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THE GENERAL ACID CATALYZED TRIFLUOROETHANOLYSIS OF ETHOXYDIMETHYLPHENYLSILANE

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Abstract. The trifluoroethanolysis of ethoxydimethylphenylsilane shows general acid catalysis by substituted acetic acids. The Bronsted α value for the reaction is 0.65.

The solvolysis of silyl ethers in protic solvents has been studied previously.[1-8] It is important to understand the mechanism of formation and/or cleavage of the silicon oxygen bond as evidenced by the importance in synthetic organic chemistry of silicon as a hydroxyl protecting group.[10] The solvolysis of silyl ethers involves cleavage of a silicon - oxygen bond and formation of a new silicon - oxygen bond. It is well known that the solvolysis of silyl ethers shows both specific[1-3] and general base catalysis[1,2,4-9] as well as specific acid catalysis.[1-3,9] We wish to report that the solvolysis of ethoxydimethylphenylsilane in 2,2,2-trifluoroethanol buffered with substituted acetic acid buffers at 30°C and ionic strength 0.05 M shows general acid catalysis. To our knowledge this is the first example of a general acid catalyzed solvolysis of a silyl ether.

Rate constants were determined by adding 1 μL of ethoxydimethylphenylsilane to 0.5 mL of a 2,2,2-trifluoroethanol solution at 30°C buffered with a substituted acetic acid buffer. The anionic form of the buffer was present as the tetramethylammonium salt and ionic strength was maintained at 0.05 M with tetramethylammonium perchlorate. The trifluoroethanol solution also contained approximately 0.2 μL of mesitylene as an internal standard. The rate constant for the disappearance of ethoxydimethylphenylsilane, k_{obs}, was determined using gas chromatography to measure the peak area of ethoxydimethylphenylsilane as a function of time.[11] Peak areas were normalized relative to the internal standard. The slope of a semilog plot of the peak area of ethoxydimethylphenylsilane against time gave the value of k_{obs}. Semilog plots were linear for over three half-lives. Rate constants were reproducible within ± 20% and were generally much better. The only product observed by gas chromatography was the (2,2,2 trifluoroethoxy)dimethylphenylsilane.

The rate constant, k_{obs}, increased with increasing buffer concentration while keeping the ratio of acidic to basic form of the buffer constant. It was demonstrated that the increase in rate was dependent on the acid form of the buffer by varying the acid/base ratio of the buffer in several experiments and determining that the rate depended only on the acid component of the buffer. For example, the observed rate constant for the disappearance of ethoxydimethylphenylsilane in a solution buffered with a chloroacetic acid buffer having an acid/base ratio of 0.05 M/0.025 M is 2.9 x 10^{-4} s^{-1}, essentially the same as the rate constant of 3.6 x 10^{-4} s^{-1} obtained with an acid/base ratio of 0.05 M/0.005 M. Rate constants for catalysis by the acidic component of the buffer, k_{HA}, were obtained from plots of k_{obs} against the concentration of the acidic form of the buffer (Figure 1). Plots of k_{obs} vs acid concentration were linear except for upward curvature at high buffer concentrations (>0.2M). This upward curvature is presumably due to a salt-induced medium effect[12] observed when tetramethylammonium acetate replaces tetramethylammonium perchlorate as the salt. Experiments were conducted with an acid/base ratio for the buffer of 10 or 2 except when dichloroacetic acid was used as the buffer acid. These experiments were performed using an acid/base ratio of 0.2 or 0.3. Experiments using dichloroacetic acid as the buffer and having a higher acid/base ratio to give more acidic solutions were not reproducible and often did not give linear semilog plots for the peak area of ethoxydimethylphenylethoxysilane *vs* time.

