J. Org. Chem. **1994,** *59,* 2523–2528 **2523**

Catalysis of the Trifluoroethanolysis of Dimethylphenylphenoxysilane

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Received December 6, 1993®

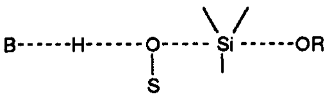
The buffer-catalyzed trifluoroethanolysis of dimethylphenylphenoxysilane was studied. The reaction exhibits general base catalysis, general acid catalysis, and bifunctional catalysis. The Bronsted values are the following: general base catalysis, $\beta_B = 0.72$; general acid catalysis, $\alpha_A = 0.65$; bifunctional catalysis $\beta_{AB} = 0$. Solvent isotope effects for the acetic acid–tetramethylammonium acetate-catalyzed trifluoroethanolysis are greater than 1.0 for all three mechanisms of catalysis. It is suggested that general acid catalysis, general base catalysis, and bifunctional catalysis are modifications of a similar mechanism.

Introduction

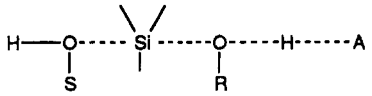
Silicon, although located immediately below carbon on the periodic table, shows quite different behavior from carbon in its reactions with nucleophilic reagents. For example, silicon, unlike carbon, is capable of forming pentavalent adducts with nucleophilic reagents. Indeed there are many documented examples of hypervalent silicon species.[1] Another difference between silicon and carbon is that tetravalent silicon compounds undergo general base-catalyzed solvolysis in protic solvents rather than direct nucleophilic substitution.[2-11] For tetravalent carbon the preferred reaction is direct substitution by the nucleophilic reagent. General base-catalyzed solvolysis at tetravalent carbon is uncommon and has been observed in only a few systems.[12]

Our research has been directed at understanding the mechanism for the solvolysis of silyl ethers in protic solvents. Results from our laboratory suggest that the alcoholysis reaction is a one-step concerted reaction with bond formation to the attacking solvent molecule occurring simultaneously with breaking of the silicon–oxygen leaving group bond.[2,4] It was demonstrated that the trifluoroethanolysis of dimethylphenylphenoxysilane does not occur by a mechanism that involves the preequilibrium formation of a pentavalent intermediate that then collapses to produce products (S_Ni-Si or $A_N + D_N$ mechanism).[2] Additional results indicate that the simultaneous bond-forming and bond-breaking process occurs on a tetravalent silicon species and not on a pentavalent silicon species formed in a preequilibrium step.[13] The reaction can best be described as an S_N2-like reaction where bond formation to the nucleophile and bond breaking to the leaving group occur simultaneously on a tetravalent silicon center (S_N2-Si or A_ND_N mechanism).[2]

When the nucleophile is a solvent molecule, the addition of solvent is catalyzed by added bases. This general base-catalyzed solvolysis of silyl ethers is well documented.[2-11] General base catalysis presumably involves a molecule of base catalyst removing a proton from the attacking solvent molecule as it forms a bond to the silicon center. The transition state for general base catalysis is depicted below where B represents the base catalyst, HOS the solvent, and OR the leaving group.



In addition it has been demonstrated that the solvolysis of silyl ethers can occur with general acid catalysis[15,16] and with bifunctional catalysis.[3,18] General acid catalysis presumably involves a molecule of the acid catalyst donating a proton to the leaving group in the transition state as depicted below, where AH represents the acid catalyst, HOS the solvent, and OR the leaving group.



Bifunctional catalysis involves both a molecule of acid and base catalyst in the transition state. It is reasonable

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® Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) For a recent review on hypervalent silicon compounds see Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993,** *93,* 1371. Also see refs cited in Dietze, P. E. *J. Org. Chem.* **1993,** *58,* 5653.

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(13) It is known that pentavalent silicon species can be more reactive than tetravalent silicon species toward nucleophilic substitution.[14] A proposed mechanism[14] for nucleophilic substitution at silicon involves the preequilibrium formation of a pentavalent adduct between the silicon compound and the nucleophilic reagent. This pentavalent species then undergoes reaction with a second molecule of the nucleophilic reagent to displace the leaving group. However, this does not appear to be the operable mechanism for the alcoholysis of silyl ethers.[2]

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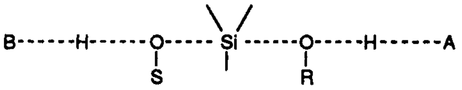
to suggest that the mechanism for bifunctional catalysis is similar to the mechanisms described above to account for general base catalysis and general acid catalysis. Presumably the mechanism for bifunctional catalysis involves a molecule of base catalyst assisting in removing a proton from the attacking solvent molecule while a molecule of acid catalyst donates a proton to the leaving group as depicted below.



In particular we have investigated the trifluoroethanolysis of silyl ethers. We have demonstrated that the trifluoroethanolysis of silyl ethers exhibits general base catalysis, general acid catalysis, and bifunctional catalysis.[3,16] There are very few examples of bifunctional catalysis in the literature.[17,18] The uncommon occurrence of bifunctional catalysis for reactions in solution is presumably due to entropic difficulties. The observation that the trifluoroethanolysis of dimethylphenylphenoxysilane exhibits bifunctional catalysis led us to investigate this reaction in more detail.

