Concerning the Mechanism for Bifunctional Catalysis in the Methanolysis of Methoxymethylphenoxyphenylsilane

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The formic acid–formate-catalyzed methanolysis of methoxy-d_3-methylphenoxyphenylsilane (**1D**) was studied. The formation of phenol and the exchange of the deuterated methoxy group with solvent was studied as a function of total buffer concentration. Both processes show bifunctional catalysis involving a molecule of acid and a molecule of base in the transition state. The observation of bifunctional catalysis suggests a mechanism in which formation of the silicon–solvent bond is concerted with breaking of the silicon–leaving group bond ($-OC_6H_5$ or $-OCD_3$). From analysis of the kinetic data it is concluded that the concerted bond-forming and bond-breaking processes do not occur on a pentavalent silicon species formed by a preequilibrium addition of solvent or formate anion to **1D**. The results are interpreted in terms of a mechanism in which solvent attack occurs on a tetravalent silicon center with simultaneous breaking of the silicon leaving group bond.

Introduction

We have been interested in the mechanism for solvolysis of silyl ethers. The solvolysis of silicon compounds is interesting from a mechanistic viewpoint since, although silicon is located immediately below carbon on the periodic table, tetravalent silicon shows quite different behavior in solvolysis reactions when compared with tetravalent carbon compounds. For example, silicon, unlike carbon, possesses d orbitals, so the possibility exists that the solvolysis of silicon compounds may involve pentavalent intermediates.[1-6] Indeed, many pentavalent silicon species have been isolated and characterized.[7] Also, in protic solvents tetravalent silicon compounds undergo general base-catalyzed addition of solvent, rather than direct nucleophilic attack.[1,8-14] This is in contrast to the solvolysis of tetravalent carbon where general base-catalyzed addition of solvent is unusual.[15] That it is important to understand the mechanism for formation and/or breaking of the silicon–oxygen bond is obvious when one considers the common usage in organic chemistry of silicon as a hydroxyl protecting group.[16,17]

In spite of many investigations, the mechanism for the solvolysis of silyl ethers and silicon compounds in general is still unclear. In particular, it has not been well established if the solvolysis of silicon compounds occurs by a one-step concerted reaction (S_N2–Si[1,9] or A_ND_N[19] mechanism), Scheme IA, or if the reaction occurs by a mechanism that involves the formation of a pentavalent silicon intermediate (S_Ni–Si[1,9] or $A_N + D_N$[19] mechanism), Scheme IB.[1,6,9,18]

Recently, Corriu has provided evidence that nucleophilic substitution at silicon may occur by a mechanism involving a preequilibrium attack of the nucleophilic reagent on the silicon substrate to form a pentavalent silicon species. This pentavalent species then undergoes reaction with a second molecule of the nucleophilic reagent in an S_N2-type reaction to displace the leaving group, Scheme 1C.[20-28]

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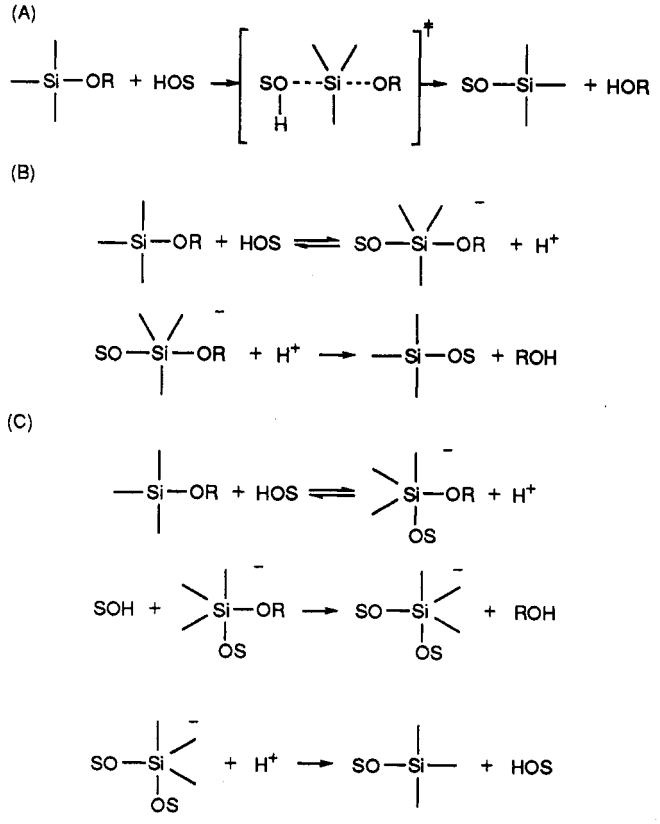
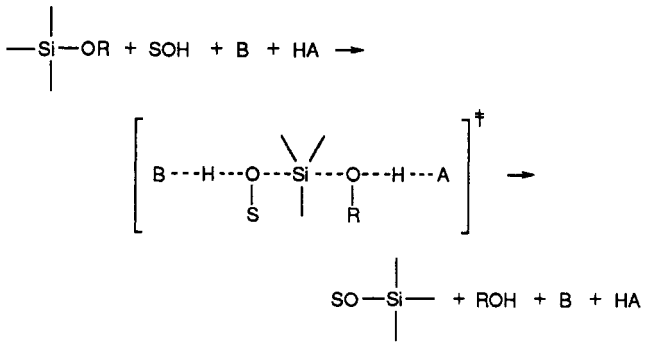
Scheme I. Possible Mechanisms for Nucleophilic Substitution at Silicon[a]



[a] Key: (A) a concerted displacement reaction (S_N2–Si mechanism); (B) a stepwise reaction involving the formation of a pentavalent silicon intermediate (S_Ni–Si mechanism); (C) a mechanism involving the preequilibrium addition of the nucleophile to the tetravalent silicon center to form a pentavalent intermediate that then undergoes rate-determining attack of a second molecule of nucleophile.

It is well established that when nucleophiles and silicon substrates react in protic solvents the commonly observed reaction is a general base-catalyzed addition of solvent; direct substitution by the nucleophilic reagent is not observed.[1,8-14] It has been demonstrated that the alcoholysis of silyl ethers can also show both general acid catalysis[31,32] and bifunctional catalysis.[14,18] The observation of bifunctional catalysis requires the involvement of both a molecule of acid and a molecule of base catalyst in the transition state and is consistent with solvolysis by a concerted mechanism that involves a molecule of solvent attacking the silicon center with a molecule of base catalyst assisting in removal of a proton from the attacking solvent molecule. The bond-forming process occurs simultaneously with cleavage of the silicon–leaving group bond; a molecule of the catalyzing acid donates a proton to the leaving group as the bond breaks. The mechanism is usually viewed as a substitution on the tetravalent silicon center[14,18] as depicted in Scheme II. It is difficult to rationalize the observation of bifunctional catalysis by a stepwise mechanism.[14,18]

Scheme II. Bifunctional Catalyzed Alcoholysis of a Silyl Ether[a]



[a] The alcoholysis occurs by a mechanism that involves a molecule of base catalyst assisting in removal of a proton from the attacking solvent molecule as it forms a bond to a tetravalent silicon center occurring simultaneously with cleavage of the silicon–leaving group bond; a molecule of the catalyzing acid donates a proton to the leaving group as the bond breaks.

However, the observation of bifunctional catalysis is also consistent with a mechanism involving the preequilibrium formation of a pentavalent silicon solvent adduct that undergoes rate-determining attack in a second step by another molecule of solvent to displace the leaving group. This second step may show bifunctional catalysis, Scheme III. In view of the results reported by Corriu,[20-28] this mechanism warrants consideration as a possible mechanism for the solvolysis of silyl ethers.

