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The Alcoholysis and Phenolysis of Isosteric Isobutyl(isopropoxy)silanethiols Catalyzed by 4-Dimethylaminopyridine or Triethylamine*

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ABSTRACT

The reaction rates of alcoholysis of isosteric silanethiols $^{i}Bu_{n}(^{i}PrO)_{3-n}SiSH$, *n* = 0–3, *in the presence of the tertiary amines, 4-dimethylaminopyridine (DMAP) or triethylamine* (NEt_3), *were measured in benzene and in acetonitrile solutions under pseudo-first-order conditions. The catalytic activity of* NEt_3 *is low. The alcoholysis catalyzed by DMAP shows features of a nucleophilic catalysis. The protonation of the catalyst (DMAP or* NEt_3*) by silanethiols causes substantial deviations from pseudo-first-order kinetics. Phenolysis of silanethiols is effectively catalyzed by both DMAP and* NEt_3. *© 1997 John Wiley & Sons, Inc. Heteroatom Chem* **8***: 245–251, 1997.*

INTRODUCTION

The investigated reaction is a nucleophilic substitution at silicon catalyzed by other nucleophiles; for review, see Ref. [2]. Alcoholysis of Si–S bonds of isosteric silanethiols $^{i}Bu_{n}(^{i}PrO)_{3-n}SiSH$, $n = 0–3$, catalyzed by medium basic pyridines, shows features of a base catalysis [1,3,4], but the efficiencies of these catalysts are low. The fast alcoholysis of silanethiols in the presence of imidazoles is a result of a very efficient nucleophilic catalysis [5], and imidazole was proved to be the most effective catalyst [6] in alcoholysis of trialkoxysilanethiols in benzene solution. The kinetics outcomes depend on the reaction environment. The pyridines and imidazoles that were studied are exemplars of low basic heterocycles. The catalytic properties of more basic amines were not studied in more detail. Only the retarding effect of Et_3N on the alcoholysis of silanethiols catalyzed by imidazoles or pyridines [5] and the high catalytic efficiency of DMAP on the alcoholysis of $^{i}Bu_{n}(^{i}PrO)_{3-n}SiSH$ in benzene solution [6] were established.

In this article, we present and compare the results of kinetics studies on alcoholysis and phenolysis of isosteric silanethiols $^{i}Bu_{n}(^{i}PrO)_{3-n}SiSH$ in the presence of NEt_3 or the very efficient supernucleophilic catalyst, 4-dimethylaminopyridine (DMAP) [7,8]. Moreover, we have compared our results with the catalytic activity of a series of nucleophiles in the alcoholysis of diphenyldichlorosilane [9] and with the abilities of these nucleophiles in formation of silylonium salts of trimethylsilyl compounds with good leaving groups [10].

Silanethiols $^{i}Bu_{n}(^{i}PrO)_{3-n}SiSH$, $n = 0–3$, represent a series of isosteric compounds of increasing acidity with increasing number of ^{i}PrO groups [11] but with similar shapes of molecules. Since silanethiols have relatively high acidities, and the two catalysts are relatively strong bases, the interactions between catalyst and silanethiol (base and acid) can play a significant role. Therefore, this set of compounds offers the possibility to study these interactions and their influence on the kinetics outcomes of

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*Contributions to the chemistry of silicon-sulfur compounds 63 [1].

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alcoholysis of silanethiols. According to our knowledge, there are no literature data available about kinetics of a similar system.

RESULTS

Alcoholysis of $^{i}Bu_n(^{i}PrO)_{3-n}SiSH$ Catalyzed with DMAP

The reactions of isosteric silanethiols $^{i}Bu_n(^{i}PrO)_{3-n}SiSH$, $n = 0–3$, with alcohols and phenols (R = Me, Et, p-ClC_6H_4, p-MeC_6H_4, C_6H_5, p-$NO_2C_6H_4$) in the presence of DMAP at room temperature proceed according to Equation 1.

$$^{i}Bu_n(^{i}PrO)_{3-n}SiSH + ROH \xrightarrow{cat} {}^{i}Bu_n(^{i}PrO)_{3-n}SiOR + H_2S \quad (1)$$

The observed kinetics behavior depends on the acidity of the silanethiol. The alcoholysis of weakly acidic $^{i}Bu_3SiSH$ and $^{i}Bu_2(^{i}PrO)SiSH$ follows the pseudo-first-order formalism [the linear regression coefficients of ln $c(^{i}Bu_n(^{i}PrO)_{3-n}SiSH)$ vs. time being generally > 0.99], and the observed pseudo-first-order rate constants k_0 for methanolysis of 0.156 and 0.026 M solutions of either $^{i}Bu_3SiSH$ or $^{i}Bu_2(^{i}PrO)SiSH$ are the same within the accuracy of our measurements.