In this paper we would like to report our results on general base catalysis, general acid catalysis, and bifunctional catalysis in the trifluoroethanolysis of dimethylphenylphenoxysilane.

Results and Discussion

Pseudo-first-order rate constants, k_{obs}, were determined for the trifluoroethanolysis of dimethylphenylphenoxysilane at 30.0 ± 0.5 °C and ionic strength 0.05 M (tetramethylammonium chloride) for a variety of amine–amine hydrochloride buffers (supplementary material). The ratio of the basic form of the buffer to acid form of the buffer, B/A, was 1.0. Values of k_{obs} were observed to increase with increasing buffer concentration. It was demonstrated that the increase in rate was dependent on the basic form of the buffer by varying the B/A ratio of the buffer in several experiments and determining that the rate depends only on the basic component of the buffer. For example, the observed rate constant for disappearance of dimethylphenoxyphenylsilane in a trifluoroethanol solution buffered with butylamine–butylamine hydrochloride having a B/A ratio of 0.05 M/0.05 M is 2.5×10^{-3} s^{-1}, is essentially the same as the rate constant of 2.3×10^{-3} s^{-1} obtained with a B/A ratio of 0.05 M/0.01 M. Similarly, the observed rate constants of 5.7×10^{-3} s^{-1} and 6.0×10^{-3} s^{-1} determined in a trifluoroethanol solution containing a butylamine–butylamine hydrochloride buffer with B/A ratios of 0.01 M/0.01 M and 0.01 M/0.002 M, respectively, are within experimental error, the same. Plots of k_{obs} vs free amine concentration are linear with intercepts equal to zero and demonstrate that amines catalyze the trifluoroethanolysis of dimethylphenylphenoxysilane. The rate law for catalysis by amines is therefore given by eq 1,

$$k_{obs} = k_B[\text{amine}] \qquad (1)$$

where k_B is the second-order rate constant for catalysis by the amine. The slope of a plot of k_{obs} vs amine concentration provides the second-order rate constant for catalysis by the amine, k_B. Values of k_B, and the pK_a values for each of the amines, determined in aqueous solution, are given in Table 1.

Table 1. Rate Constants, k_a, for General Base Catalysis by Amines for Reaction of Trifluoroethanol with Dimethylphenylphenoxysilane at 30.0 ± 0.5 °C and Constant Ionic Strength of 0.05 M (tetramethylammonium chloride)

amine	pK_a[a]	k_a (× Ms)
butylamine	10.59	4.9×10^{-2}
piperidine	11.22	2.3×10^{-1}
morpholine	8.36	2.6×10^{-3}
methoxyethylamine	9.20	8.6×10^{-3}
propargylamine	8.15	6.4×10^{-4}

[a] Reference 19.

Pseudo-first-order rate constants, k_{obs}, for the trifluoroethanolysis of dimethylphenylphenoxysilane at 30.0 ± 0.5 °C and ionic strength 0.05 M (tetramethylammonium trifluoroacetate) were determined for a variety of substituted acetic acid–acetate buffers and are reported in Table 2. The anion of the acid was present as the tetramethylammonium salt. Methoxyacetic acid, cyanoacetic acid, dichloroacetic acid, and trifluoroacetic acid were used in this study. Data for acetic acid has been reported earlier.[3] For experiments with trifluoroacetic acid–tetramethylammonium trifluoroacetate buffers ionic strength was not maintained. However, it was demonstrated in experiments with acetic acid–tetramethylammonium acetate buffers that ionic strength does not have a large effect on k_{obs}.[3] Experiments performed with methoxyacetic acid–tetramethylammonium methoxyacetate buffers and with cyanoacetic acid–tetramethylammonium cyanoacetate buffers, having an acid–base ratio, A/B, of 10, gave the same values for k_{obs} when ionic strength was maintained with tetramethylammonium trifluoroacetate as was obtained when ionic strength was not maintained. These experiments support the earlier observation[3] that ionic strength does not have a large effect on k_{obs} (see data in Table 2). For all buffer systems values of k_{obs} were measured for acid–base ratios, A/B, of 5, 10, 15, and 20.

For all substituted acetic acid buffers the value for k_{obs} was observed to increase with increasing buffer concentration while the ratio of acidic to basic form of the buffer, A/B, was kept constant. For methoxyacetic acid and cyanoacetic acid buffers this increase in rate with increasing buffer concentration is not linear and shows upward curvature. This nonlinear dependence of observed rate on total buffer concentration, $[\text{buffer}]_{total}$, is the same as reported earlier for the trifluoroethanolysis of dimethylphenylphenoxysilane in acetic acid–tetramethylammonium acetate buffers.[3] A plot of k_{obs} vs $[\text{buffer}]_{total}$, for methoxyacetic acid buffers (Figure 1) depicts the increase in rate with increasing buffer concentration and the curvature. For dichloroacetic acid and trifluoroacetic acid buffers the values of k_{obs} also increase with increasing buffer concentration; however, the plots showed no detectable deviation from linearity. Figure 2 depicts a plot of k_{obs} vs $[\text{buffer}]_{total}$ for trifluoroacetic acid buffers. In Figure 2 only data for A/B ratios of 20 and 5 are plotted in order that the linear dependence on total buffer concentration can be easily seen. Plots of k_{obs} vs total buffer concentration for A/B ratios of 10 and 15 (not shown) are also linear.