An additional mechanism that will also have a rate law first order in both acid and base (i.e., show bifunctional catalysis) and must be considered as a possible mechanism to account for the observed bifunctional catalysis is shown in Scheme IV. This mechanism involves reaction of a molecule of the base catalyst with the silyl ether leading to the preequilibrium formation of a pentavalent silicon species. The pentavalent species, being an anion, is protonated on the leaving group. The protonated pentavalent species than undergoes a general base-catalyzed addition of solvent in the rate-determining step, followed by cleavage of the silicon–base bond leading to the tetravalent product.

Thus, there are three possible mechanism (Schemes II–IV) that can reasonably account for the observed bifunctional catalysis of silyl ethers. In this paper we report experiments on the methanolysis of methoxy-d_3-methylphenoxyphenylsilane, **1D**, catalyzed by formic acid and formate anion. We also report experiments on the methoxide-catalyzed methanolysis of methoxymethylphenoxyphenylsilane. By employing methoxy-d_3-methylphenoxyphenylsilane, **1D**, we were able to monitor the loss of phenol from **1D** and exchange of the deuteriomethoxy

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(29) (a) The rate constants k^{OPh} and k^{OMe} are pseudo-third-order rate constants since the rate laws involve a molecule of methoxymethylphenoxyphenylsilane, a molecule of formic acid, a molecule of formate anion, and a molecule of methanol solvent. Since the concentration of methanol is a constant and is included in the rate constants k^{OPh} and k^{OMe} they are pseudo-third-order rate constants. (b) Similarly, the rate constant k'^{OPh} is a pseudo-second-order rate constant since the rate law involves a molecule of methoxymethylphenoxyphenylsilane, a molecule of methoxide, and a molecule of methanol solvent. The methoxide is acting as a general base to facilitate the addition of a methanol molecule to the silyl ether. Since the concentration of methanol is a constant and is included in the rate constant k'^{OPh}, it is a pseudo-second order rate constant.

(30) Another possible mechanism, suggested by a reviewer, that is also consistent with the results involves formate anion removing a proton from a reversibly formed adduct between methanol and the silyl ether at the same time as a molecule of formic acid donates a proton to the phenoxy leaving group. However, as was pointed out by Schowen et al., this mechanism is unlikely since it requires the "oxonium proton not to be rapidly transferred to an adjacent solvent molecule but wait for the arrival of a formate ion."[18]

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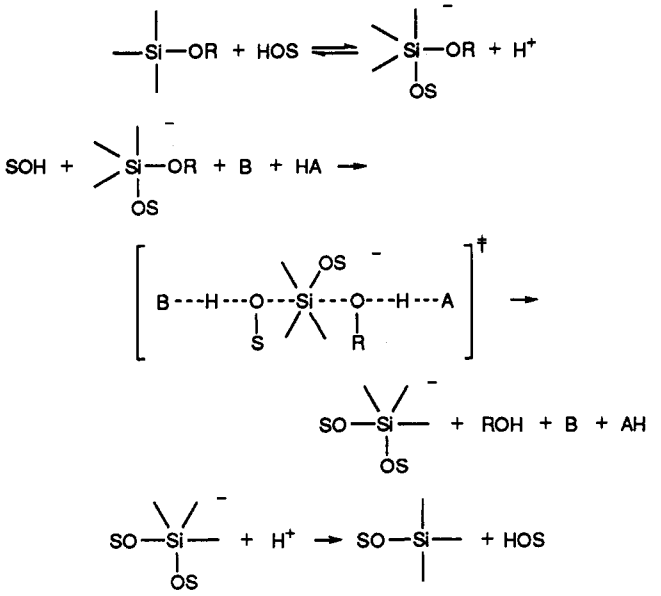
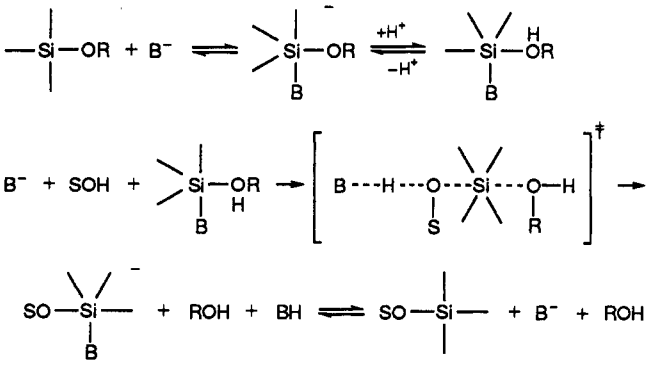
Scheme III. Bifunctional-Catalyzed Alcoholysis of a Silyl Ether[a]



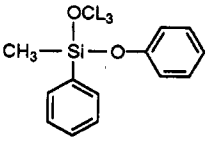
[a] The alcoholysis occurs by a mechanism involving the preequilibrium formation of a pentavalent silicon solvent adduct that undergoes rate-determining attack in a second step by another molecule of solvent to displace the leaving group. The second step shows bifunctional catalysis.

Scheme IV. Bifunctional-Catalyzed Alcoholysis of a Silyl Ether[a]



[a] The alcoholsis occurs by a mechanism involving the preequilibrium formation of a pentavalent silicon adduct with the base catalyst, followed by protonation on the oxygen of the leaving group, OR. This protonated intermediate than undergoes rate-determining attack by solvent in a general base-catalyzed step.

group with the solvent. These experiments were designed to establish if the observed bifunctional catalysis in the solvolysis of silyl ethers is more consistent with a mechanism involving solvent attack on tetravalent silicon (Scheme II) or on a pentavalent silicon species (Scheme III or IV). The results are inconsistent with the mechanism involving a pentavalent silicon species; thus, the mechanism is best described as a simple S_N2–Si mechanism (Scheme II).



1D, L = D
1H, L = H

Table I. Pseudo-First-Order Rate Constants for Formation of Phenol, k_{obs}, and for Loss of the Deuteriomethoxy Group, k'_{obs}, from Methoxy-d_3-methylphenoxyphenylsilane, 1D, in Methanol at 30 ± 0.5 °C Buffered with Formic Acid/Sodium Formate and Constant Ionic Strength of 0.5 M ($NaClO_4$)

formic acid, M	sodium formate, M	$k_{obs} \times 10^5$ s	$k'_{obs} \times 10^4$ s
0.05	0.05	5.3	2.6
0.03	0.03	2.2	1.1
0.15	0.05	13.7	8.7, 6.3[a]
0.1275	0.0425		7.5
0.12	0.04	9.4	
0.105	0.035		4.4, 4.4
0.09	0.03	5.5	
0.06	0.02	2.6	1.8, 2.0, 1.9[a]
0.50	0.05	43.5	
0.40	0.04	26.7	
0.30	0.03	16.0	
0.20	0.02	7.7	
0.10	0.01	2.4	
0.75	0.05	54.5	
0.60	0.04	37.7	
0.45	0.03	23.0	
0.30	0.02	11.2	

[a] Rate constant determined by the extraction method as described in the Experimental Section.

