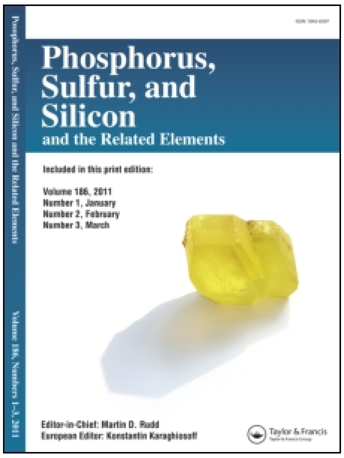

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CONTRIBUTIONS TO THE CHEMISTRY OF SILICON-SULPHUR COMPOUNDS 62. THE ALCOHOLYSIS AND PHENOLYSIS OF ISOBUTYL(ISOPROPOXY)SILANETHIOLS $^{i}Bu_{<i>n</i>}(^{<i>i</i>}PrO)_{3-n}SiSH$ CATALYZED WITH SUBSTITUTED PYRIDINES

Jerzy Pikies[a]; Wieslaw Wojnowski[a]
[a] Department of Chemistry, Technical University of Gdansk, Gdańsk, PL, Poland

To cite this Article Pikies, Jerzy and Wojnowski, Wieslaw(1993) 'CONTRIBUTIONS TO THE CHEMISTRY OF SILICON-SULPHUR COMPOUNDS 62. THE ALCOHOLYSIS AND PHENOLYSIS OF ISOBUTYL(ISOPROPOXY)SILANETHIOLS $^{i}Bu_{<i>n</i>}(^{<i>i</i>}PrO)_{3-n}SiSH$ CATALYZED WITH SUBSTITUTED PYRIDINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 78: 1, 133 — 140

To link to this Article: DOI: 10.1080/10426509308032429

URL: http://dx.doi.org/10.1080/10426509308032429

Phosphorus, Sulfur, and Silicon, 1993, Vol. 78, pp. 133–140
Reprints available directly from the publisher
Photocopying permitted by license only

CONTRIBUTIONS TO THE CHEMISTRY OF SILICON-SULPHUR COMPOUNDS 62.†

THE ALCOHOLYSIS AND PHENOLYSIS OF ISOBUTYL(ISOPROPOXY)SILANETHIOLS $^i\mathrm{Bu}_n(^i\mathrm{PrO})_{3-n}\mathrm{SiSH}$ CATALYZED WITH SUBSTITUTED PYRIDINES

JERZY PIKIES and WIESŁAW WOJNOWSKI
Department of Chemistry, Technical University of Gdańsk,
PL 80-952 Gdańsk, Poland

(Received November 2, 1992)

The reaction rates of alcoholysis and phenolysis of isosteric silanethiols $^i\mathrm{Bu}_n(^i\mathrm{PrO})_{3-n}\mathrm{SiSH}$ $n = 0 \div 3$ catalyzed by pyridine and its moderately basic derivatives in acetonitrile solutions were measured under pseudo-first order conditions. The reactions are first order in respect to pyridine, to alcohol and to thiol. A positive Hammett correlation with ρ value of 0.616 was obtained in the case of phenolysis of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ and with ρ value of 0.881 in the case of $^i\mathrm{Bu}_3\mathrm{SiSH}$. A mechanism of general base catalysis was postulated. The spontaneous alcoholysis seems also to proceed according to general base catalysis. The catalytic rate constants k_c for methanolysis catalyzed by pyridine fall in sequence:

$$(^i\mathrm{PrO})_3\mathrm{SiSH} > {}^i\mathrm{Bu}(^i\mathrm{PrO})_2\mathrm{SiSH} \geqslant {}^i\mathrm{Bu}_2(^i\mathrm{PrO})\mathrm{SiSH} > {}^i\mathrm{Bu}_3\mathrm{SiSH}.$$

The rate constants for spontaneous methanolysis follow the sequence:

$${}^i\mathrm{Bu}(^i\mathrm{PrO})_2\mathrm{SiSH} > {}^i\mathrm{Bu}_2(^i\mathrm{PrO})\mathrm{SiSH} > {}^i\mathrm{Bu}_3\mathrm{SiSH} \geqslant (^i\mathrm{PrO})_3\mathrm{SiSH}$$

The anomeric effect operating on silicon center in the ground state and (or) in the transition state (steroelectronic catalysis) seem to be responsible for these reactivity trends.