Plots of k_{obs} vs $[\text{buffer}]_{total}$ exhibiting curvature indicate a greater than first-order dependence of the rate on buffer

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Table 2. Pseudo-First-Order Rate Constants for the Solvolysis of Dimethylphenylphenoxysilane at 30.0 ± 0.5 °C in Trifluoroethanol Buffered with Substituted Acetic Acid–Tetramethylammonium Acetate Buffers and Constant Ionic Strength of 0.05 M Maintained with Tetramethylammonium Trifluoroacetate

acid (M)/ base (M)	k_{obs} (× 10⁴ s)	acid (M)/ base (M)	k_{obs} (× 10⁴ s)	acid (M)/ base (M)	k_{obs} (× 10⁴ s)	acid (M)/ base (M)	k_{obs} (× 10⁴ s)
Methoxyacetic Acid							
0.25/0.05	0.86, (0.79)[a]	0.40/0.04	1.1, (0.95)[a]	0.40/0.0267	0.80, (0.64)[a]	0.20/0.01	0.26, (0.15)[a]
0.20/0.04	0.60, (0.51)[a]	0.30/0.03	0.67, (0.56)[a]	0.30/0.02	0.54, 0.51, 0.48, (0.40)[a]	0.10/0.005	0.11
0.15/0.03	0.38, (0.27)[a]	0.20/0.02	0.36, 0.40, (0.25)[a]	0.20/0.0133	0.28, (0.22)[a]	0.005/0.05	0.079, 0.082
0.10/0.02	0.20	0.10/0.01	0.14	0.50/0.025	0.93, (0.75)[a]	0.003/0.03	0.029, 0.058
0.05/0.01	0.066	0.50/0.033	1.2, (1.0, 0.98)[a]	0.40/0.02	0.68, (0.50)[a]	0.001/0.01	0.031, 0.036
0.50/0.05	1.5, 1.4			0.30/0.015	0.47, 0.40, (0.30)[a]		
Dichloroacetic Acid							
0.25/0.05	4.8	0.50/0.05	9.1, 11.6	0.50/0.033	9.5	0.50/0.025	9.6
0.20/0.04	4.2	0.40/0.04	7.4, 9.4	0.40/0.0267	7.4	0.40/0.02	7.6
0.15/0.03	3.1	0.20/0.02	4.5, 4.6	0.30/0.02	5.6, 6.4	0.30/0.03	5.3, 6.8
0.10/0.02	2.1	0.10/0.01	2.4	0.20/0.0133	3.9, 4.9	0.20/0.01	3.9
0.05/0.01	1.1			0.10/0.0067	2.2, 2.9	0.10/0.005	2.2
Cyanoacetic Acid							
0.25/0.05	2.4	0.40/0.04	3.2, (3.1)[a]	0.40/0.0267	2.8	0.30/0.015	2.0
0.20/0.04	1.8	0.30/0.03	2.3, 2.3, (2.0)[a]	0.30/0.02	2.0	0.20/0.01	1.3
0.15/0.03	1.2	0.20/0.02	1.4, 1.4, (1.0)[a]	0.20/0.0133	1.3	0.10/0.005	0.62
0.10/0.02	0.72	0.10/0.01	0.63, 0.70, (0.36)[a]	0.10/0.0067	0.61	0.005/0.05	0.070
0.05/0.01	0.32	0.5/0.033	3.6	0.50/0.025	3.3	0.003/0.03	0.029
0.50/0.05	4.3, (4.5)[a]			0.40/0.02	2.6		
Trifluoroacetic Acid							
0.25/0.05	30	0.50/0.05	64	0.50/0.033	64	0.50/0.025	65, 59
0.20/0.04	21	0.40/0.04	51	0.40/0.0267	46	0.40/0.02	51, 55
0.15/0.03	14	0.30/0.03	34	0.30/0.02	34	0.30/0.015	38, 40
0.10/0.02	9.6	0.20/0.02	19	0.20/0.0133	25	0.20/0.01	22, 26
0.05/0.01	4.4	0.10/0.01	14	0.10/0.0067	14	0.10/0.005	16, 15

[a] Values in parenthesis are for rate constant k_{obs}, determined without using tetramethylammonium trifluoroacetate to control ionic strength.