Results

The pseudo-first-order rate constant, k_{obs}, for the methanolysis of 1D in a variety of formic acid–sodium formate buffers at 30 °C and constant ionic strength of 0.05 M ($NaClO_4$) are reported in Table I. The rate constants, k_{obs}, were determined by measuring the change in absorbance at 281 nm due to the formation of phenol as a function of time. Our rate constants agree well with those obtained by Schowen[18] under slightly different conditions (25 °C and ionic strength 0.05 M with $LiClO_4$). A plot of k_{obs} against the product of the concentrations of formic acid and formate anion is provided in Figure 1. Figure 1 shows that the formation of phenol is dependent on the concentration of both buffer species, consistent with bifunctional catalysis and a rate law of eq 1. The

$$k_{obs} = k^{OPh}[HOCOOH][NaOOCH] \quad (1)$$

near-zero intercept indicates that terms in the rate law not involving both acid and base catalysts are negligible. The slope of this plot, 1.64×10^{-2} M^{-2} s^{-1}, provides the pseudo-third-order rate constant, k^{OPh}, for the bifunctional-catalyzed methanolysis of 1D.[29a]

Also given in Table I are the pseudo-first-order rate constants, k'_{obs}, for exchange of the deuteriomethoxy group of 1D with solvent methanol in the same formic acid–sodium formate buffers. The pseudo-first-order rate constants k'_{obs} were determined by mass spectral analysis which gave the ratio of methoxy-d_3-methylphenoxyphenylsilane (1D) to total methoxymethylphenoxyphenylsilane (1D and 1H) as a function of time. A plot of k'_{obs} against the product of formic acid concentration and formate concentration, Figure 2, indicates that exchange of the deuteriomethoxy group in 1D also shows bifunctional catalysis, similar to that observed for loss of the phenoxy group. The slope of this plot, k^{OMe}, gives the pseudo-third-order rate constant for exchange of the deuteriomethoxy group in 1D with solvent of 1.25×10^{-1} M^{-2} s^{-1}.[29a] The error bars in Figure 2 were estimated from visual inspection of linear semilog plots of the ratio of methoxy-d_3-methylphenoxyphenylsilane to the total methoxymethylphenoxyphenylsilane present, 1D/(1D + 1H), vs time. The slopes of these plots give pseudo-first-order

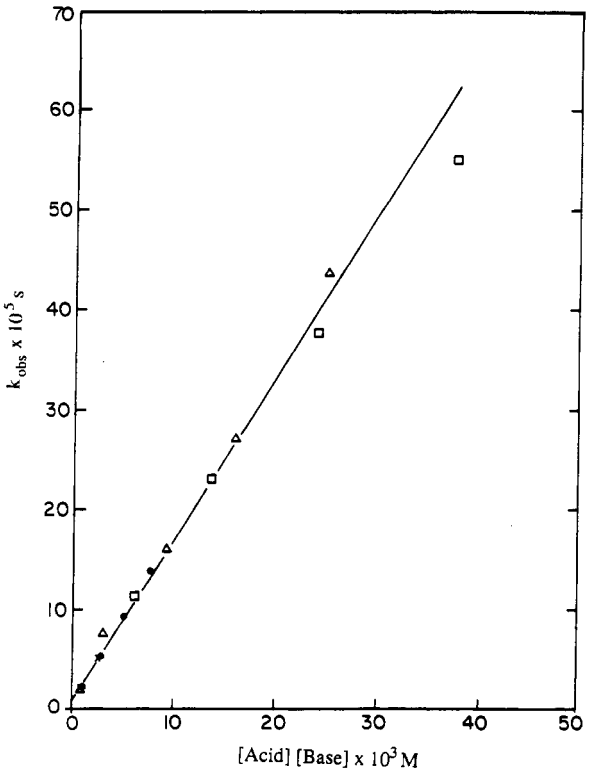


Figure 1. Plots of the pseudo-first-order rate constants, k_{obs}, for formation of phenol against the product of formic acid concentration and sodium formate concentration for reaction of methoxy-d_3-methylphenoxyphenylsilane, **1D**, in buffered methanol at 30 °C and constant ionic strength of 0.05 M ($NaClO_4$): (x) A/B = 1; (○) A/B = 3; (△) A/B = 10; and (□) A/B = 15.

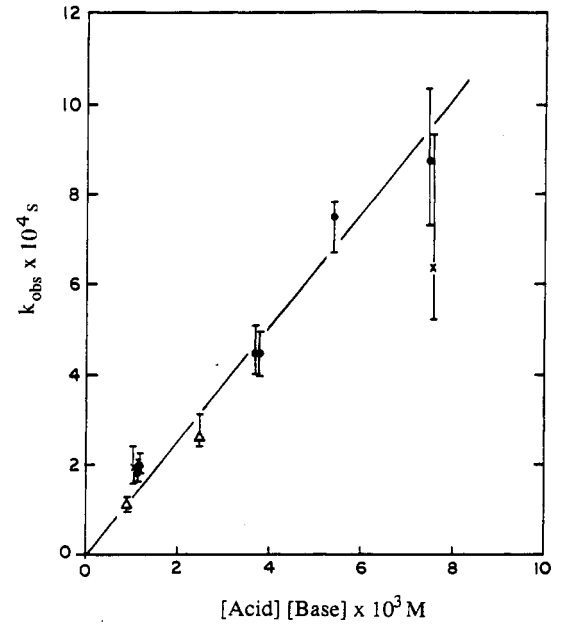


Figure 2. Plot of the pseudo-first-order rate constants, k'_{obs}, for loss of the deuteriomethoxy group from methoxy-d_3-methylphenoxyphenylsilane, **1D**, against the product of formic acid concentrations and sodium formate concentration in buffered methanol at 30 °C and constant ionic strength of 0.05 M ($NaClO_4$): (△) A/B = 1; (●) A/B = 3; and (x) A/B = 3 (with rate constants determined using the extraction technique as described in the Experimental Section).

rate constants for exchange of the deuteriomethoxy group with solvent (see Experimental Section).

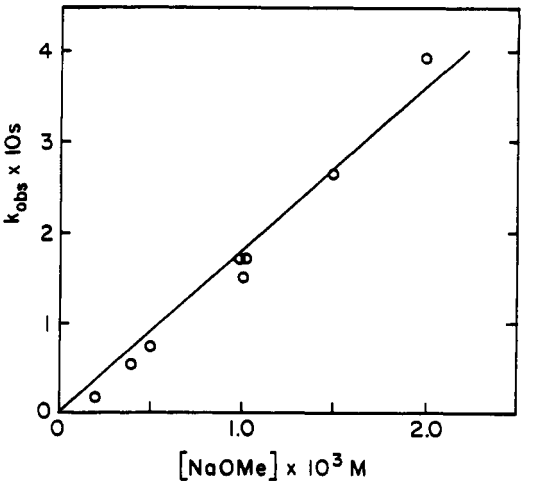


Figure 3. Plots of the pseudo-first-order rate constants, k_{obs}, for formation of phenol against sodium methoxide concentration for reaction of methoxymethylphenoxyphenylsilane, **1H**, in methanol at 10 °C and constant ionic strength of 0.05 M ($NaClO_4$).

Table II. Pseudo-First-Order Rate Constants for Formation of Phenol, k_{obs}, from Methoxymethylphenoxyphenylsilane, *1H*, in Methanol Containing Sodium Methoxide at 10 °C and Constant Ionic Strength of 0.05 M ($NaClO_4$)

methoxide × 10^4 M	k_{obs} × 10^2 s	methoxide × 10^4 M	k_{obs} × 10^2 s
2.0	1.8	10.0	15, 17, 17
4.0	5.5	15.0	26
5.0	7.4	20.0	39

In Table II is given the pseudo-first-order rate constants, k_{obs}, for the formation of phenol from **1H** catalyzed by methoxide at 10 °C and constant ionic strength of 0.05 M ($NaClO_4$). The rate constants, k_{obs}, were determined by measuring the change in absorbance at 281 nm due to the formation of phenol as a function of time. A plot of k_{obs} against the concentration of methoxide is provided in Figure 3 and demonstrates that the rate of reaction is dependent on the first order in methoxide. The slope of this plot, 1.8 × 10^2 M^{-1} s^{-1}, gives the pseudo-second-order rate constant, k'^{OPh}, for the methoxide-catalyzed methanolysis of *I*.[29b]

We also examined the initially formed dimethoxymethylphenylsilane product produced from the methoxide-catalyzed methanolysis of **1D**. To a methanol solution containing sodium methoxide at 10 °C was added **1D** and the mixture shaken. After an appropriate time the solution was quenched and the product analyzed by GC/MS as described in the Experimental Section. Reactions were performed in solutions that were 1 × 10^{-3} and 4 × 10^{-4} M in methoxide, and each mixture was analyzed after times of 5 and 10 s. GC/MS analysis of the dimethoxymethylphenylsilane product isolated from the 1 × 10^{-3} M solution after times of 5 and 10 s indicated that it was 91% and 87% $C_6H_5SiCH_3(OCD_3)(OCH_3)$, respectively. Under these conditions, times of 5 and 10 s corresponded to approximately 52% and 76% disappearance of **1D** (see Table II). A similar experiment in methanol that was 4 × 10^{-4} M in methoxide showed that product isolated after times of 5 and 10 s was 97% and 95% $C_6H_5SiCH_3(OCD_3)(OCH_3)$. Under these conditions times of 5 and 10 s correspond to approximately 25% and 42% disappearance of **1D** (see Table II).