Key words: Silicium; silanethiols; alcoholysis; catalysis.

INTRODUCTION

It is known that the protolytic splitting of Si—SR bond is subject to basic catalysis.[2,3] We have found that the fast cleavage of Si—S bonds of isosteric silanethiols $^i\mathrm{Bu}_n(^i\mathrm{PrO})_{3-n}\mathrm{SiSH}$ $n = 0 \div 3$ in the presence of imidazoles is a result of nucleophilic catalysis.[4] The properties of these silanethiols[5] and the reactivity trends[4] are best explained in terms of the anomeric effect involving silicon center.[6,7] The catalytic influence of substituted pyridines and azoles on the alcoholysis and phenolysis of trialkoxysilanethiols in benzene solution was investigated and imidazole was proved to be the most effective one.[8,9] In the case of medium basic pyridines as catalysts the reaction rates of ethanolysis of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ are dependent only on pK_a and independent on the steric hindrance of catalysts.[8]

In this paper we present the results of kinetic studies of alcoholysis and phenolysis of isosteric silanethiols $^i\mathrm{Bu}_n(^i\mathrm{PrO})_{3-n}\mathrm{SiSH}$ in the presence of pyridine (Py) and its derivatives of medium basicity and of different steric hindrance in order to distin-

---

†For Part 61 see Reference 1.

guish between base and nucleophilic catalysis which can operate in this case. The reaction kinetics were measured mainly in the acetonitrile solutions, because the solute—solvent and solute—solute interactions in this system are relative simple and the kinetic outcomes are easier to understand than in benzene solutions.[4]

RESULTS

The reactions of isosteric silanethiols $^t\mathrm{Bu}_n(^t\mathrm{PrO})_{3-n}\mathrm{SiSH}$, $n = 0 \div 3$, with alcohols (R = Me, Et,) and with phenols ($R = p\mathrm{X}\text{-}\mathrm{C_6H_4}$, X = Me, H, Cl, $\mathrm{NO_2}$) in the presence of pyridines in MeCN solution at room temperature proceed smoothly according to Equation (1).

$$^t\mathrm{Bu}_n(^t\mathrm{PrO})_{3-n}\mathrm{SiSH} + \mathrm{ROH} \xrightarrow{\mathrm{cat}} {}^t\mathrm{Bu}_n(^t\mathrm{PrO})_{3-n}\mathrm{SiOR} + \mathrm{H_2S} \qquad (1)$$

Ethanolysis and phenolysis of $^t\mathrm{Bu_3SiSH}$ were always accompanied by hydrolysis and $^t\mathrm{Bu_3SiOH}$ was found (≈ 20% of $^t\mathrm{Bu_3SiOR}$).

1. *Spontaneous Alcoholysis*

The uncatalysed alcoholysis of $^t\mathrm{Bu}_n(^t\mathrm{PrO})_{3-n}\mathrm{SiSH}$ in MeCN solution (Figure 1) exhibits the external order in respect to ROH ≈ 2.2 and is first order in respect to $^t\mathrm{Bu}_n(^t\mathrm{PrO})_{3-n}\mathrm{SiSH}$ (k_0 values were calculated from the linear relationships ln $c(^t\mathrm{Bu}_n(^t\mathrm{PrO})_{3-n}\mathrm{SiSH})$ vs. reaction time). Methanolysis of $^t\mathrm{Bu_3SiSH}$ in MeCN solution (Figure 1d) is about 5-times faster than ethanolysis (Figure 1e). MeCN