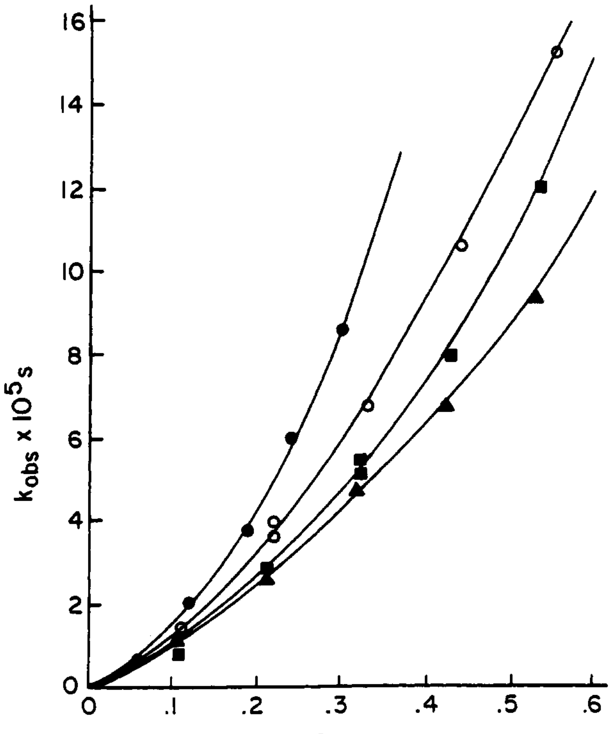

Figure 1. Plot of k_{obs} against total buffer concentration for solvolysis of dimethylphenylphenoxysilane at 30 °C in trifluoroethanol buffered with methoxyacetic acid–tetramethylammonium methoxyacetate at various buffer ratios A/B and constant ionic strength (tetramethylammonium trifluoroacetate): ●, A/B = 5; ○, A/B = 10; □, A/B = 15; △, A/B = 20.

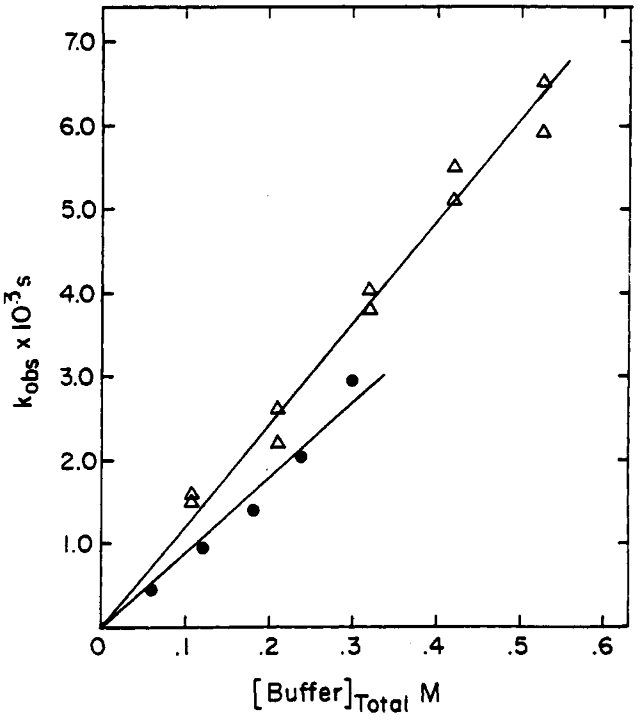

Figure 2. Plot of k_{obs} against total buffer concentration for solvolysis of dimethylphenylphenoxysilane at 30 °C in trifluoroethanol buffered with trifluoroacetic acid–tetramethylammonium trifluoroacetate at buffer ratios A/B of 20 (△) and 5 (●).

concentration. The upward curvature can be accounted for by a rate law containing a term in both the acidic and basic form of the buffer. The same explanation was offered to account for the upward curvature observed with acetic acid–tetramethylammonium acetate buffers.[3] An earlier study of the acetic acid–tetramethylammonium acetate-catalyzed reaction supports the suggestion that the observed curvature is due to a term in the rate law containing both the acidic and basic forms of the buffer, i.e. bifunctional catalysis.[3] Evidence was provided to suggest that other possible causes for the curvature were unlikely.[3] It is reasonable that the observed curvature in plots of k_{obs} vs $[\text{buffer}]_{total}$ for methoxyacetic acid and cyanoacetic acid buffers is also due to bifunctional

Table 3. Rate Constants for General Acid Catalysis, k_A, and for Bifunctional Catalysis, k_{AB}, by Substituted Acetic Acid–Tetramethylammonium Acetate Buffers for the Reaction of Trifluoroethanol with Dimethylphenylphenoxysilane at 30.0 ± 0.5 °C and Constant Ionic Strength of 0.05 M (tetramethylammonium trifluoroacetate)

acetic acid buffer	pK_a	k_A (× Ms)	k_{AB} (× Ms)
trifluoroacetic	0.23	$(1.2 \pm .04) \times 10^{-2}$ $((1.2 \pm 0.2) \times 10^{-2})$[a]	$(0 \pm 1.2) \times 10^{-2}$
dichloroacetic	1.29	$(1.9 \pm 0.1) \times 10^{-3}$ $((1.9 \pm 0.3) \times 10^{-3})$[a]	$(0 \pm 4.0) \times 10^{-3}$
cyanoacetic	2.43	$(4.9 \pm 0.2) \times 10^{-4}$ $((5.4 \pm 2.2) \times 10^{-4})$[a]	$(5.7 \pm 0.5) \times 10^{-3}$ $((5.5 \pm 0.6) \times 10^{-3})$[a]
methoxyacetic	3.53	$(8.3 \pm 0.8) \times 10^{-5}$ $((7.9 \pm 1.0) \times 10^{-5})$[a]	$(4.6 \pm 0.2) \times 10^{-3}$ $((4.9 \pm 0.8) \times 10^{-3})$[a]
acetic[b]	4.76	$(1.7 \pm 0.3) \times 10^{-5}$ $((2.3 \pm 1.0) \times 10^{-5})$[a]	$(1.6 \pm 0.1) \times 10^{-3}$ $((1.6 \pm 0.3) \times 10^{-3})$[a]