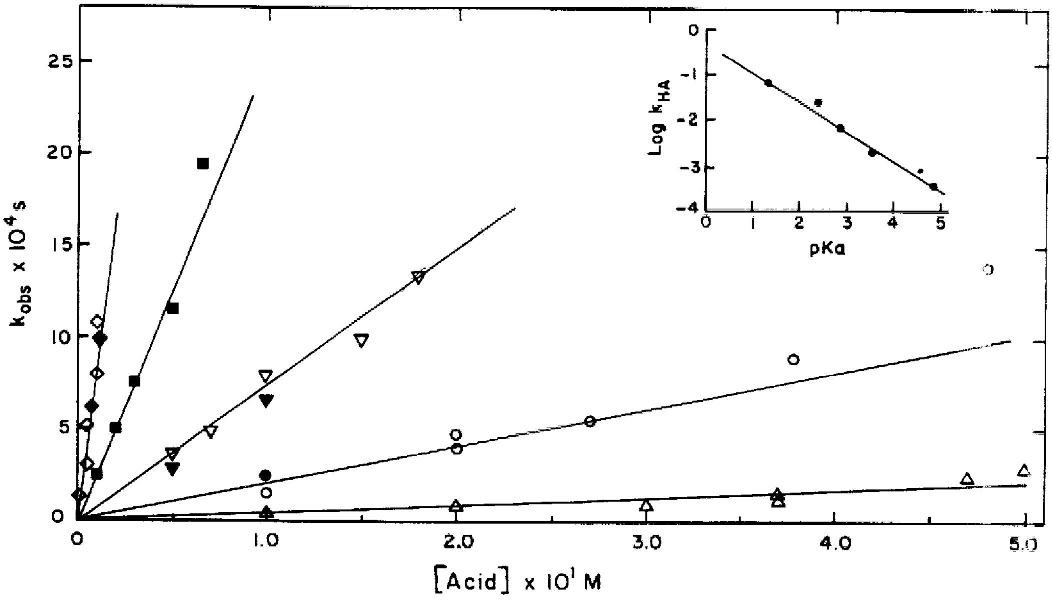
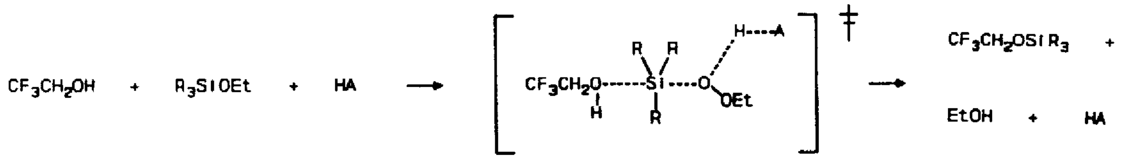


Figure 1. Pseudo-first order rate constants, k_{obs}, for reaction of ethoxydimethylphenylsilane in 2,2,2-trifluoroethanol at 30°C and ionic strength 0.05M buffered with substituted acetic acids plotted against the concentration of the acidic component of the buffer. The acids are as follows: (△) CH_3COOH, (○) CH_3OCH_2COOH, (▽) $ClCH_2COOH$, (□) $NCCH_2COOH$, (◇) $Cl_2CHCOOH$. The solid points represent an acid/base ratio of 2 and the open points an acid/base ratio of 10 except for $Cl_2CHCOOH$ where the open points represent an acid/base ratio of 0.2 and the solid points a ratio of 0.3. The insert shows a Bronsted plot of log k_{HA} vs. pK_a (determined in water[14]) of the catalyzing acid.

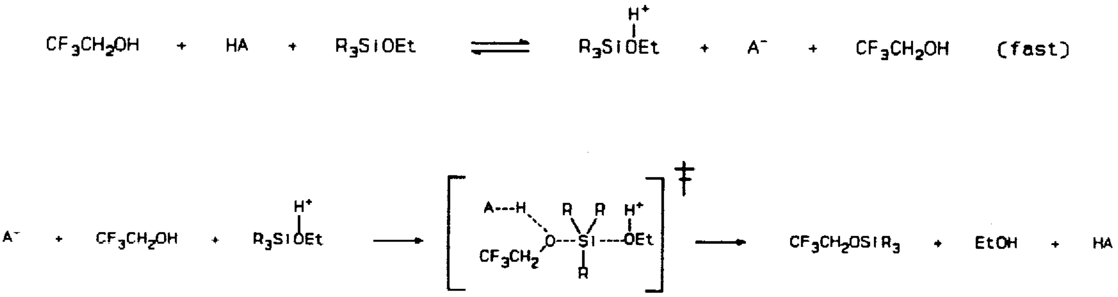
The plots of k_{obs} against acid concentration have intercepts close to zero. The principal term in the rate law for this reaction is therefore rate = k[R_3SiOEt][HA] where R_3SiOEt represents ethoxydimethylphenylsilane and HA represents the acid form of the buffer. This rate equation corresponds to true general acid catalysis[13] and is depicted in Mechanism 1.

Mechanism 1



This rate law, however, is kinetically indistinguishable from rate = $k[R_3SiOEtH^+][A^-]$ where A^- is the basic form of the buffer and $R_3SiOEtH^+$ is the protonated ethoxydimethylphenylsilane. This latter rate equation corresponds to specific acid - general base catalysis and is depicted by Mechanism 2.[13]

Mechanism 2



A Bronsted plot of log k_{HA} against pK_a of the buffer acid (pK_a values determined in water[14]) has a slope of -0.65 and is shown in the insert of Figure 1. The slope of the Bronsted plot, $-\alpha$, is a measure of the degree of proton transfer in the transition state and suggests that the proton is approximately 65% transferred in the transition state.

These results demonstrate that the trifluoroethanolysis of ethoxydimethylphenylsilane shows general acid catalysis by substituted acetic acids. However, this work does not distinguish between the kinetically equivalent mechanisms of true general acid catalysis and specific acid - general base catalysis. Additional experiments are in progress to determine the mechanistic details of this reaction.

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