The slopes ln k_c vs. ln c(ROH) for $^{i}Bu_2(^{i}PrO)SiSH$ and for $^{i}Bu_3SiSH$ are shown in Figure 1; $k_c = k_0/c(\text{cat})$, k_0 = observed pseudo-first-order rate constant. The k_c values were not corrected for the possible concomitant occurrence of the uncatalyzed process; the uncatalyzed processes were slow compared to the catalyzed ones. The external order with respect to ROH in MeCN solution is slightly more than zero, and the rate differences between methanolysis and ethanolysis are about two-fold. The k_c values for methanolysis carried out in benzene solution depend substantially on the concentration of alcohol (slope e). The comparison of k_c values in MeCN and in benzene solution clearly indicates an accelerating effect of MeCN on the alcoholysis of these two silanethiols catalyzed by DMAP.

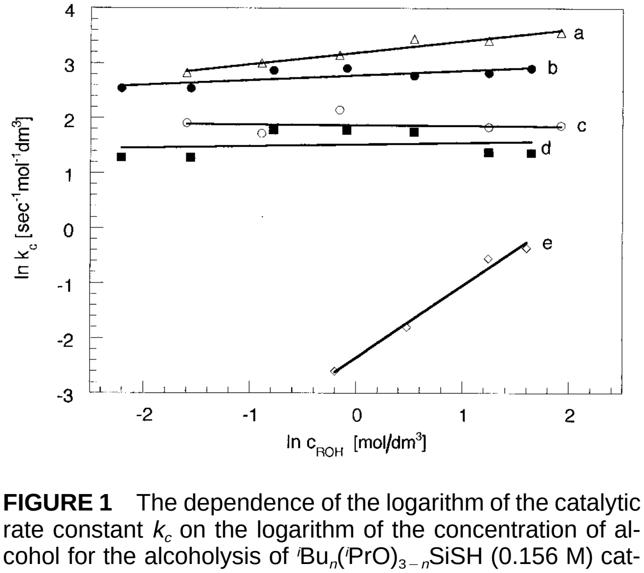

FIGURE 1 The dependence of the logarithm of the catalytic rate constant k_c on the logarithm of the concentration of alcohol for the alcoholysis of $^{i}Bu_n(^{i}PrO)_{3-n}SiSH$ (0.156 M) catalyzed with DMAP (1.25×10^{-3} M): (a) $^{i}Bu_2(^{i}PrO)SiSH$ MeOH in MeCN, (b) $^{i}Bu_2(^{i}PrO)SiSH$ EtOH in MeCN, (c) $^{i}Bu_3SiSH$ MeOH in MeCN, (d) $^{i}Bu_3SiSH$ EtOH in MeCN, and (e) $^{i}Bu_3SiSH$ 0.210 M MeOH in benzene.

The plots of k_0 vs. concentration of DMAP are shown in Figure 2; the reaction is first order (external) with respect to DMAP. Thus, the kinetics relationships and reaction rates of alcoholysis of these two silanethiols catalyzed by the relatively strongly basic DMAP (pK_a = 9.51) are very similar to those of the alcoholysis of $^{i}Bu_n(^{i}PrO)_{3-n}SiSH$, $n = 0–3$, catalyzed by the moderately basic imidazole (pK_a = 6.95) and by N-methylimidazole (pK_a = 7.33) [5]. The reaction rates can be described as follows:

$$v = k[\text{DMAP}]\,[^{i}Bu_n(^{i}PrO)_{3-n}SiSH] = k_0[^{i}Bu_n(^{i}PrO)_{3-n}SiSH] \quad (2)$$

Hence, it seems to be very probable that the mechanism of alcoholysis in the presence of DMAP is the same as that established for alcoholysis catalyzed by imidazoles and assumes the formation of quaternary silylonium salts $[^{i}Bu_n(^{i}PrO)_{3-n}Si–DMAP]^+\ SH^-$ as reactive intermediates; see Ref. [5] for a detailed discussion. The small deviations from