[a] Determined by the graphical procedure as described in ref 3. [b] Taken from ref 3.

catalysis. A complete rate law including catalysis by all acidic and basic species present in solution is given by eq 2.

$$k_{obs} = k_o + k_H[H^+] + k_{TO}[TO^-] + k_A[A] + k_B[B] + k_{AB}[A][B] \quad (2)$$

In eq 2 k_o is the rate constant for the uncatalyzed reaction, k_H and k_{TO} are the rate constants for reaction catalyzed by hydronium ion and trifluoroethoxide ion, respectively, and k_A and k_B are rate constants for catalysis by the acidic form of the buffer (general acid catalysis) and the basic form of the buffer (general base catalysis). The term k_{AB} represents the rate constant for bifunctional catalysis. Plots of k_{obs} vs [buffer]$_{total}$ for all the buffers studied have intercepts close to zero (for example see Figures 1 and 2). This indicates that the terms involving k_o, k_H, and K_{TO} are small, and their contribution to k_{obs} is negligible so that eq 1 can be simplified to eq 3.

$$k_{obs} = k_A[A] + k_B[B] + k_{AB}[A][B] \quad (3)$$

The absence of curvature in plots of k_{obs} vs [buffer]$_{total}$ for trifluoroacetic acid and dichloroacetic acid buffers suggest that for these buffers the k_{AB} term must also be small relative to k_A and/or k_B. For these buffers the equation for k_{obs} can therefore be further simplified to eq 4.

$$k_{obs} = k_A[A] + k_B[B] \quad (4)$$

Values of k_A and k_{AB} for each of the buffers were obtained from a computer-generated least-squares fit of the data according to eq 3 and are reported in Table 3 along with the pK_a values, determined in aqueous solution,[19] for each of the acids. Values for k_A and k_{AB} obtained by graphical treatment of the data as described in ref 3 gave similar values as those obtained from the least-squares analysis and are also reported in Table 3. For all the substituted acetic acid buffers used in this study the value of k_B obtained from the computer-generated least squares fit of the data according to eq 3, was too small to be accurately determined. The substituted acetate anions are not sufficiently strong bases to exhibit detectable general base catalysis. The values of k_B were found to be 0 within experimental error and are therefore not reported. Graphical treatment of the data also demonstrate that the values of k_B (obtained from the intercept of the appropriate plot, see ref 3) are close to 0 and too small to be accurately determined.

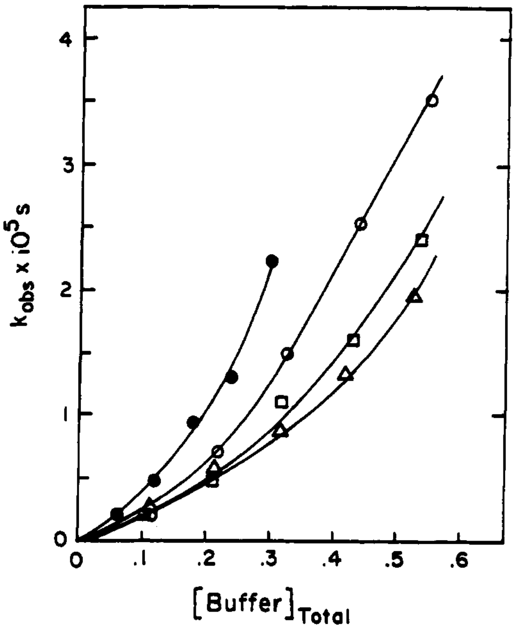

Figure 3. Plot of k_{obs} against total buffer concentration for solvolysis of dimethylphenylphenoxysilane at 30 °C in deuterated trifluoroethanol buffered with acetic acid-*d*–tetramethylammonium acetate at various buffer ratios A/B and constant ionic strength (tetramethylammonium trifluoroacetate): ●, A/B = 5; □, A/B = 10; ○, A/B = 15; △, A/B = 20.

For trifluoroacetic acid and dichloroacetic acid buffers, where no curvature was observed, values of k_{AB} were obtained by a computer-generated least-squares fit of the data according to eq 4. When the data for these buffers is treated according to eq 3, the same values for k_A are obtained as were obtained using eq 4 and the value of k_{AB} is found to be, within experimental error, 0. In Table 3 is reported the range of values for the k_{AB} term obtained from analysis of the data using eq 3.