Discussion

We now consider the three mechanisms consistent with the rate law described above for the formic acid–formate-catalyzed methanolysis of **1D** that are depicted in Schemes II–IV. Two of these possibilities involve the preequilibrium formation of a pentavalent intermediate that then undergoes rate-determining substitution of the leaving group (Schemes III and IV). The first possibility involves the preequilibrium addition of solvent to **1D** leading to a pentavalent silicon intermediate. This intermediate then reacts with another molecule of solvent in a second bifunctional catalyzed step to displace the phenoxy group or the deuteriomethoxy group, Scheme III.

The second possible mechanism involves the preequilibrium addition of formate anion to **1D** leading to a pentavalent intermediate that is then protonated on the oxygen of the phenoxy or deuteriomethoxy group. This protonated intermediate then undergoes, in the rate-determining step, a general base-catalyzed addition of solvent to displace the phenoxy group or the deuteriomethoxy leaving group as depicted in Scheme IV, where B represents formate anion and OR represents either the phenoxy leaving group or the deuteriomethoxy group. In view of the results reported by Corriu[20-28] we felt that these mechanisms, involving substitution on a pentavalent silicon species, were possible and warranted consideration for cleavage of silicon oxygen bonds in compounds such as **1D**.

The third possible mechanism involves two competing pathways for displacement of the phenoxy group and the deuteriomethoxy group of **1D**. Both of these are concerted displacements on the tetravalent silicon center and exhibit bifunctional catalysis, as described in Scheme II, where OR is either a phenoxy leaving group or a deuteriomethoxy leaving group.

We now provide evidence that the mechanisms for bifunctional catalysis involving a pentavalent intermediate, as described in Schemes III and IV, are inconsistent with the reported results. The results are, however, consistent with the mechanism described in Scheme II involving solvent attack on the tetravalent silicon.

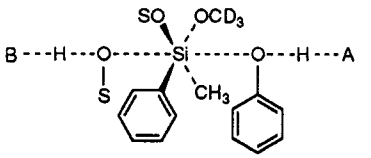
We first consider the mechanism described in Scheme III which is described more completely in Scheme V. Scheme V gives a detailed mechanism for loss of phenol and loss of the deuteriomethoxy group during the methanolysis of **1D** according to the mechanism that involves the preequilibrium addition of solvent to **1D** (K_A and K_W) to form a pentavalent silicon intermediate. This pentavalent species then undergoes reaction with a second molecule of solvent leading to the substitution of the phenoxy group (k_B) or substitution of the deuteriomethoxy group (k_X). The steps k_B and k_X are catalyzed by both a molecule of acid and a molecule of base.

The right-hand side of Scheme V describes the pathway for bifunctional-catalyzed substitution of the phenoxy group, and the left-hand side of Scheme V depicts the pathway for bifunctional-catalyzed substitution of the deuteriomethoxy group. In scheme V the pentavalent intermediates **I** and **II** are depicted such that electronegative oxygen substituents are placed in the apical positions. Electronegative substituents prefer to occupy apical positions. It is possible that the pentavalent structures **I** and **II** could be interconverted by a pseudorotation; however, the occurrence of a pseudorotation will not affect the interpretation of our results.

Consider the mechanism for bifunctional-catalyzed formation of phenol according to Scheme V. The mechanism involves preequilibrium formation of the pentavalent intermediate **I** followed by a bifunctional catalyzed step, k_B, that leads to phenol production and the formation of another pentavalent intermediate that rapidly collapses to the dimethoxy-substituted product (k_C and k_D). The rate constant for the formation of phenol according to Scheme V is given by eq 2, where [A] and [B] represent

$$k^{OPh} = k_A k_B[A][B]/(k_{-A} + k_B[A][B]) \qquad (2)$$

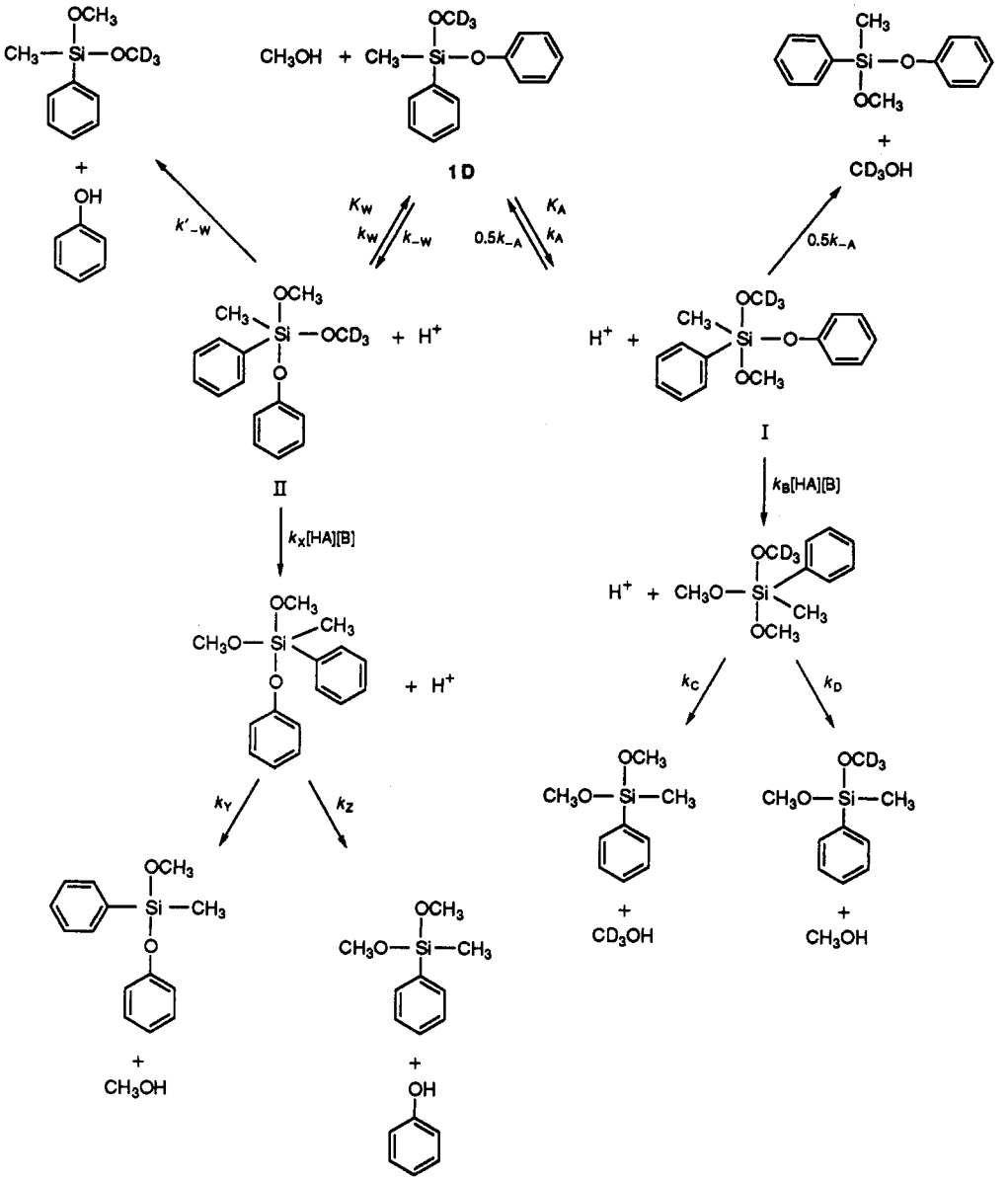
the concentrations of the acidic and basic forms of the buffer, respectively. Since the reaction exhibits bifunctional catalysis k_B must be the rate-determining step ($k_{-A} > k_B$) and eq 2 can be rewritten as $k^{OPh} = k_A k_B[A][B]/k_{-A}$. As was pointed out by Schowen[18] and us[14] the observation of bifunctional catalysis strongly supports concerted bond formation and bond breaking of the silicon–oxygen bonds; a possible transition state for the bifunctional-catalyzed substitution of phenol, k_B, is shown below.