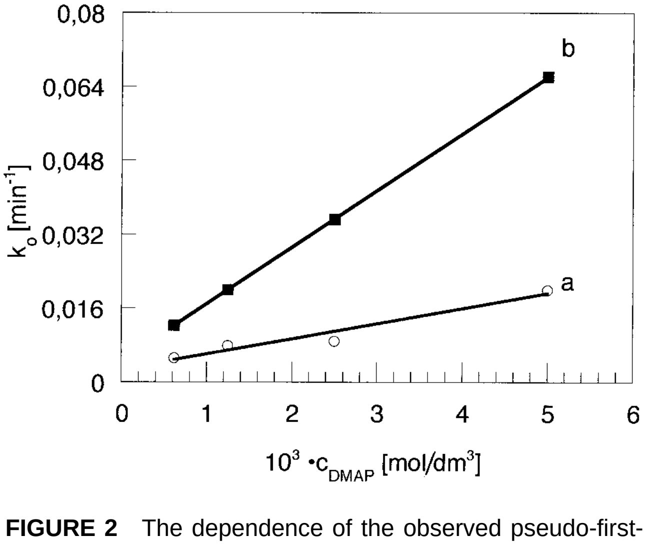

FIGURE 2 The dependence of the observed pseudo-first-order rate constant k_0 in MeCN solution on the initial concentration of DMAP—c(DMAP): (a) $^{i}Bu_3SiSH$ (0.026 M), MeOH (3.43 M) and (b) $^{i}Bu_2(^{i}PrO)SiSH$ (0.026 M), EtOH (3.43 M).

external zero order with respect to alcohol in this case (Figures 1a–1d) are probably due to parallel base catalysis. The first order with respect to DMAP implies that the hydrogen-bonded complex $^i\text{Bu}_n(^i\text{PrO})_{3-n}\text{SiSH}\cdots\text{DMAP}$ is of similar catalytic activity as free DMAP or (more probably) that the concentration of non-hydrogen-bonded DMAP is not significant. The conductivity studies imply that the dissociation of catalyst (Equation 3) is of minor importance for these two silanethiols.

The alcoholysis of the two most acidic thiols, $(^i\text{PrO})_3\text{SiSH}$ and $^i\text{Bu}(^i\text{PrO})_2\text{SiSH}$ [11], catalyzed by DMAP, does not follow the pseudo-first-order formalism, and therefore the time dependencies of concentration of these silanethiols at various MeOH concentrations are shown graphically, in Figure 3 for the $(^i\text{PrO})_3\text{SiSH}$ case and in Figure 4 for the $^i\text{Bu}(^i\text{PrO})_2\text{SiSH}$ case. It is evident that the slopes of c $[(^i\text{PrO})_3\text{SiSH}]$ vs. reaction time for reaction in MeCN represent close to zero-order kinetics with respect to the silanethiol (Figures 3a–3d) reaction. A similar trend is observed to some extent for the $^i\text{Bu}(^i\text{PrO})_2\text{SiSH}$ reaction (Figures 4a–4d).

These outcomes can be explained assuming the correctness of Equation 2 for both the $(^i\text{PrO})_3\text{SiSH}$ and $^i\text{Bu}(^i\text{PrO})_2\text{SiSH}$ reactions. The departures from first-order kinetics are best explained by significant protonation of DMAP according to Equation (3). Protonated DMAP shows no catalytic activity [6]. The protonation of DMAP should not be considered as a pre-equilibrium phenomenon because the fraction of unprotonated DMAP is a function of the nonconstant R_3SiSH concentration.

Conductivity studies of DMAP (1.25×10^{-3} M) in the presence of an excess of $^i\text{Bu}_n(^i\text{PrO})_{3-n}\text{SiSH}$ (0.156 M) in MeCN solution indicate the presence of charged species. The degree of dissociation of DMAP in the presence of $^i\text{Bu}_n(^i\text{PrO})_{3-n}\text{SiSH}$ in MeCN solution, β, falls in the following series: $(^i\text{PrO})_3\text{SiSH}(\beta = 0.37) > {}^i\text{Bu}(^i\text{PrO})_2\text{SiSH}(\beta = 0.17) > {}^i\text{Bu}_2(^i\text{PrO})\text{SiSH}(\beta = 0.04) > {}^i\text{Bu}_3\text{SiSH}(\beta = 0.014)$. $\beta = [\text{DMAPH}^+]/c(\text{DMAP})$ and $c(\text{DMAP})$ = initial con-