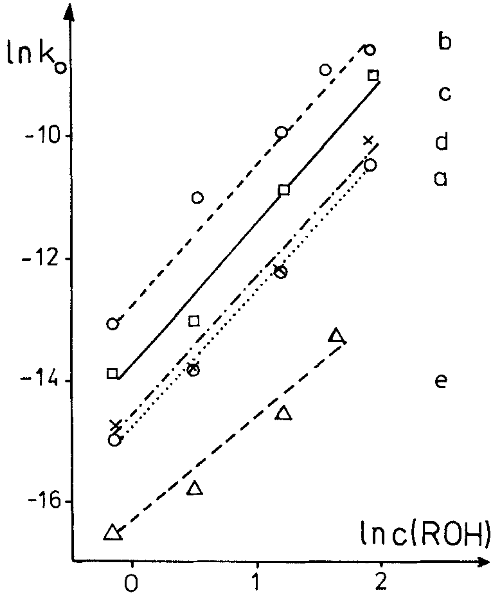

FIGURE 1 Plots of ln k_0 vs. ln c(ROH) for spontaneous alcoholysis of $^t\mathrm{Bu}_n(^t\mathrm{PrO})_{3-n}\mathrm{SiSH}$ (0.156 M) in MeCN solution: a) $(^t\mathrm{PrO})_3\mathrm{SiSH}$ (MeOH), b) $^t\mathrm{Bu}(^t\mathrm{PrO})_2\mathrm{SiSH}$ (MeOH), c) $^t\mathrm{Bu}_2(^t\mathrm{PrO})\mathrm{SiSH}$ (MeOH), d) $^t\mathrm{Bu_3SiSH}$ (MeOH), e) $^t\mathrm{Bu_3SiSH}$ (EtOH).

(compared to C_6H_6) exerts little effect upon the uncatalyzed process, for ^{t}Bu$_3$SiSH and for 3.43 M MeOH in C_6H_6 solution $k_0 = 5 \cdot 10^{-6}\ s^{-1}$, in MeCN solution $k_0 = 4.3 \cdot 10^{-6}\ s^{-1}$.

The reactivities of isosteric silanethiols in MeCN solution fall in sequence (k_{rel} for 3.43 M MeOH in parentheses): ^{t}Bu(^{i}PrO)$_2$SiSH (13) > ^{t}Bu$_2$(^{i}PrO)SiSH (4.9) > ^{t}Bu$_3$SiSH (1.2) ≥ (^{i}PrO)$_3$SiSH (1).

2. *Alcoholysis and Phenolysis Catalyzed by Moderately Basic Pyridines*

The catalytic rate constants k_c for alcoholysis were calculated assuming that the uncatalyzed process (k_0) is a parallel pseudo-first-order reaction. The reaction rates of spontaneous alcoholysis in this system were taken into account because they are comparable to the rates of catalyzed reactions, at the low concentrations of catalysts especially.

Alcoholysis of ^{t}Bu$_n$(^{i}PrO)$_{3-n}$SiSH in MeCN or C_6H_6 solution is first order in respect to thiol—the linear regression coefficient of ln c(^{t}Bu$_n$(^{i}PrO)$_{3-n}$SiSH) vs. time generally > 0.99, first order in respect to Py (external) (Figure 2a–2d) and first order in respect to ROH (external) (Figure 3). Methanolysis of (^{i}PrO)$_3$SiSH in MeCN solution (Figure 3a) is about 5-times faster than ethanolysis (Figure 3e). The comparison of k_c values in MeCN and benzene clearly indicates an accelerating effect of MeCN on the alcoholysis catalyzed with pyridine. For ^{t}Bu$_3$SiSH (cat. = Py) and for 3.43 M MeOH in C_6H_6 solution, $k_c = 0.43 \cdot 10^{-4}\ s^{-1}\ mol^{-1}\ dcm^3$, in MeCN solution $k_c = 12 \cdot 10^{-4}\ s^{-1}\ mol^{-1}\ dcm^3$.

The k_c values for methanolysis (cat. = Py) in MeCN solution follow the sequence (k_{rel} for 3.43 M MeOH in parentheses): (^{i}PrO)$_3$SiSH (3.0) > ^{t}Bu(^{i}PrO)$_2$SiSH (2.7) > ^{t}Bu$_2$(^{i}PrO)SiSH (2.1) > ^{t}Bu$_3$SiSH (1.0). The reaction rates for phenolysis of