Increasing the concentration of buffer species leads to an increase in the rate of formation of phenol and can be represented by lowering the height of the energy barrier associated with the microscopic rate constant k_B. Eventually, at high enough buffer concentration $k_B[A][B]$ will become faster than k_{-A}, and there will be a change to k_A as the rate-determing step. At high buffer concentrations $k_B[A][B] > k_{-A}$ and eq 2 reduces to $k^{OPh} = k_A$. The consequence of this change in the rate-determining step is that a plot of k_{obs} vs [A][B] will eventually level off at a rate constant of k_A. From an examination of Figure 1 it is obvious that there is no evidence for curvature in a plot of k_{obs} vs [A][B] for values of [A][B] up to 38×10^{-3} M^2. Therefore, k_A must be much greater than the highest value of k_{obs} measured. Thus, we can set a lower limit for the value of k_A at $k_A \geq 55 \times 10^{-5}$ s^{-1}.

When the pentavalent intermediate, **I**, collapses to starting material it can do so by the loss of an $-OCH_3$ group or by loss of the $-OCD_3$ group (k_{-A}). The rate of loss of the deuteriomethoxy group from **1D** according to this pathway will be $k'_{OMe} = k_A^{0.5}k_{-A}/k_{-A} = k_A/2$. Exchange of the deuteriomethoxy group by this pathway must occur with a rate constant $k'_{OMe} \geq 2.75 \times 10^{-4}$ s^{-1}. This lower limit for k'_{OMe} is obtained from the minimum rate constant of 55×10^{-5} s^{-1} imposed on k_A. This is a minimum value for exchange of the deuteriomethoxy group. The positive slope in Figure 2 indicates that exchange of the deuteriomethoxy group also occurs by a mechanism that involves bifunctional catalysis. This pathway is depicted on the left-hand side of Scheme V through intermediate **II** and will increase the rate of deuteriomethoxy exchange above the minimum value of 2.75×10^{-4} s^{-1}. If the mechanism proposed in Scheme V were correct then the intercept of Figure 2 should be $\geq 2.75 \times 10^{-4}$ s^{-1} in order to account for the minimum amount of exchange required by the pathway described by the right-hand side of Scheme IV. It is clear from Figure 2 that the intercept is much lower than the

Scheme V. Detailed Mechanism Depicting the Bifunctional-Catalyzed Loss of Phenol and Loss of the Deuteriomethoxy Group from Methoxy-d_3-methylphenoxyphenylsilane, 1D[a]



[a] The reaction occurs by a mechanism that involves the preequilibrium formation of a pentavalent silicon solvent adduct that undergoes rate-determining attack in a second step by another molecule of solvent to displace the leaving group. The second step shows bifunctional catalysis.

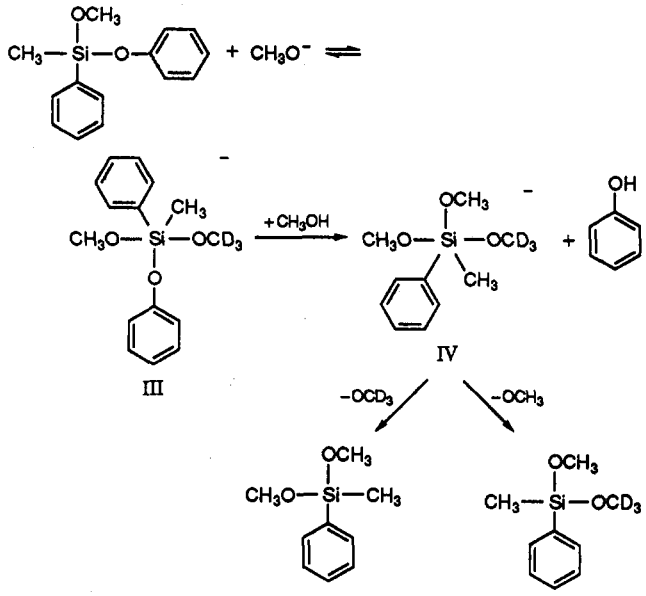
minimum value of 2.75×10^{-4} s^{-1} required by this mechanism.

The above results are therefore inconsistent with the mechanism described in Scheme V (or in the more simplified version of Scheme III) which involves the preequilibrium addition of solvent to **1D** followed by general base-catalyzed addition of a second solvent molecule.

The second possible mechanism involving a pentavalent silicon species (Scheme IV) involves the preequilibrium reaction of the silyl ether with a molecule of formate anion in the first step. In Scheme IV B represents formate anion and OR represents the phenoxy or deuteriomethoxy leaving group. Now, if formate anion can react with the silyl ether to form a pentavalent species it is reasonable that methoxide anion, being many orders of magnitude more basic than formate anion and therefore more nucleophilic, will also lead to the formation of a pentavalent species. It is for this reason that we examined the methoxide catalyzed solvolysis of **1D**.

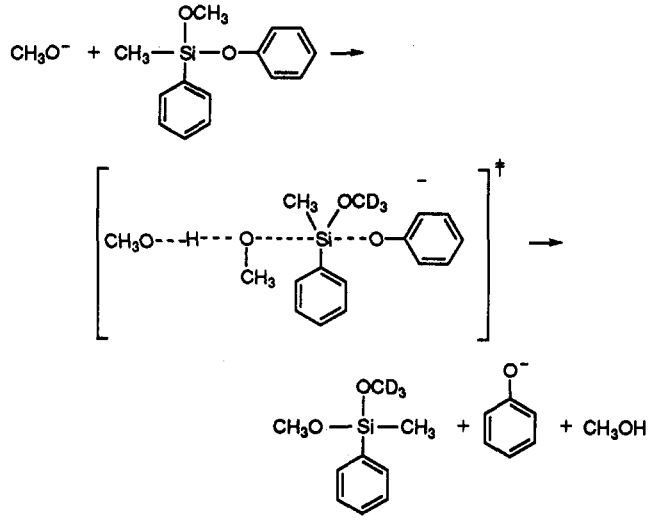
The data in Table II and Figure 3 clearly show that the formation of phenol from **1** is indeed catalyzed by methoxide. In Scheme VI is depicted the mechanism for formation of phenol from **1D** according to a mechanism involving the preequilibrium addition of methoxide ion to **1D** leading to a pentavalent intermediate, **III**, that then undergoes nucleophilic attack by a molecule of methanol leading to phenol formation and to formation of another pentavalent intermediate, **IV**. The pentavalent species **IV** then loses a molecule of methoxide or deuteriomethoxide giving the final product. In Scheme VI the intermediate **III** is depicted as resulting from axial entry of methoxide anion. If pseudorotation does not occur in intermediates **III** and **IV** then intermediate **IV** will have the deuteriomethoxide and a methoxide group in axial positions. According to the principal of microscopic

Scheme VI. Detailed Mechanism Depicting the Methoxide-Catalyzed Loss of Phenol from Methoxy-d_3-methylphenoxyphenylsilane, 1D[a]



[a] The loss occurs by a mechanism that involves the preequilibrium formation of a pentavalent silicon solvent adduct, **III**, which than undergoes nucleophilic attack by a molecule of solvent to displace the phenol leaving group.