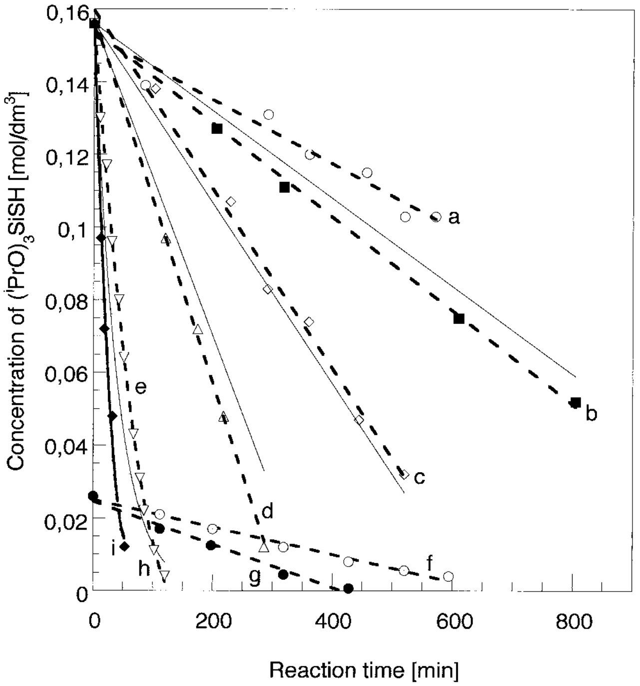

FIGURE 3 The dependence of concentration of $(^i\text{PrO})_3\text{SiSH}$ on the reaction time for methanolysis catalyzed with DMAP. Run e in benzene solution, the other in MeCN solution. Dashed lines: (a) DMAP 1.25×10^{-3} M, MeOH 3.43 M; (b) DMAP 1.50×10^{-3} M, MeOH 3.43 M; (c) DMAP 2.5×10^{-3} M, MeOH 3.43 M; (d) DMAP 3.75×10^{-3} M, MeOH 3.43 M, (e) DMAP 3.75×10^{-3} M, MeOH 3.43 M; (f) DMAP 1.25×10^{-3} M, MeOH 6.86 M; and (g) DMAP 1.25×10^{-3} M, MeOH 0.86 M. Continuous lines: (b,c,d) dependencies calculated according to Equation 4 using $k_c = 20$ min^{-1} mol^{-1} dm^3, $K_1 = 84$, $K_2 = 0.018$; (h) dependence calculated according to simple first-order reaction, $k_c = 20$ min^{-1} mol^{-1} dm^3, DMAP 1.25×10^{-3} M; and (i) dependence calculated according to Equation 5, $k_c = 20$ min^{-1} mol^{-1} dm^3, DMAP 3.75×10^{-3} M, $K = 0.011$.

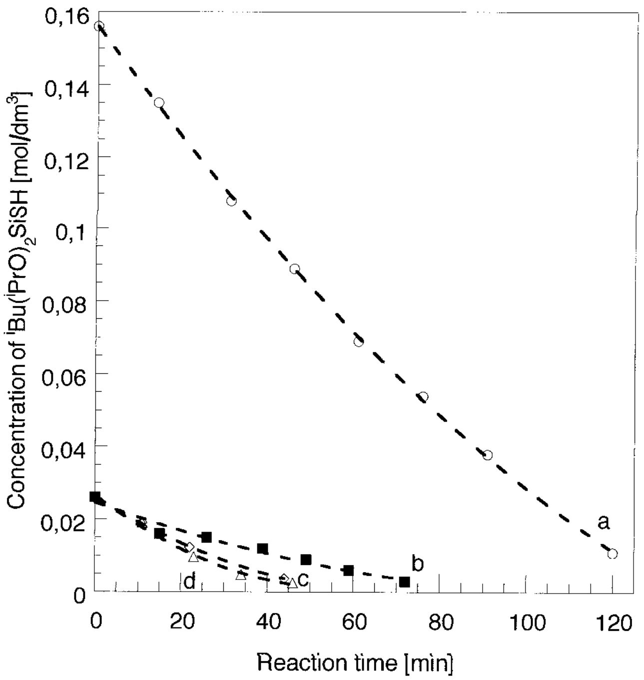

FIGURE 4 The dependence of concentration of $^i\text{Bu}(^i\text{PrO})_2\text{SiSH}$ on the reaction time for methanolysis catalyzed with DMAP 1.25×10^{-3} M in MeCN solution: (a) MeOH 3.43 M, (b) MeOH 6.86 M, (c) MeOH 3.43 M, and (d) MeOH 1.72 M.