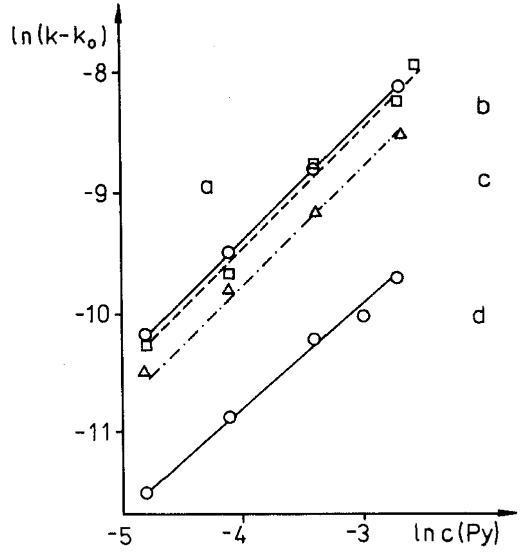

FIGURE 2 Plots of ln($k - k_0$) vs. ln c(Py) for methanolysis of ^{t}Bu$_n$(^{i}PrO)$_{3-n}$SiSH in MeCN solution (cat. = Py, MeOH = 3.43 M): a) (^{i}PrO)$_3$SiSH (0.026 M), b) ^{t}Bu(^{i}PrO)$_2$SiSH (0.156 M), c) ^{t}Bu$_2$(^{i}PrO)SiSH (0.156 M), d) ^{t}Bu$_3$SiSH (0.026 M).

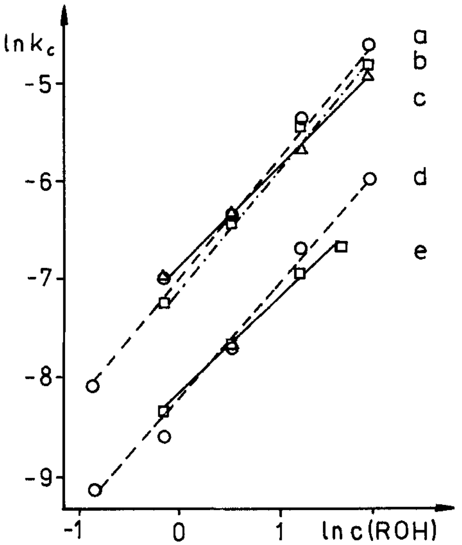

FIGURE 3 Plots of ln k_c vs. ln c(ROH) for alcoholysis of ^{t}Bu$_n$(^{i}PrO)$_{3-n}$SiSH (0.026 M in MeCN) catalyzed with Py: a) (^{i}PrO)$_3$SiSH, MeOH, Py = $16.8 \cdot 10^{-3}$ M. b) ^{t}Bu(^{i}PrO)$_2$SiSH, MeOH, Py = $16.8 \cdot 10^{-3}$ M. c) ^{t}Bu$_2$(^{i}PrO)SiSH, MeOH, Py = $16.8 \cdot 10^{-3}$ M. d) ^{t}Bu$_3$SiSH, MeOH, Py = $16.8 \cdot 10^{-3}$ M. e) (^{i}PrO)$_3$SiSH, EtOH, Py = $33.6 \cdot 10^{-3}$ M.

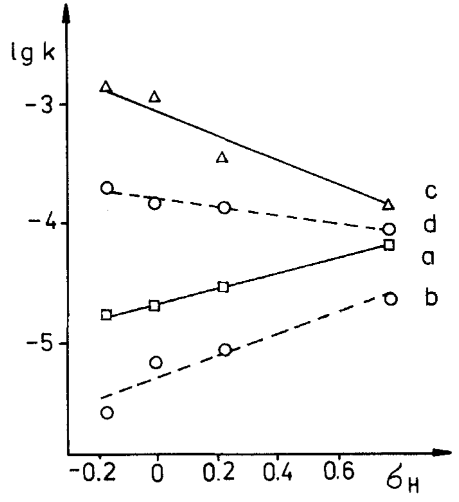

FIGURE 4 Plots of lg k vs. Hammet σ_H constants for catalyzed phenolysis of ^{t}Bu$_n$(^{i}PrO)$_{3-n}$SiSH (0.078 M) in MeCN solution, (p-XC$_6$H$_4$OH = 1.73 M): a) (^{i}PrO)$_3$SiSH, Py = $50 \cdot 10^{-3}$ M, b) ^{t}Bu$_3$SiSH, Py = $50 \cdot 10^{-3}$ M, c) (^{i}PrO)$_3$SiSH, N-MeIm = $8.4 \cdot 10^{-3}$ M, d) ^{t}Bu$_3$SiSH, N-MeIm = $8.4 \cdot 10^{-3}$ M.

(^{i}PrO)$_3$SiSH and ^{t}Bu$_3$SiSH respectively in presence of Py (Figure 4a and b) and in the presence of N-methylimidazole (N-MeIm) (Figure 4c and d) are dependent on the nature of the *para* substituents of phenols. The reaction rate constants were not corrected for uncatalyzed reaction, because the uncatalyzed process was very slow in this case.