Scheme VII. Detailed Mechanism Depicting the Methoxide-Catalyzed Loss of Phenol from Methoxy-d_3-methylphenoxyphenylsilane, 1D[a]



[a] The loss occurs by a mechanism involving methoxide ion acting as a general base for nucleophilic attack by another molecule of methanol at the silicon center.

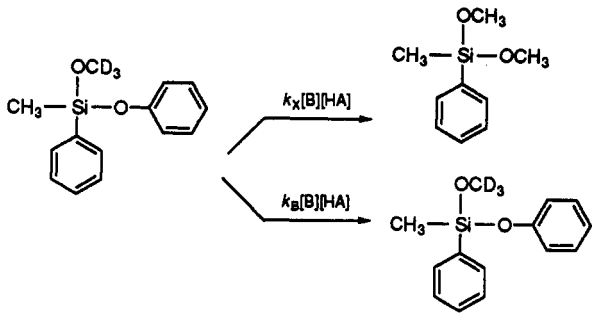
reversibility axial entry requires axial departure of a methoxide; therefore collapse of intermediate **IV** could occur by loss of a methoxide or a deuteriomethoxide group. This will lead to the initial formation of dimethoxymethylphenylsilane that is 50% $C_6H_5SiCH_3(OCD_3)(OCH_3)$ and 50% $C_6H_5SiCH_3(OCH_3)_2$. If pseudorotation can occur in intermediates **III** or **IV** this would lead to equivalence of all the methoxy groups in the pentavalent structure **IV** so that collapse of the intermediate leading to the final product could occur by loss of either methoxy group or by loss of the deuteriomethoxy group. The initially formed dimethoxymethylphenylsilane product will then be 67% $C_6H_5SiCH_3(OCD_3)(OCH_3)$ and 33% $C_6H_5SiCH_3(OCH_3)_2$. However, as was indicated in the Results the percentage of $C_6H_5SiCH_3(OCD_3)(OCH_3)$ is well above the amounts of 50% or 67% predicted by the mechanism involving the addition of methoxide in a preequilibrium step leading to formation of a pentavalent intermediate that then undergoes substitution by another molecule of solvent. This result is therefore inconsistent with the mechanism described in Scheme VI. The mechanism described in Scheme VI involving methoxide as the nucleophile reagent is analagous to Scheme IV where the nucleophilic reagent, B, is formate anion. If methoxide anion does not act as a nucleophilic reagent toward the silicon center leading to a pentavalent species it is unlikely that the less nucleophilic formate anion will act as a nucleophilic reagent. For this reason we believe that Scheme IV is unlikely as a reasonable mechanism to account for the observed bifunctional catalysis.

Since evidence is presented against mechanisms involving a pentavalent intermediate as depicted in Scheme III (or the more detailed version shown in Scheme V) and Scheme IV we are left with Scheme II. Scheme II involves a concerted substitution on the tetravalent silicon center. The mechanism of Scheme II adequately accounts for the bifunctional catalysis and is also consistent with the results from the methoxide catalysis experiments.

Consider the results expected if the reaction occurs by a concerted displacement on the tetravalent silicon species with a molecule of methoxide acting as a general base to facilitate the addition of another molecule of methanol to the silyl ether. It has been well established that methoxide acts as a general base to assist in the addition of a second methanol molecule.[1,8-14] This mechanism is depicted in Scheme VII. According to this mechanism every molecule of dimethoxymethylphenylsilane formed will contain one methoxy group and one deuteriomethoxy group; the initially formed product will be 100% $C_6H_5SiCH_3(OCD_3)(OCH_3)$. As indicated in the Results the percentages are indeed close to 100% as predicted by this mechanism. That the percentages of $C_6H_5SiCH_3(OCD_3)(OCH_3)$ are slightly less then the 100% predicted by the general base-catalyzed mechanism (Scheme VII) is probably due to the fact that both **1D** and the product, $C_6H_5SiCH_3(OCD_3)(OCH_3)$, undergo methoxide-catalyzed loss of the deuteriomethoxy group. In fact, GC/MS analysis of the methoxyphenoxymethylphenylsilane remaining after partial solvolysis of **1D** did indeed indicate that the deuteriomethoxy group had been partially replaced by a methoxy group from the solvent. In addition, it was shown by adding dimethoxy-d_6-methylphenylsilane to methanol solution (1×10^{-3} M in methoxide) that after 10 s the dimethoxy-d_6-methylphenylsilane had undergone partial exchange of the deuteriomethoxy groups with solvent.

In Scheme II formate anion acts as a general base to remove a proton from the attacking methanol molecule, and a molecule of formic acid acts as a general acid to donate a proton to the leaving group. The methoxide-catalyzed reaction is similar in that methoxide acts as a general base removing a proton from the attacking methanol molecule. Presumably, another molecule of methanol assists in the departure of the phenoxy leaving group by hydrogen bonding. However, since the phenoxy leaving group is of lower pK_a than methanol the methanol molecule can only stabilize the transition state by hydrogen

Scheme VIII. Bifunctional-Catalyzed Loss of Phenol and Loss of the Deuteriomethoxy Group from Methoxy-d_3-methylphenoxyphenylsilane, 1D[a]



[a] The loss occurs by parallel concerted mechanisms that involve general base-catalyzed attack of methanol and general acid-catalyzed protonation of the leaving group occurring in a single step.

bonding to the leaving group because there is no thermodynamic advantage to proton transfer.

It is also of interest to note that in the formic acid–sodium formate catalyzed reaction the more basic leaving group, methoxide, reacts faster than the less basic phenoxide leaving group. This must mean that there is a substantial amount of protonation of the leaving group in the transition state and that this is larger for the more basic leaving group.

The results described above suggest that nucleophilic attack on a pentavalent silicon species is not the operable mechanism for alcoholysis of simple silyl ethers. The experimental results, however, are adequately described by competing S_N2–Si (A_ND_N) mechanisms that both involve nucleophilic attack of a solvent molecule on the tetravalent silicon species, **1D**, leading to replacement of the phenol group or of the deuteriomethoxy group, with both of these reactions exhibiting bifunctional catalysis (Scheme VIII).[30]

The mechanisms in Schemes V and VI involving nucleophilic attack on a pentavalent silicon species are similar to the mechanism proposed by Corriu for the racemization of chlorosilanes and the solvolysis of chlorosilanes in aprotic solvents containing small amounts of water with catalysis by added "nucleophilic solvents".[20,22] Hydrolysis of chlorosilanes in anisole containing small amounts of water occurs only in the presence of small amounts of "nucleophilic solvents."[20] The proposed mechanism to account for this catalysis is prior coordination of the "nucleophilic solvent" with the silicon atom to form a pentavalent intermediate; the pentavalet silicon species then undergoes substitution by a molecule of water. No reaction was observed in the absence of the nucleophilic solvent. Typical nucleophilic catalysts used in these studies were oxygen-containing compounds such as dimethylformamide, hexamethylphosphoric triamide, and dimethyl sulfoxide. Indeed, 1:1 adducts between halolsilanes and hexamethylphosphoric triamide have been isolated.[32] The rate of hydrolysis of chlorosilanes in anisole, containing small amounts of water and nucleophilic solvents, is first order in the chlorosilane, first order in the "nucleophilic solvent", and first order in water, consistent with the proposed mechanism.[20,22] The change in stereochemistry from inversion of configuration, which is typically observed in the hydrolysis of alcoholysis of silyl chlorides, to retention of configuration for chlorosilane solvolysis in the presence of "nucleophilic solvents" is consistent with the mechanism involving an intermediate that undergoes nucleophilic attack.

The racemization of chlorosilanes catalyzed by hexamethylphosphorictriamide in carbon tetrachloride is first order in the chlorosilane and second order in hexamethylphosphoric triamide.[26] The proposed mechanism involves addition of a "nucleophilic solvent" to the chlorosilane to form the pentavalent intermediate, which than reacts with another molecule of the "nucleophilic solvent" to displace the chloride ion leading to racemization.