centration of DMAP. $c(^i\mathrm{Bu}_n(^i\mathrm{PrO})_{3-n}\mathrm{SiSH}) \gg c(\mathrm{DMAP})$.

$$\mathrm{R_3SiSH} + \mathrm{DMAP} \overset{K_1}{\rightleftarrows} \mathrm{R_3SiS^-} \cdot \mathrm{DMAPH^+} \overset{K_2}{\rightleftarrows} \mathrm{R_3SiS^-} + \mathrm{DMAPH^+} \quad (3)$$

On the basis of available data concerning hydrogen bond equilibria in organic solvents, it should be expected that an increasing amount of alcohol in solution should facilitate the proton transfer to amine (with formation of $\mathrm{R_3SiS^-} \cdot \mathrm{DMAPH^+}$) due to specific interactions [12,13] connected with properties of alcohols as hydrogen donors in hydrogen bonding systems. Moreover, the process of dissociation is enabled by the shift of the equilibrium K_2 to the right with increasing influence of the same specific interactions. Conductivity studies of a system DMAP (1.25×10^{-3} M), $(^i\mathrm{PrO})_3\mathrm{SiSH}$ (0.156 M), and MeOH (various concentrations) in MeCN solution clearly confirm this assumption. For [MeOH] = 0 M, $\beta = 0.37$; for [MeOH] = 0.22 M, $\beta = 0.44$; for [MeOH] = 0.43 M, $\beta = 0.49$; for [MeOH] = 0.87 M, $\beta = 0.55$; for [MeOH] = 1.74 M, $\beta = 0.64$; for [MeOH] = 3.45 M, $\beta = 0.68$; for [MeOH] = 6.90 M, $\beta = 0.74$. Any influence of dielectric permeability on these equilibria (K_1, K_2) is ruled out in the isodielectric system MeCN—MeOH.

When x is regarded as the concentration of free DMAP and y is regarded as the concentration of silanethiol, k_c is the catalytic rate constant and $y \gg c(\mathrm{DMAP})$; thus, $[\mathrm{R_3SiS^-} \cdot \mathrm{DMAPH^+}] = c - x - c\beta$; $[\mathrm{R_3SiS^-}] = [\mathrm{DMAPH^+}] = c\beta$; $K_1 = (c - x - c\beta)/xy$; $K_2 = c^2\beta^2/(c - x - c\beta)$, and therefore, the reaction rate v is

$$v = -\frac{dy}{dt} = k_c xy = k_c \frac{c^2\beta^2}{K_1K_2} \quad (4)$$

β depends on K_1, K_2, y, and c

$$\beta = \frac{\sqrt{(K_1K_2y)^2 + 4K_1K_2yc(1 + K_1y)} - K_1K_2y}{2c(1 + K_1y)} \quad (5)$$

If $K_1 \gg K_2$ ($K_1 = 84$, $K_2 = 0.0018$) and if $y \gg c$, β is almost constant up to 85% of completion of reaction. This explains the observed linear dependence of concentration of silanethiol (y) on the reaction time.

On the assumption that x is small compared to $c(1 - \beta)$ at concentration of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ $y = 0.156$ M, there results $K_2 = 0.0018$. Assuming the probable value of the catalytic rate constant for DMAP, $k_c = 20\ \mathrm{min^{-1}\ mol^{-1}\ dm^3}$, being the same as the k_c for methanolysis of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ catalyzed by N-methylimidazole (N-meim) under the same conditions, and considering Figure 3a, we obtained $K_1 = 84$. The slopes b, c, and d can be explained well by using the evaluated K_1 and K_2 values. The slope 3h shows the calculated dependence of concentration of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ vs. reaction time for methanolysis according to the simple first-order formalism using $k_c = 20\ \mathrm{min^{-1}\ mol^{-1}\ dm^3}$ and $c(\mathrm{DMAP}) = 1.25 \times 10^{-3}$ M. This mechanism explains also the puzzling influence (Figures 3f and 3g and Figures 4b–4d) of alcohol concentration on reaction rates. The overall reaction rate for $c_0(^i\mathrm{PrO})_3\mathrm{SiSH}$ 0.026 M, $c_0(\mathrm{DMAP})$ 1.25×10^{-3} M has a maximum at MeOH ≈ 0.86 M (Figure 3g); for the $^i\mathrm{Bu}(^i\mathrm{PrO})_2\mathrm{SiSH}$ case, such a maximum is at MeOH ≈ 1.72 M (Figure 4d). The increasing degree of protonation of DMAP if $c(\mathrm{ROH})$ increases and the external order with respect to alcohol (slightly more than zero) are responsible for this finding. Methanolysis of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ in benzene solution catalyzed by DMAP (Figure 3e) is approximately first order with respect to thiol concentration, and DMAP shows high catalytic activity ($k_c = 7.7\ \mathrm{min^{-1}\ mol^{-1}\ dm^3}$). This means that protonation of DMAP in this system is slight. This finding can be explained in terms of the dependence of the proton transfer equilibrium (3) upon environmental nonspecific interactions that are dependent on the Onsager parameter of the reaction medium [12]; MeCN, compared to benzene, retards the alcoholysis of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ catalyzed by DMAP (Figures 3e and 3d). In the system $(^i\mathrm{PrO})_3\mathrm{SiSH}$ and N-methylimidazole ($\mathrm{p}K_a = 7.33$), the dissociation degree being $\beta = 0.023$, the tendency to linear time dependence of concentration of $(^i\mathrm{PrO})_3\mathrm{SiSH}$ is not visible within the accuracy of our measurements.