Pseudo-first-order rate constants, k_{obs}, for trifluoroethanolysis of dimethylphenylphenoxysilane at 30.0 ± 0.5 °C and ionic strength 0.05 M determined in deuterated trifluoroethanol buffered with acetic acid-*d*–tetramethylammonium acetate are reported as supplementary material. Plots of k_{obs} vs [buffer]$_{total}$ at a fixed ratio of A/B, Figure 3, indicate a nonlinear increase in k_{obs} with increasing buffer concentration, the plots showing upward curvature. Values for k_A, k_B, and k_{AB} were determined by a computer-generated least squares fit of the data according to eq 3. Values of k_A, k_B, and k_{AB} for acetic acid-*d*–tetramethylammonium acetate in deuterated trifluoroethanol are $(6.5 \pm 1.7) \times 10^{-6}$ M^{-1} s^{-1}, $(1.2 \pm 0.2) \times 10^{-4}$ M^{-1} s^{-1} and $(1.0 \pm 0.1) \times 10^{-3}$ M^{-2} s^{-1}, respectively. These values agree well with those obtained by a graphical treatment of the data: $k_A = (1.9 \pm 0.8) \times 10^{-5}$ M^{-1} s^{-1}, $k_B = (3.0 \pm 0.3) \times 10^{-4}$ M^{-1} s^{-1}, and $(9.5 \pm 2.0) \times 10^{-4}$ M^{-2} s^{-1}. Values for k_A, k_B, and k_{AB} determined in non-deuterated trifluoroethanol are $(1.7 \pm 0.3) \times 10^{-5}$ M^{-1} s^{-1}, $(2.2 \pm 0.3) \times 10^{-4}$ M^{-1} s^{-1}, and $(1.6 \pm .1) \times 10^{-3}$ M^{-2} s^{-1}, respectively.[3]

Comparison of the rate constants (determined from the computer-generated least squares fit) obtained in deuterated and in non-deuterated solvent[3] provide solvent deuterium isotope effects, k_H/k_D, for each mechanism of catalysis. The k_H/k_D values for k_A, k_B, and k_{AB}, with the

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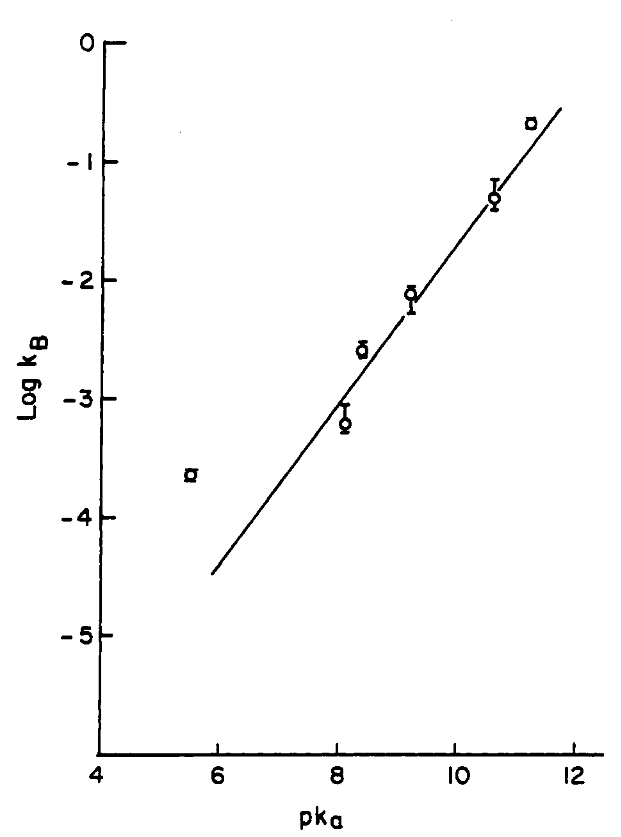

Figure 4. Bronsted plot of log k_B vs the pK_a of the base catalyst for the base-catalyzed trifluoroethanolysis of dimethylphenylphenoxysilane. The bases in order of increasing pK_a are acetate anion, propargylamine, morpholine, methoxyethylamine, *n*-butylamine, and piperidine.

range of values provided in parenthesis, are 2.6 (1.7–4.3), 1.8 (1.4–2.5) and 1.5 (1.3–1.7), respectively.

Discussion

A Bronsted plot of log k_B vs pK_a of the base catalyst is shown in Figure 4. The slope of the plot (drawn through the points for primary amines), β_B, is 0.72 and is a measure of the amount of proton transfer to the catalyzing base in the transition state. A Bronsted value, β, of 0.7 is similar to that observed by others for the general base-catalyzed solvolysis of silyl ethers. The general base-catalyzed reaction presumably involves a molecule of base catalyst removing a proton from the attacking trifluoroethanol molecule, and the value of β_B suggests that the proton is approximately 70% transferred in the transition state. Also included on Figure 4 is the point corresponding to general base catalysis by acetate anion. The point corresponding to acetate shows a positive deviation from the line defined by amine bases and indicates that the acetate anion is a more-effective catalyst than an amine of comparable pK_a. The reason(s) for this is not clear; however, in the transition state for the solvolysis reaction a positive charge is developed on the oxygen of the attacking solvent molecule. This positive charge may be stabilized by an electrostatic interaction with the negative charge on the acetate anion. Such electrostatic stabilization is not possible when the base is a neutral amine.

Similarly a Bronsted plot of log k_A vs pK_a of the catalyzing acid (Figure 5) has a slope, $-\alpha_A$, of 0.65 and is similar to the α value observed for the general acid-catalyzed trifluoroethanolysis of dimethylphenylethoxysilane. For the general acid-catalyzed reaction the acid catalyst is presumably donating a proton to the phenoxide leaving group in the transition state. A value for α_A of 0.65 suggests that for general acid catalysis the proton is also approximately 70% transferred in the transition state.