Pentavalent silicon species are reasonable as intermediates in these reactions. It has been demonstrated that in methylene chloride aldehydes will form pentavalent complexes with tetravalent siliconates.[34] Pentavalent silicon species do exist, and many have been isolated and characterized by NMR and X-ray crystallography.[7] Corriu has also provided evidence that pentavalent silicon species are more reactive than tetravalent silicon in reactions with nucleophilic reagents.[24-27] It has been suggested that this enhanced reactivity is due to increased length and greater loosening of the silicon–leaving group bond (as well as the other bonds) in the pentavalent structure and an increased electrophilicity of the pentavalent silicon center.[4,24] These factors must outweigh the increased steric hindrance for substitution at a pentavalent reaction center.

The results reported by Corriu[20,22] for the hydrolysis and racemization of chlorosilanes in aprotic solvents are consistent with, but do not require, a mechanism involving nucleophilic attack on a pentavalent intermediate. The results are also consistent with a double displacement mechanism.[33] The hydrolysis reaction could involve substitution of the chloride group from nucleophilic attack by a "nucleophilic solvent" molecule followed by a second nucleophilic attack involving a molecule of water to give the product. This double displacement would account for the second-order dependence, first order in both the "nucleophilic solvent" and water. This double displacement would lead to product of retained configuration and is therefore consistent with the observed change of stereochemistry from inversion, in the absence of added "nucleophilic solvents", to retention in the presence of "nucleophilic solvents." In fact, this mechanism has been proposed to account for the alcoholysis of silyl chlorides in toluene catalyzed by amines.[35]

The double displacement reaction just described for substitution at silicon is similar to that observed for substitution of the mesylate group of 2-octyl mesylate in dioxane/water and acetone/water mixtures.[36] In 100% water, solvolysis of 2-octyl mesylate gives 2-octanol as product, with complete inversion of configuration. In dioxane/water mixtures, however, some 2-octanol of retained configuration is formed. This racemization cannot be due to carbocation formation since dioxane/water is less polar than 100% water, where complete inversion of configuration was observed. The reaction is best explained as initial attack of dioxane on the carbon center to form an oxonium ion intermediate followed by attack by water.[36]

That the racemization of chlorosilanes is second order in "nucleophilic solvent" and first order in the chlorosilane is also consistent with a double displacement mechanism.[31] The chlorosilane undergoes attack by a molecule of

(34) Stevenson, W. H.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6352.
(35) Chu, H. K.; Johnson, M. D.; Frye, C. L. *J. Organomet. Chem.* **1984**, *271*, 327.
(36) Weiner, H.; Sneen, R. A. *J. Am. Chem. Soc.*, **1965**, *87*, 287.

"nucleophilic solvent" followed by attack of a second molecule of the "nucleophilic solvent". The resulting oxonium is than attacked by the chloride leaving group to reform starting material of inverted configuration.

Finally, while adducts of "nucleophilic solvents" such as hexamethylphosphoric triamide with halosilanes have been isolated,[23,33] there is no evidence that this is a pentavalent silicon species containing covalent bonds to all five ligands. It is reasonable that they could be ionic, saltlike structures, as was suggested for the adduct between hexamethylphosphorictriamide and trimethylsilyl bromide or iodide, tris(dimethylamino)(trimethylsiloxy)-phosphonium halide, $[(Me_2N)_3POSiMe_3]^+X^-$.[33] The ionic nature of these compounds was supported by conductivity measurements. Corriu has criticized these conductivity measurements as being due to HX formed from hydrolysis of the halosilane with trace amounts of water present in the methylene chloride used for the conductivity measurements.[23] However, lack of a large conductance does not disprove the ionic structure. Low conductivity does not demonstrate the nonexistence of a salt structure for the adduct. The low conductance may merely be due to the fact that the saltlike adduct is not dissociated in methylene chloride but exists as an ion pair.

In conclusion, our results suggest that the mechanism for the solvolysis of silyl ethers in protic solvents can best be described as a concerted displacement on the tetravalent silicon center, S_N2–Si or A_ND_N mechanism. The results reported in this paper are inconsistent with a mechanism that involves solvent attack on a performed pentavalent silicon species as has been proposed for other substitutions at silicon.

Experimental Section

Methods. Gas chromatography–mass spectral (GC/MS) analysis was performed on a Hewlett-Packard Model 5988 GC/MS/DS. The GC was equipped with a 30-m × 0.257-mm J&W fused silica DB-5 capillary column. The MS was operated in the electron impact mode. Proton NMR spectra were recorded on a GE QE-300 instrument. Measurements of UV absorbance were made on a Shimadzu UV-160 spectrophotometer equipped with a thermostated cell holder.

Materials. Methanol, formic acid, sodium formate, and sodium perchlorate used to make buffer solutions, were commercially available, and were used without further purification. Phenol, triethylamine, methanol-d_4 (99.8 atom% D), diethyl ether (anhydrous), toluene, and dichloromethylphenylsilane were commercially available.

Sodium methoxide solution was prepared by dissolving enough freshly cleaned sodium metal in methanol to give a solution of approximately 0.1 M. The resulting methoxide solution was titrated against standardized hydrochloric acid to determine the exact concentration of methoxide. The resulting methoxide solution was than diluted with an appropriate amount of methanol to provide a 0.05 M solution of sodium methoxide.

Dimethoxy-d_6-methylphenylsilane was prepared from dichloromethylphenylsilane by modification of a previously described procedure.[37] Dichloromethylphenylsilane (9.6g, 0.05 mol) in 30 mL of anhydrous diethyl ether was added with stirring to 80 mL of anhydrous diethyl ether containing methanol-d_4 (3.6 g, 0.10 mol) and triethylamine (10.1 g, 0.10 mol) over a period of 20 min. The solution was allowed to stir for 1.5 h and filtered and the diethyl ether removed under reduced pressure to give a colorless liquid. The resulting liquid was distilled using a small Vigereux column under reduced pressure (1.25 mmHg). The fraction boiling between 59 and 62 °C was collected to yield 6.7 g of dimethoxy-d_6-methylphenylsilane (71% yield). The NMR spectrum was consistent with the desired product. Mass spectral analysis indicated >99.5% deuteration.

Methoxy-d_3-methylphenoxyphenylsilane (**1D**) was prepared from dimethoxy-d_6-methylphenylsilane according to a previously described procedure[37] with slight modification. To 10 mL of anhydrous toluene containing dimethoxy-d_6-methylphenylsilane (2.06 g, 0.011 mol) and phenol (1.034 g, 0.011 mol) was added with stirring 0.0048 g of sodium metal (2.1×10^{-4} mol) dissolved in 0.4 mL of methanol-d_4 followed by an additional 5 mL of toluene. The resulting solution was heated, and the methanol/toluene azeotrope was continually removed. When the head temperature reached 85 °C the heat was removed and the solution allowed to stir for an additional 1.5 h. The solution was heated again until the head temperature reached 85 °C, the heat removed, and the solution stirred for 1.5 h. The solution was cooled in an ice/water bath and washed three times with 3 mL of cold water, dried ($MgSO_4$), and filtered and the solvent removed under reduced pressure. The resulting pale yellow liquid was distilled under reduced pressure (1.2 mmHg), and the fraction boiling between 113 and 124 °C was collected. A clear liquid (1.3 g) was obtained (45% yield based on dimethoxy-d_6-methylphenylsilane). The NMR spectrum was consistent with the desired product. Mass spectral analysis indicated >99.5% deuteration.