On the assumption that the concentration of the ion—pair ($\mathrm{R_3SiS^-} \cdot \mathrm{DMAPH^+}$) is low, the solutions of Equations 2 and 3 result in Equation 5 where $K = K_1K_2 \approx c\beta^2/y(1 - \beta) = 0.011$.

$$\left.\frac{Ky}{2c} + \frac{\sqrt{4Kyc + K^2y^2}}{2c} + \ln y + \ln\left(Ky + 2c + \sqrt{4Kyc + K^2y^2}\right)\right|_{y}^{y_0} = k_c ct \quad (6)$$

The slope according to Equation 6 (Figure 3i) differs substantially from the experimental slope 3d. It is evident that Equation 6 cannot explain our results, and the kinetic outcome is due to DMAP consumption, both by ion-pair formation and by ionization. However, the literature data indicate that the majority of salts consisting of guaternized organic cations and perchlorate or picrate anions are almost completely dissociated [14]; this is not the case for silanothiolate anions.

Alcoholysis of ^{i}Bu$_n$(^{i}PrO)$_{3-n}$SiSH (n = 0–3) catalyzed by NEt$_s$

The methanolysis of ^{i}Bu$_3$SiSH follows the pseudo-first-order formalism (Figures 5a and 5b), but NEt$_3$ exerts only a very weak catalytic effect; i.e., for methanolysis, k_c = 0.05 min^{-1} mol^{-1} dm^3 (in MeCN), k_c = 0.031 min^{-1} mol^{-1} dm^3 (in $C_2H_4Cl_2$), and $k_c \approx 0$ min^{-1} mol^{-1} dm^3 (in C_6H_6). The k_c values were corrected with regard to the uncatalyzed process. For ethanolysis in MeCN solution, k_c = 0.012 min^{-1} mol^{-1} dm^3. Thus, the rate of this reaction is more sensitive to steric hindrance of the alcohol, and the k_c value for methanolysis is fourfold greater than that for ethanolysis. This ratio is similar to a base-catalyzed alcoholysis of R$_3$SiCl [15]. These outcomes are consistent with conductivity studies of a system: NEt$_3$ (0.014 M) and ^{i}Bu$_3$SiSH (0.074 M) in MeCN solution, the degree of dissociation of NEt$_3$ being β = 0.004, according to Equation 3.

The time dependencies of concentration of (^{i}PrO)$_3$SiSH in methanolysis catalyzed by NEt$_3$ are shown graphically in Figures 5c and 5d. The catalytic activity of NEt$_3$ in this reaction is low. The curve 5c (in MeCN) shows a tendency to be linear, due to protonation of the catalyst (Equation 3). The slope 5d (in C_6H_6) reflects first-order kinetics (with low K$_1$, K$_2$ values according to Equation 3). The degree of dissociation of NEt$_3$ (1.25 × 10^{-3} M) at a (^{i}PrO)$_3$SiSH concentration of 0.156 M in MeCN is substantially lower (β = 0.18) than that of DMAP (β = 0.37), in spite of the higher basicity of NEt$_3$ (pK_a = 10.75).

