSi(CH_3)_3$ (Table I) are essentially equal to the relative constants k^B (equation (1), because methanolysis under neutral conditions is relatively slow. The constants k_{rel} follow equation (3), where σ^* and E_s are Taft's polar and steric constants, respectively, of the $(CH_2)_nR^{15}$ group, and r is the correlation coefficient. The important influence of the steric effect on the reaction site (the Si

$$\log k_{rel} = \rho^*(\sigma^* + 0.10) + \delta(E_s + 0.07) + c \quad (3)$$

$$\log k_{rel} = \log k^{ROSi(CH_3)_3} - \log k^{C_2H_5OSi(CH_3)_3},$$

$$\rho^* = 4.64, \quad \delta = 0.62, \quad c = -0.07, \quad r = 0.96.$$

atom) is similar to that in the base-catalysed hydrolysis of the structurally similar esters of acetic acid ($\delta = 0.644$ ref.¹⁶). The positive constant ρ^* is consistent with the mechanism of solvolysis recently discussed by Boe⁶. This high value of ρ^* is consistent with the high polarizability of the Si—O bond; this value is apparently augmented by the fact the $(CH_2)_nR$ group can, because of its location on the oxygen, influence in the same manner both X—Si bond-making and also Si—O bond-breaking in transition state (I).

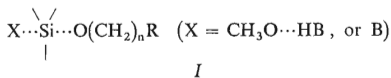


TABLE I

Relative Rate Constants of Base-Catalysed Methanolysis of Trimethylsiloxyalkanes $R(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$

R	n						
	0	1	2	3	4	5	6
CH ₃	—	1.00 ^a	0.60 ^a	0.53 ^a	0.54	0.52	0.53 ^b
(CH ₃) ₃ C	0.010 ^{a,c}	0.049 ^a	0.52	0.52	0.51	—	—
(CH ₃) ₃ Ge	—	0.30	0.54	0.52	0.53	—	—
(CH ₃) ₃ Si	—	0.15 ^d	0.49	0.50	0.52	0.50	0.49
C ₆ H ₅	—	1.48 ^a	—	—	—	—	—
CH ₂ =CH	—	3.27	—	—	—	—	—
CH ₃ O	—	—	2.10 ^a	0.87	0.52	0.55	0.51
Cl	—	—	3.23 ^a	0.82	0.56	0.51	0.52

^a These values were also considered in correlation (3); ^b $n = 7$, 0.52; $n = 8$, 0.49; ^c 0.078 for $(\text{CH}_3)_2\text{HC}$ (see footnote^a); ^d 0.11 for $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{Si}$.

(If the group were positioned on silicon, it could not simultaneously *e.g.* facilitate both bond-making and bond-breaking.)

This knowledge of the relative importance of the steric and the polar effects now makes possible an interpretation of k_{rel} for those compounds in which the proposed intramolecular interactions can occur. An interaction $(p - d)_\sigma$ was considered to be the cause of the cyclization of the $(\text{C}_2\text{H}_5\text{O})_m(\text{CH}_3)_{3-m}\text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ compounds¹⁰ and it is thus also possible for this interaction to occur in the analogous $\text{X}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ [for $\text{X} = (\text{CH}_3)_3\text{M}$ ($\text{M} = \text{Si}, \text{Ge}$), $0 \rightarrow \text{M}$; for $\text{X} = \text{OCH}_3$ or Cl , $\text{X} \rightarrow \text{Si}$] compounds. The relative basicity of the oxygen in $\text{X}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($\text{X} = (\text{CH}_3)_3\text{M}$, Cl , $n > 2$) compounds obtained as the shift of the IR absorption band $\nu(\text{OH})$ of phenol during Lewis acid-base interaction with these compounds, does not differ from that in the corresponding $\text{R}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($\text{R} = \text{CH}_3$, $\text{C}(\text{CH}_3)_3$) compounds¹⁷. The basicity, however, is not such a sensitive means of indication of $(p - d)_\sigma$ interaction as is the nucleophilic attack on the atom adjacent to the oxygen¹⁸ (in this case Si). However, the essentially identical values of k_{rel} of the $\text{X}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ compounds with $\text{X} = (\text{CH}_3)_3\text{M}$, Cl , OCH_3 and $\text{R}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($\text{R} = \text{alkyl}$) compounds with $n > 2$ (Table I) do not indicate the presence of a coordination interaction. In the event of $(p - d)_\sigma$ interactions it might have been expected that the increased electron density at silicon would significantly

decrease nucleophilic bond-making at silicon; a lesser effect would be observed for bond-breaking.