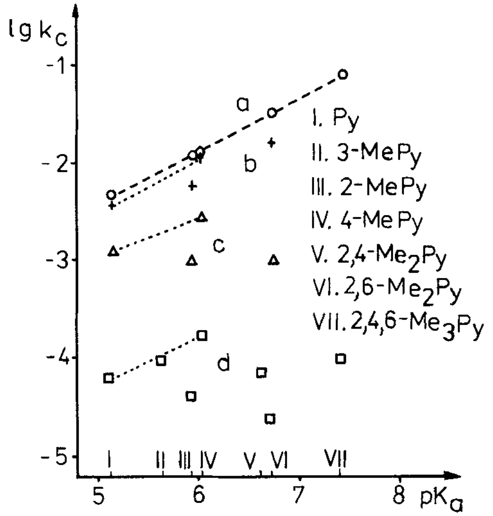

FIGURE 5 Plots of lg k_c vs. pK_a of catalysts for methanolysis of ^{t}Bu$_n$(^{i}PrO)$_{3-n}$SiSH (MeOH = 3.43 M): a) (^{i}PrO)$_3$SiSH 0.026 M, MeCN, b) ^{t}Bu(^{i}PrO)$_2$SiSH 0.026 M, MeCN, c) ^{t}Bu$_3$SiSH 0.026 M, MeCN, d) ^{t}Bu$_3$SiSH 0.21 M, C_6H_6.

Positive Hammett correlations with ρ value of 0.881 for (^{i}PrO)$_3$SiSH and ρ value of 0.616 for ^{t}Bu$_3$SiSH were obtained for phenolysis in the presence of pyridine in MeCN solution. A positive Hammett correlation for ethanolysis of (^{i}PrO)$_3$SiSH in C_6H_6 solution (cat. = Py) can be also deduced.[9] The rate constants for phenolysis in the presence of *N*-MeIm result negative Hammett correlations with ρ value of -1.11 for (^{i}PrO)$_3$SiSH and ρ value of -0.323 for ^{t}Bu$_3$SiSH (Figure 4c and d).

Figure 5 shows the relationships lg k_c vs. pK_a of catalysts for methanolysis of (^{i}PrO)$_3$SiSH in MeCN solution (5a), for ^{t}Bu(^{i}PrO)$_2$SiSH in MeCN solution (5b), for ^{t}Bu$_3$SiSH in MeCN solution (5c) and for ^{t}Bu$_3$SiSH in C_6H_6 solution (5d). The introduction of methyl groups in α positions in pyridine ring causes an increased catalytic efficiency during alcoholysis of (^{i}PrO)$_3$SiSH and in some extent during alcoholysis of ^{t}Bu(^{i}PrO)$_2$SiSH in MeCN solution. The same trend was reported for ethanolysis of (^{i}PrO)$_3$SiSH in benzene solution.[8] The steric hindrance of one or two α-methyl groups is not substantial and the k_c values differ approximately according to the pK_a values of these amines. In the case of ^{t}Bu$_3$SiSH the introduction of α-Me groups decreases the k_c values despite of increased basicity of the catalyst both in MeCN and in benzene solution.

DISCUSSION

Data concerning the structure of MeOH—MeCN system given by Uniquac Associated Solution Theory[10,11] and IR studies[12] indicate that in this system the monomeric MeOH exists at very low concentration and that dominating form of MeOH up to the concentration of MeOH 1.72 M is the associate MeOH—MeCN. The concentration of $(\text{MeOH})_n \cdot (\text{MeCN})_m$, ($n > 1$) increases however with increasing MeOH concentration. Taking into account the external order in respect to methanol for uncatalyzed process in MeCN solution > 2 it seems therefore reliable that the reactive form is $(MeOH)_n \cdot (MeCN)_m$ where $n > 1$, or that two associates MeOH—MeCN are acting in the activated complex. It means that the second molecule of MeOH is acting as a base catalyst.

The important problem in the case of reaction catalyzed by pyridines is to distinquish between two possible mechanisms:

a. Nucleophilic catalysis which assumes $[{}^{t}Bu_n({}^{i}PrO)_{3-n}SiNC_5H_5]^+SH^-$ as a reactive intermediate.
b. General base catalysis assuming proton abstracting from alcohol or phenol in the rate determining step.