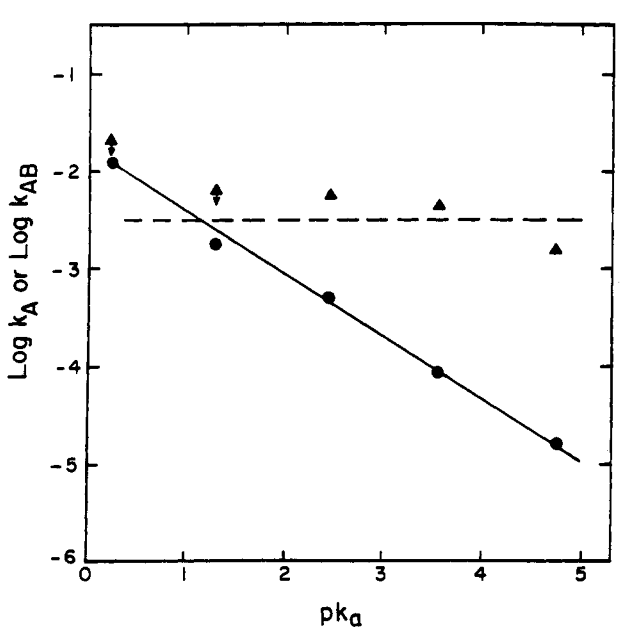

Figure 5. Bronsted plot of log k_A (circles) and of log k_{AB} (triangles) vs the pK_a of the acid catalyst for the acid-catalyzed and for bifunctional catalysis of the trifluoroethanolysis of dimethylphenylphenoxysilane.

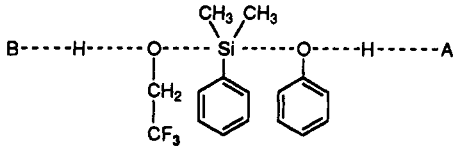

Figure 6.

A Bronsted plot may also be constructed for the bifunctional catalysis term using the values of k_{AB} available for acetic acid, methoxyacetic acid, and cyanoacetic acid and is included on Figure 5. The slope of this plot, β_{AB}, is consistent with a value for β_{AB} of 0. Upper limits on the value of k_{AB} for trifluoroacetic acid and dichloroacetic acid buffers are included in Figure 5 and show that within experimental error these acids also fit on a Bronsted plot with β_{AB} of 0. A value of 0 for β_{AB} indicates that for a given acid–base pair any increase in the effectiveness of the base catalyst is offset by a decrease in the effectiveness of the acid catalyst. This is consistent with a mechanism where the catalyzing base assists in removal of a proton from the attacking trifluoroethanol molecule as the silicon–oxygen bond forms occurring simultaneously with proton donation to the phenoxide leaving group by the catalyzing acid as depicted in Figure 6.

The reaction under study is essentially a symmetrical reaction having an oxygen nucleophile and an oxygen leaving group. For a symmetrical reaction, the degree of proton transfer between the catalyzing acid and the oxygen of the leaving group must be the same as the amount of proton transfer between the oxygen of the attacking solvent molecule and the catalyzing base. As the basicity of the acetate anion increases making it a more effective catalyst, there is a corresponding decrease in the acidity of the acid making it a less-effective catalyst, these two factors offset each other so that there is no observed increase in k_{AB} with changing pK_a of the catalyst and the value of β_{AB} is 0.

The solvent deuterium isotope effect on the base-catalyzed reaction, k_B, the acid-catalyzed reaction, k_A, and the bifunctional catalyzed reaction, k_{AB}, are all greater than 1.0. Although the values of k_H/k_D have reasonably large errors, they are all greater than 1.0. Values for k_H/k_D larger than 1.0 are consistent with a mechanism where a proton is being transferred in the rate-determining step. The value of the solvent deuterium isotope effect for the base-catalyzed reaction is 1.8. This value is similar in magnitude to that observed for the methanolysis of phenoxytriphenylsilanes.[9]

Larger values for the solvent deuterium isotope effect might be expected for a proton under going transfer between electronegative atoms in the transition state. However, as was pointed out by Schowen[9] solvation of the base catalyst can lead to an inverse secondary isotope effect that will diminish the observed isotope effect. It is also possible that the isotope effects could be reduced by coupling of the motion of the proton(s) and heavy atoms in the transition state.[20]

We suggest that bifunctional catalysis, general base catalysis, and general acid catalysis of the trifluoroethanolysis of dimethylphenylphenoxysilane all occur by a similar mechanism. The transition state for general base catalysis is the same as the transition state depicted in Figure 6 for bifunctional catalysis except that a trifluoroethanol molecule, rather than a molecule of acid catalyst, assists in the departure of the leaving group. The transition state can be depicted as in Figure 6 with HA representing a molecule of trifluoroethanol. The trifluoroethanol molecule, however, can only stabilize the negative charge developing on the phenoxide oxygen by hydrogen bonding since there is no thermodynamic advantage for proton transfer. Similarly, in the general acid-catalyzed reaction a trifluoroethanol molecule assists another trifluoroethanol molecule, by hydrogen bonding, as the nucleophile oxygen–silicon bond is formed; this occurs as the general acid donates a proton to the departing phenoxide anion. Again the transition state can be depicted as in Figure 6 with B representing a molecule of trifluoroethanol. According to this interpretation, one would expect the value of $\beta_{AB} = \beta_B - \alpha_A$, as is the case, within experimental error.