Kinetics. Rate constants, k_{obs}, for the formic acid–formate-catalyzed solvolysis of **1D** in methanol were determined at 30 °C and at ionic strength 0.05 M with $NaClO_4$. Pseudo-first-order rate constants were determined by measuring the increase in absorbance at 281 nm due to the formation of phenol as a function of time. Reaction solutions were prepared by combining known volumes of stock solutions of formic acid/sodium formate in methanol with a known volume of 0.05 M $NaClO_4$ in methanol to give a final volume of 2.5 mL. The stock solutions of formic acid/formate buffer in methanol used to make the reaction solutions were 0.15 M/0.05 M, 0.05 M/0.05 M, 0.5 M/0.05 M, and 0.75 M/0.05 M. The cuvettes containing the reaction solutions were placed in the thermostated cell holder of the spectrophotometer. After temperature equilibration (30 ± 0.5 °C), 0.6 μL of **1D** was added, the cuvette was shaken, and the appearance of phenol was monitored as a function of time. The spectrophotometer was interfaced to a personal computer, and the pseudo-first-order rate constants, k_{obs}, were obtained by a nonlinear regression analysis of absorbance vs time data. Reactions were followed for more than 5 half-lives. The nonlinear regression analysis calculated the best end point. For reactions that were followed to completion, the observed end points always agreed well with the calculated end points. Good pseudo-first-order kinetics were followed, and semilog plots of $(A_\infty - A_t)$ were linear. Rate constants were generally reproducible within better than 10%.

The rate constants for the formic acid–formate-catalyzed exchange of the deuteriomethoxy group of **1D** with solvent, k'_{obs}, were determined by measuring the ratio **1D**/(**1D** + **1H**) as a function of time. The percent of **1D** was determined by GC/MS analysis. Reaction solutions (2 mL) were prepared as described above in a 4-mL vial sealed with a rubber septum cap. The vial was placed in a (30 ± 0.5 °C) constant temperature bath. After temperature equilibration, 0.5 μL of **1D** was added and the solution shaken and returned to the temperature bath. At various time intervals 2–3-μL volumes of the reaction mixture were removed and injected on the GC/MS system. The GC was operated with an injector temperature of 200 °C; the oven was set at an initial temperature of 90 °C for 3 min followed by temperature programming at a rate of 10 °C/min to a final temperature of 220 °C, and the final temperature was maintained for 3 min. The peak corresponding to methoxymethylphenoxyphenylsilane eluted at approximately 14 min. The peaks of interest in the mass spectrum of methoxyphenoxymethylphenylsilane are the m/z 244 and 247 (parent peaks for nondeuterated and deuterated methoxymethylphenoxyphenylsilane, respectively) and m/z 229 and 232 (presumably resulting from loss of a methyl group from the parent silane). The intensities of these peaks were measured by using the average of scans taken over the entire GC peak after appropriate background correction. The ratio 247/(247 + 244) or 232/(232 + 229) gives the percentage of **1D** in each sample. The first data point was usually obtained

(37) Corriu, R. J. P.; Lanneau, G. F.; Royo, G. *J. Organomet. Chem.* 1972, *35*, 35.

after 1 min, and reactions were followed for more than 3 half-lives. Semilog plots of the ratio 1D/(1D + 1H) against time were linear. The slopes of these plots give the pseudo-first-order rate constants for loss of the deuteriomethoxy group in 1D.

Since the initial percentage of $-OCD_3$ present in 1D was shown to be greater than 99.5% one would expect that extrapolation of the semilog plots to $t = 0$ should give an intercept corresponding to close to 100% 1D. However, the semilog plots, although linear, always gave intercepts significantly lower than 100%, generally corresponding to 60–80% 1D. It was demonstrated by two methods that this discrepancy is due to the method of analysis, presumably from a reaction of 1D with methanol at the elevated temperature of the injector. In the first experiment it was demonstrated that when the rate of reaction was determined in a formic acid/formate buffer, A/B = 0.06 M/0.02 M the first data point obtained at 1 min indicated about 60% 1D; this corresponds to an intercept of approximately 60% 1D. However, if the same data point (1 min) is determined after removal of methanol and buffer species by extraction, the resulting percentage of 1D from mass spectral analysis is now >99%. This experiment was performed by adding 1 μL of 1D to 1 mL of buffer solution at 30 °C. After 1 min the reaction mixture was poured into 4 mL of diethyl ether and the solution extracted twice with 2-mL volumes of water. The diethyl ether solution was dried ($MgSO_4$), filtered, and concentrated to a volume of approximately 0.5 mL with a stream of air. The resulting ether solution was analyzed by GC/MS.

In a second experiment, entire rate determinations were conducted using the extraction technique. Reactions were initiated as described above by adding 5.0 μL of 1D to 10 mL of buffer solution incubated at 30 °C. At various time intervals 0.5-mL aliquots of the reaction mixture were removed and placed in 2 mL of diethyl ether, the ether was extracted with 2 mL of water and then twice with 1-mL volumes of water, dried ($MgSO_4$), filtered, and concentrated to a volume of approximately 0.5 mL, and the diethyl ether solutions were analyzed by GC/MS. Semilog plots of 1D/(1D + 1H) against time were linear and had intercepts of >99% 1D at $t = 0$. The slopes of these plots were the same, within experimental error, as in experiments that employed direct injection of the reaction mixture without prior extraction. For A/B = 0.06 M/0.02 M $k'_{obs} = (1.6 - 2.1) \times 10^{-4}$ s^{-1} with direct injection of the sample and $(1.7 - 1.9) \times 10^{-4}$ s^{-1} for reaction employing the extraction technique; similarly for A/B = 0.15 M/0.05 M, $k'_{obs} = (7.3 - 10.0) \times 10^{-4}$ s^{-1} and $(5.2 - 9.3) \times 10^{-4}$ s^{-1} for analysis by direct injection of the sample and for analysis employing the extraction technique, respectively. These experiments show that the low intercepts obtained by direct injection are an artifact due to the method of analysis. However, this artifact does not affect the measured rate constants for loss of deuteriomethoxy group in 1D.

Rate constants, k_{obs}, for the methoxide-catalyzed solvolysis of 1H, at 10 °C and ionic strength 0.05 M with $NaClO_4$, were determined using the undeuterated compound employing a similar procedure as described for the formic acid-formate-catalyzed reactions. Reaction solutions were prepared by combining known volumes of stock solutions of 0.05 M sodium methoxide with a known volume of 0.05 M $NaClO_4$. The cuvettes containing 2.5 mL of the reaction solution were placed in a thermostated cell holder at 10 °C, and after temperature equilibration 0.6 μL of 1H was added and the reaction followed by measuring the change in absorbance at 281 nm as described above for reactions in formic acid–formate solutions.

Analysis of the dimethoxymethylphenylsilane product from the methoxide-catalyzed methanolysis of 1D was performed by adding 1 μL of 1D to 1 mL of methanol at 10 °C containing a known concentration of methoxide, the mixture was shaken, and after an appropriate amount of time (5 or 10 s) the reaction mixture was poured into 4 mL of ethyl ether and 4 mL of water at 0 °C. The aqueous layer was removed and the ether washed two times with 3 mL of ice cold water. The ether layer was dried ($MgSO_4$) and filtered. The resulting ether solution was concentrated to a volume of less than 0.5 mL, and a 2-μL volume injected on the GC/MS. The GC was operated with an injector temperature of 200 °C; the oven was set at an initial temperature of 90 °C for 3 min followed by temperature programming at a rate of 10 °C/min to a final temperature of 220 °C, and the final temperature was maintained for 3 min. The peak corresponding to dimethoxymethylphenylsilane eluted at approximately 7 min. The peaks of interest in the mass spectrum of dimethoxymethylphenylsilane are the m/z 182 and 185 (parent peaks for dimethoxymethylphenylsilane and for dimethoxy-d_3-methylphenylsilane, respectively) and m/z 167 and 172 (presumably resulting from loss of a methyl group from the parent silane). Each sample was injected twice. For the first injection the MS was operated in the scan mode, and for the second injection the MS was operated in the single ion monitoring (SIM) mode. The intensities of the peaks were measured using the average of scans taken over the entire GC peak after appropriate background correction. For single ion monitoring, m/z of 167, 172, 182, and 185 were measured. The ratio 172/(172 + 167) or 185/(185 + 182) gives the percentage of dimethoxy-d_3-methylphenylsilane in each sample.

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