Investigation of steric effects on the efficiency of catalyst, known as a test for nucleophilic catalysis[13] gives ambiguous results. The isosteric silanethiols show different susceptibility to steric hindrance on the catalyst; ${}^{t}Bu_3SiSH$ is the most susceptible and the reaction shows features of nucleophilic catalysis, $({}^{i}PrO)_3SiSH$ is not susceptible and the reaction shows features of a general base catalysis. It is known that general base catalysis is also influenced by steric hindrance on the catalyst.[14] Thus this observation is in agreement with a mechanism of nucleophilic catalysis and with general base catalysis as well.

Acetonitrile exerts an accelerating effect upon the catalyzed reaction. It accelerates strongly the formation of acetyl imidazolium or pyridonium salts, which are the reactive intermediates in nucleophilic catalyzed hydrolysis or aminolysis of acetyl anhydride.[15] It accelerates the Menschutkin reaction[16,17] which is similar to the formation of reactive intermediate in mechanism a. From the other side the activated complex in mechanism b with structure of trigonal bipyramide is more polar than substrates and therefore the reaction according to mechanism b can also be accelerated by more polar acetonitrile. Thus the acceleration with MeCN of catalyzed alcoholysis speaks on favour of mechanism a and b as well. On the other hand the alcoholysis catalyzed by medium basic pyridines in MeCN solution exhibits substantial differences in kinetic relationships compared to the alcoholysis of ${}^{t}Bu_n({}^{i}PrO)_{3-n}SiSH$ catalyzed by *N*-MeIm which is known to be nucleophilic catalyzed.[4] These differences are:

1. The k_c values ratio for methanolysis vs. ethanolysis (cat. = Py) is ≈ 5 but this ratio for imidazole (Im) or *N*-MeIm catalyzed alcoholysis is ≈ 2.[4]
2. The phenolyses catalyzed by Py show positive Hammett correlations but in the presence of *N*-MeIm negative ones.
3. The methanolysis in the presence of pyridines is first-order but in the presence of Im or *N*-MeIm, respectively, is about zero-order in respect to MeOH.[4]

Taking into account the factors determining the stability of proposed reactive intermediate $[{}^{t}Bu_n({}^{i}PrO)_{3-n}SiNC_5H_5]^+SH^-$ compared to the related intermediates with stronger nucleophiles Im or *N*-MeIm (see Reference 15 for detailed discussion) the reaction order in respect to alcohol in the case of nucleophilic catalysis by Py should be zero.

Thus, the general base catalysis appears to be more probable as a mechanistic model to explain the outcome of the alcoholysis in the presence of medium basic pyridines. The arguments mentioned in p.1 and p.2 speak also on favour of a base catalysis.

The first order in respect to Py and to $^{t}Bu_n(^{i}PrO)_{3-n}SiSH$ implies, that the pyridinium silanothiolate formation is of no importance for the kinetic of this system. Moreover it implies that the hydrogen bonded complex $^{t}Bu_n(^{i}PrO)_{3-n}SiSH$—Py is of similar catalytic activity as free Py or that this complex is the kinetically significant form of catalyst (more probably).

The introduction of electronegative ^{i}PrO groups in place of isosteric ^{t}Bu groups does not significantly change the nature of the Si—S bond in $^{t}Bu_n(^{i}PrO)_{3-n}SiSH$ and the polar effects of alkoxygroups should not be significant in determining the reactivities of these compounds.[4,5]

The reactivity trends for spontaneous alcoholysis and for alcoholysis catalyzed with Im or *N*-MeIm[4] point out $^{t}Bu(^{i}PrO)_2SiSH$ as a most reactive one. For the reaction catalyzed with pyridine $(^{i}PrO)_3SiSH$ is the most reactive one. This phenomena seem to be of steric origin and were understandable regarding the smaller steric hindrance of $^{t}Bu_n(^{i}PrO)_{3-n}Si$ moieties ($n = 0 \div 2$) compared with $^{t}Bu_3Si$ moiety caused by hindered rotation of ^{i}PrO—groups due to the anomeric interaction $p_\pi(O) \rightarrow \sigma^*(Si—O)$, $p_\pi(S) \rightarrow \sigma^*(Si—O)$ and $p_\pi(O) \rightarrow \sigma^*(Si—S)$. These interactions can take place in $(^{i}PrO)_3SiSH$,$^{t}Bu(^{i}PrO)_2SiSH$ and $^{t}Bu_2(^{i}PrO)SiSH$ as well.[15,18] Kinetic data obtained for methanolysis of $^{t}Bu_n(^{i}PrO)_{3-n}SiSH$ catalyzed by substituted pyridines (Figure 5) are in good agreement with above explanation. $^{t}Bu_3SiSH$ with only weak anomeric interactions $p_\pi(S) \rightarrow \sigma^*(Si—C)$ is very susceptible to steric hindrance on the catalyst. $(^{i}PrO)_3SiSH$ with strong anomeric interactions $p_\pi(O) \rightarrow \sigma^*(Si—O)$, $p_\pi(S) \rightarrow \sigma^*(Si—O)$ and $p_\pi(O) \rightarrow \sigma^*(Si—S)$ is not susceptible to steric hindrance of catalyst. $^{t}Bu(^{i}PrO)_2SiSH$ with strong mutual anomeric interactions $p_\pi(O) \rightarrow \sigma(Si—0)$ is moderately susceptible to steric hindrance on the catalyst.