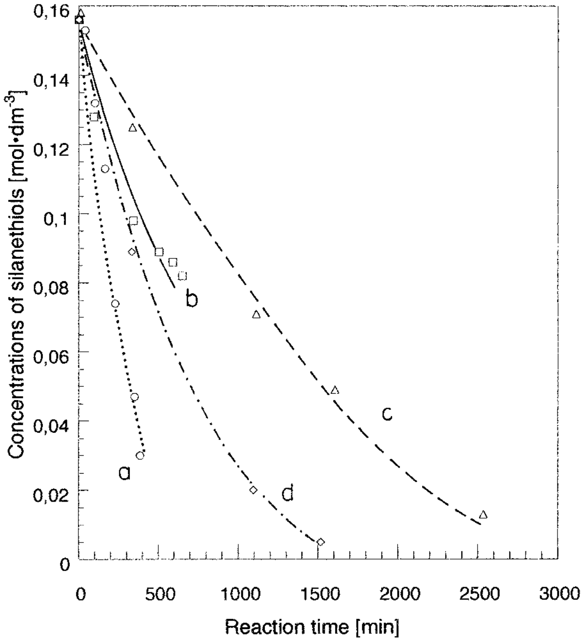

FIGURE 5 The dependence of concentration of silanethiol on the reaction time for methanolysis (MeOH = 3.43 M) catalyzed with NEt$_3$ (16.6 × 10^{-3} M): (a) ^{i}Bu$_3$SiSH in MeCN, (b) ^{i}Bu$_3$SiSH in benzene, (c) (^{i}PrO)$_3$SiSH in MeCN, (d) (^{i}PrO)$_3$SiSH in benzene.

Phenolysis of ^{i}Bu$_n$(^{i}PrO)$_{3-n}$SiSH (n = 0–3)

Figures 6a through 6c show the plots of lg k_c vs. Hammett σ_H constants of substituents for phenolysis of ^{i}Bu$_3$SiSH with *para*-substituted phenols. The similar and high catalytic activity of NEt$_3$ (pK_a = 10.75), DMAP (pK_a = 9.51), and N-meim (pK_a = 7.33) appears to be the most striking phenomenon. The Hammett relationships lg k_c vs the σ_H constant for phenolysis of ^{i}Bu$_3$SiSH with *para*-substituted phenols are not linear. These dependencies for NEt$_3$ and DMAP can be explained in terms of a specific base catalysis (with phenolate ion as the nucleophile) and can be a result of the concentrations of phenolate ions and their reactivity, but the result is not in accord with the similar catalytic activity of N-meim. The conductivity studies of a system, NEt$_3$ (0.014 M)

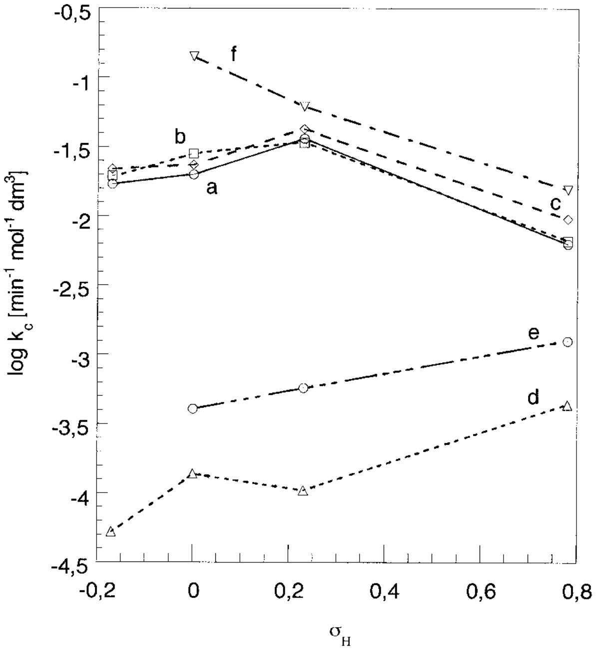

FIGURE 6 The dependence of the logarithm of the catalytic rate constants k_c on the Hammett σ_H constants for phenolysis of ^{i}Bu$_n$(^{i}PrO)$_{3-n}$SiSH (c_0 = 0.078 M) in MeCN solution with *para*-substituted phenols, (p-XC$_6$H$_4$OH = 1.73 M): (a) ^{i}Bu$_3$SiSH, DMAP = 8.4 × 10^{-3} M; (b) ^{i}Bu$_3$SiSH, NEt$_3$ = 16.8 × 10^{-3} M; (c) ^{i}Bu$_3$SiSH, N-Meim = 8.4 × 10^{-3} M; (d) ^{i}Bu$_3$SiSH. Py = 5.0 × 10^{-2} M; (e) (^{i}PrO)$_3$SiSH, Py = 5.0 × 10^{-2} M; and (f) (^{i}PrO)$_3$SiSH, N-Meim = 8.4 × 10^{-3} M.