The values of k_{rel} of the $(CH_3)_3MCH_2OSi(CH_3)_3$ ($M = Si, Ge$) and $(CH_3)_3.CCH_2OSi(CH_3)_3$ compounds are not identical (as they were for the compounds where $n > 2$). The interpretation of the order of their reactivities ($C < Si < Ge$; Table I) is more difficult because the E_s constants for the $(CH_3)_3MCH_2$ -groups were not determined because of the decomposition of the $(CH_3)_3MCH_2CO_2R$ esters during acid-catalysed hydrolysis¹⁹. The $(CH_3)_3MCH_2-$ ($M = Si, Ge$) groups are generally considered strong electron donors^{20,21}, stronger than the $(CH_3)_3.CCH_2$ -group. The higher electron donor ability of $(CH_3)_3MCH_2$ -groups in comparison with the $(CH_3)_3CCH_2$ -group would be expected to cause a lower reactivity of $(CH_3)_3MCH_2OSi(CH_3)_3$ compounds. However, the contrary is true. Therefore, the question arises of whether the order of reactivities $C < Si < Ge$ can indeed be satisfactorily explained by the different steric effect of the $(CH_3)_3MCH_2$ - and $(CH_3)_3C.CCH_2$ -groups. The steric effect could modify reactivities based on the inductive effect in two ways: 1) the application of the overall similarity between constant E_s and Van der Waal's radius would produce an additional decrease of k_{rel} for $(CH_3)_3.MCH_2OSi(CH_3)_3$ compounds, and 2) the relatively higher value of k_{rel} of these compounds could be brought about only by the relatively smaller steric effect of the $(CH_3)_3MCH_2$ -groups, as was pointed out *e.g.* in the reactions of alcohols $(CH_3)_3.MCH_2OH$ ^{22,23}. Considering the inductive effect of both $(CH_3)_3MCH_2$ -groups to be the same ($\sigma^* = 0.26$), the determination of the E_s constants for these groups from Eq. (3) leads to the unlikely values of -0.09 (Si) and $+0.40$ (Ge). It thus follows that the relatively higher k_{rel} of $(CH_3)_3MCH_2OSi(CH_3)_3$ cannot be explained solely on the basis of the relatively smaller steric effect of the $(CH_3)_3MCH_2$ -groups; these values are higher than can be assumed on the basis of the electron donor abilities of the $(CH_3)_3MCH_2$ -groups as exhibited in $(CH_3)_3MCH_2CO_2X$ ($X = R^{15}, H^{24,25}$) and p - $(CH_3)_3MCH_2-C_6H_4CO_2H$ ²⁵ compounds. It would be consistent with the mechanism of base-catalysed methanolysis to interpret these results by means of an intramolecular interaction between the oxygen and atom M, which would lead to a decrease of the electron density on the silicon of the $(CH_3)_3SiO$ -group in the ground state of these compounds. The same interpretation could also be applied in the case of the $C_2H_5(CH_3)_2SiCH_2OSi(CH_3)_3$ compound.

REFERENCES

1. Akerman E.: Acta Chem. Scand. 10, 298 (1956).
2. Akerman E.: Acta Chem. Scand. 11, 373 (1957).
3. Schowen R. L., Latham K. S.: J. Am. Chem. Soc. 88, 3795 (1966).
4. Schowen R. L., Latham K. S.: J. Am. Chem. Soc. 89, 4677 (1967).
5. Humffray A. A., Ryan J. J.: J. Chem. Soc. B 1969, 1138.
6. Bøe B.: J. Organometal. Chem. 43, 275 (1972).

7. Voronkov M. G., Fešin V. O., Mironov V. F., Michajlanc S. A., Gar T. K.: *Ž. Obšč. Chim.* **41**, 2211 (1971).
8. Pola J., Schraml J., Chvalovský V.: *This Journal* **38**, 3158 (1973).
9. Rivière P., Satge J.: *J. Organometal. Chem.* **49**, 157 (1973).
10. Pola J., Bažant V., Chvalovský V.: *This Journal* **38**, 1528 (1973), and references included therein.
11. Bažant V., Chvalovský V., Rathouský J.: *Organosilicon Compounds*, Vol. 2. Academia, Prague 1965.
12. Bažant V., Chvalovský V., Rathouský J.: *Organosilicon Compounds*, Vol. 4. Inst. of Chemical Process Fundamentals, Czechoslov. Acad. of Sci., Prague 1973.
13. Pola J., Chvalovský V.: *This Journal* **38**, 1674 (1973).
14. Eckschlager K.: *Chyby chemických rozborů*. Published by Státní nakladatelství technické literatury, Prague 1961.
15. Taft R. W. in *Steric Effects in Organic Chemistry* (M. S. Newman, Ed.). Wiley, New York 1956.
16. Hancock C. K., Yager B. J., Falls C. P., Schreck J. O.: *J. Am. Chem. Soc.* **85**, 1297 (1963).
17. Pola J., Chvalovský V.: Unpublished results.
18. Pola J., Chvalovský V.: *This Journal* **39**, 2247 (1974)
19. Gold J. R., Sommer L. H., Whitmore F. C.: *J. Am. Chem. Soc.* **70**, 2874 (1948).
20. Jarvie A. W. P.: *Organometal. Chem. Rev.* **A 6**, 153 (1970).
21. Ebsworth E. A. V. in *Organometallic Compounds of the Group IV Elements*, (A. G. Mac Diarmid, Ed.), Vol. I, Part I, Ch. 1. M. Dekker, New York 1968.
22. Krumpolc M., Bažant V., Chvalovský V.: *This Journal* **38**, 711 (1973).
23. Pola J., Bažant V., Chvalovský V.: *This Journal* **37**, 3885 (1972).
24. Sommer L. H., Gold J. R., Goldberg G. M., Marans N. S.: *J. Am. Chem. Soc.* **71**, 1509 (1949).
25. Bott R. W., Eaborn C., Pande K. C., Swaddle T. W.: *J. Chem. Soc.* **1962**, 1217.