We would like to point out here that one or more alkoxy substituents can additionally decrease the energy of pentavalent transition states ("stereoelectronic catalysis"), if these substituents are at the basal positions of trigonal bipyramide, such as was suggested for hydrolysis of phosphate esters.[19] Therefore the enhanced reactivity of silanethiols with at least one alkoxy substituent at silicon is understandable on this way.

EXPERIMENTAL

Solvents and reagents used in kinetic studies were prepared as described.[4,5] All runs were carried out as described.[4] The progress of reaction was monitored with GC.[4] The ionic strength of MeCN solutions was maintained by $4 \cdot 10^{-4}$ M LiCl. The kinetic investigations were performed at 21 ± 1°C under pseudo-first order conditions ($k = s^{-1}$ and $k_c = s^{-1}\ mol^{-1}\ dcm^3$).

ACKNOWLEDGEMENTS

The authors are grateful to the Polish Academy of Sciences (CPBP 01.13.3.6) for financial support. We are grateful to Dr. J. Zielkiewicz for carrying out Uniquac calculations.

LITERATURE CITED

1. Part 61. B. Becker, W. Wojnowski, K. Peters, E-M. Peters and H.G. v. Schnering, *Polyhedron*, **11**, 613 (1992).

2. R. Danielli and A. Ricci, *J. Chem. Soc., Perkin Trans. II*, 1471 (1972).
3. S. Kozuka and T. Kitamura, *Bull. Chem. Soc. Jpn.*, **52,** 3384 (1979).
4. J. Pikies and W. Wojnowski, *J. Organometal. Chem.*, **386,** 305 (1990).
5. J. Pikies and W. Wojnowski, *J. Organometal. Chem.*, **378,** 317 (1989).
6. Y. Apeloig and A. Stanger, *J. Organometal. Chem.*, **346,** 305 (1988).
7. A. Reed, C. Schade, P. v. Raque-Schleyer, P. Kamath and J. Chandrasekhar, *J. Chem. Soc., Chem. Commun.*, 67 (1988).
8. J. Pikies, K. Przyjemska and W. Wojnowski, *Z. Anorg. Allg. Chem.*, **551,** 209 (1987).
9. K. Przyjemska and W. Wojnowski, *Z. Anorg. Allg. Chem.*, **551,** 203 (1987).
10. J. Nagata, *Fluid Phase Equilibria*, **19,** 153 (1985).
11. J. Nagata, *Thermochim. Acta*, **157,** 95 (1990).
12. S. Mitra, *J. Chem. Phys.*, **36,** 3286 (1962).
13. W. Stańczyk and J. Chojnowski, *J. Organometal. Chem.*, **117,** 219 (1976).
14. M. Akiyama, Y. Hara and M. Tanabe, *J. Chem. Soc., Perkin Trans. II*, 281 (1978).
15. A. Fersht and W. Jencks, *J. Am. Chem. Soc.*, **92,** 5432 (1970).
16. M. Abraham and P. Grellier, *J. Chem. Soc., Perkin Trans. II*, 1735 (1976).
17. E. Arnett and R. Reich, *J. Am. Chem. Soc.*, **102,** 5892 (1980).
18. J. Pikies and W. Wojnowski, *J. Organometal. Chem.*, **393,** 87 (1990).
19. D. Gorenstein, *Chem. Rev.*, **87,** 1047 (1987).