and p-XC_6H_4OH (0.83 M) in CH_3CN solution, indicate the presence of charged species as depicted in Equation 7. The degrees of dissociation of NEt_3, γ, where $\gamma = [HNEt_3^+]/c(NEt_3)$, decreases in the series $X = p NO_2$ ($\gamma = 0.37$), $X = p Cl$ ($\gamma = 0.29$), $X = H$ ($\gamma = 0.10$), $X = p Me$ ($\gamma = 0.05$).

$$NEt_3 + XC_6H_4OH \rightleftarrows HNEt_3^+ \cdot XC_6H_4O^- \rightleftarrows HNEt_3^+ + XC_6H_4O^- \quad (7)$$

The Hammett relationships for phenolysis of $^iBu_3SiSH$ (Figure 6d) and for $(^iPrO)_3SiSH$ (Figure 6e), catalyzed by pyridine, show features of a basic catalysis (a positive Hammett correlation). Because of the low basicity of pyridine, the influence of equilibria according to Equation 7 on the kinetics outcomes should not be substantial. The phenolysis of $(^iPrO)_3SiSH$, catalyzed by N-meim, shows a negative Hammett correlation (Figure 6f). This can be a result of a change of catalytic mechanism (nucleophilic catalysis), but the influence of equilibria according to Equation 7 can be substantial.

CONCLUSION

The nitrogen heterocycles exhibit in the alcoholysis of silanethiols different catalytic abilities [1,5] that are not related to pK_a, but strictly to nucleophilic properties of these catalysts. This means that nucleophilic catalysis is much more effective than basic catalysis in this case. The ability of the Si–S bond to be stretched by electron donation to the silicon atom is only modest [16] (see apicophilicity series). This means that only the most powerful nucleophiles can act as a catalyst. From the group of nitrogen heterocycles that were investigated by us, imidazole and N-methylimidazole are the best σ and π donors. Thus, despite the moderate basicity, they efficiently stabilize the five valent silicon species that are formed in the initial step in nucleophile-catalyzed substitution at silicon. Moreover, the small steric hindrance of imidazoles promotes the advantage of nucleophilic catalysis. DMAP acts also in alcoholysis of silanethiols as a nucleophilic catalyst, but pyridine is acting as a basic catalyst in this reaction [1].

Our results favor a mechanism with a four-valent silylonium salt as a reactive intermediate [17]. A high steric hindrance of investigated silanethiols should favor the silylonium salt structure [18]. Similar pyridinium salts $[R_3Si - Py]^+X^-$ ($X = I^-, Br^-$) were isolated [19,20] and have high electrophilic reactivity. Our results are in agreement with the results of Chu *et al.* [9], who reported the very high catalytic activity of DMAP in alcoholysis of chlorosilanes. Our results are also in agreement with the results of Bassindale and Stout [10], who report a very high ability of DMAP and N-meim to form silylonium salts with trimethylsilyl compounds with good leaving groups.

The strongest base NEt_3 is acting as a base catalyst in the alcoholysis of silanethiols, but with low efficiency. In the case of phenolysis, the specific base catalysis by NEt_3 or DMAP is efficient due to the formation of a significant phenolate ion concentration.

EXPERIMENTAL

Solvents and reagents used in kinetics studies were prepared as described in the literature [5]. All runs in MeCN solution were carried out with ionic strength maintained at 4×10^{-4} M LiCl [5]. The kinetics investigations were performed at (21 ± 1)°C under pseudo-first-order conditions. The progress of reaction was monitored with GC [5].

The conductivity measurements were carried out in MeCN solution using Conductivity Meter Radelkis OK—102/1 at 22°C. The β values were calculated using Λ_∞ for picric anion 77.3 Ω^{-1} cm^2 mol^{-1} and Λ_∞ for pyridinium cation 90 Ω^{-1} cm^2 mol^{-1} [21]. Concentration of $^iBu_n(^iPrO)_{3-n}SiSH$ was 0.156 M, of DMAP, 1.25×10^{-3} M, and of N-methylimidazole, 5×10^{-3} M. The γ values were calculated using Λ_∞ for tetraethylammonium picrate 164.6 Ω^{-1} cm^2 mol^{-1} [22].

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