Experimental Section

Materials. Trifluoroethanol, deuterium oxide (99.8 atom % *d*), dimethylphenylsilyl chloride, phenol, tetramethylammonium hydroxide pentahydrate, tetramethylammonium chloride, the substituted acetic acids, and the amines and amine hydrochlorides were all commercially available. Trifluoroethanol was stored over 4-Å molecular sieves.

The tetramethylammonium salts of the substituted acetic acids were prepared by adjusting the pH of an aqueous solution of the appropriate acid to 1 pH unit above the pK_a of the acid with the addition of an aqueous solution of tetremethylammonium hydroxide. The water was removed under vacuum and the resulting wet solid was recrystallized. Tetramethylammonium trifluoroacetate and tetramethylammonium dichloroacetate were recrystallized from acetone, and tetramethylammonium cyanoacetate and tetramethylammonium methoxyacetate were recrystallized from acetone/ethanol. The recrystallized tetramethylammonium salts were dried overnight in a vacuum desiccator. The pH of an aqueous solution of the salt was 7.

Dimethylphenylphenoxysilane was prepared from dimethylphenylsilyl chloride as described earlier.[7]

Trifluoroethanol-*d* was prepared according to the following procedure. To approximately 500 mL of trifluoroethanol was added slowly, with stirring, under an atmosphere of argon approximately 30 g of sodium metal. After all of the sodium metal had dissolved, the excess trifluoroethanol was removed under reduced pressure, the resulting white solid was dissolved in D_2O (60 mL) and the mixture distilled using a small Vigereaux column, the fraction boiling between 79–84 °C was collected. A volume of 130 mL of the resulting solution was then combined with 100 mL of trifluoroethanol and 40 mL of D_2O and the solution distilled using a small Vigereaux column. The fraction boiling between 79–84 °C was collected. This procedure was repeated five times. The resulting trifluoroethanol was dried with anhydrous calcium sulfate, filtered, and distilled using a 55-cm concentric tube distillation apparatus with a return to a collection ratio of 10. The distillate was stored under argon. The resulting trifluoroethanol was shown to be greater than 99% deuterated by NMR and to contain less than 0.5% water by volume. The percentage of water in the trifluoroethanol was determined by GC analysis using a Shimadzu Model GC-8A gas chromatograph equipped with a 4 ft × $^1/_4$ in. 20% Carbowax 20M column and a thermal conductivity detector. The GC was operated with a helium carrier gas, a column temperature of 100 °C, a column pressure of 1.5 kg/cm^2, and a detector temperature of 200°C. Solutions, having known volumes, of water and trifluoroethanol were used to determine response factors. It was demonstrated with known solutions that 0.5% water by volume could easily be detected.

Kinetics. Pseudo-first-order rate constants for the trifluoroethanolysis of dimethylphenylphenoxysilane in trifluoroethanol solutions buffered with substituted acetic acid–tetramethylammonium acetate buffers or amine–amine hydrochloride buffers was determined by monitoring the increase in absorbance due to the formation of phenol at 280 nm as a function of time on a Shimadzu UV-160 spectrophotometer equipped with a thermostated cell holder. The substituted acetic acid buffers were prepared by combining known volumes of a 1.0 M trifluoroethanol solution of the acid, a known volume of a 0.1 M trifluoroethanol solution of the tetramethylammonium salt of the acid, a known volume of a 0.1 M tetramethylammonium trifluoroacetate solution in trifluoroethanol, and trifluoroethanol such that the final volume was 2.4 mL and the final ionic strength was 0.05 M. For the amine buffers a known volume of a trifluoroethanol solution containing both the amine (0.05 M) and the amine hydrochloride (0.05 M) was combined with a 0.05 M trifluoroethanol solution of tetramethylammonium chloride to give a final volume of 2.4 mL. After temperature equilibration (30.0 ± 0.5 °C), 0.6–1.0 μL of phenyldimethylphenoxysilane was added to the buffer solution. The rate of solvolysis was determined by monitoring the increase in absorbance due to the formation of phenol at 280 nm as a function of time. The spectrophotometer was interfaced to a personal computer and k_{obs} values were obtained by a nonlinear regression analysis of absorbance vs time data. Reactions were followed for greater than three half-lives. The nonlinear regression analysis resulted in the best end points. 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 10%.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and to the University of Maryland for an institutional DRIF grant.

Supplementary Material Available: Pseudo-first-order rate constants for the trifluoroethanolysis of phenoxydimethylphenylsilane catalyzed by amine buffers and pseudo-first-order rate constants for the trifluoroethanolysis of phenoxydimethylphenylsilane in deuterated trifluoroethanol catalyzed by acetic acid-*d*–tetramethylammonium acetate buffers (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) Engdahl, K. A.; Bivehed, H.; Ahlberg, P.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 4767.