Experimental and Theoretical Study of Oxygen Insertion into Trialkylsilanes by Methyltrioxorhenium Catalyst

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Among the reactions of hydrogen peroxide that are catalyzed by methyltrioxorhenium, the oxidation of alkylsilanes is unique. It is not a reaction in which an oxygen atom is added to a substrate, but one featuring a net insertion, $R_3Si-H + H_2O_2 \rightarrow R_3Si-OH + H_2O$. Kinetics studies were carried out on 10 compounds. Rate constant were determined for the bimolecular reaction of the silane with the peroxo compound $CH_3Re(O)(\eta^2\text{-}O_2)_2(H_2O)$. The variation of rate constant with the alkyl groups R follows two trends: the values of $\log(k)$ are linear functions of (a) the stretching frequency of the Si−H group and (b) the total Taft constant for these substituents. The reactions of $(n\text{-}Bu)_3Si-H$ and $(n\text{-}Bu)_3Si-D$ exhibit a kinetic isotope effect of 2.1 at 0 °C. From these data, a model for the transition state was formulated in which O−H and Si−O bond making accompany Si−H bond breaking. Quantum mechanical calculations have been carried out on the gas-phase reaction between Et_3SiH and $CH_3Re(O)_2(\eta^2\text{-}O_2)$. These results support this structure, calculating a structure and energy that are in agreement. The theoretical activation energy is 28.5 kcal mol^{-1}, twice the experimental value in aqueous acetonitrile, 12.4 kcal mol^{-1}. The difference can be attributed to the solvation of the polar transition state in this medium.

Introduction

Much evidence accumulated during this decade, as recently reviewed,[1−5] has shown that methyltrioxorhenium (CH_3ReO_3, abbreviated as MTO) is an effective and selective catalyst for oxidation reactions that utilize hydrogen peroxide. In nearly all of these cases, the chemistry entails the addition of an oxygen atom (shown by isotopic labeling to be that of the peroxide[6]) to a substrate directly. That substrate is thus converted to a stable product, for example $R_2S \rightarrow R_2SO$.

In contrast, oxidation reactions that cannot proceed by O atom addition are, at best, quite slow and often require a cocatalyst. An example is the oxidation of secondary alcohols with hydrogen peroxide; without MTO no reaction occurs. With the catalyst oxidation takes place very slowly,[7] unless bromide ions are added as a cocatalyst, in which case the mechanism changes entirely.[8] As interesting as the action of the cocatalyst is, the original mechanism for inserting an oxygen atom into a C−H bond remains obscured by the difficulty of studying such slow events. Because C−H bonds proved to be so inert, we have turned to the weaker Si−H bonds of silanes.

The oxidation of silanes (in our case, trialkylsilanes, R_3SiH) yields silanols, although in many media disiloxanes are an accompanying side product. Methods for the selective preparation of silanols are limited, because traces of acid or base will dimerize them.[9] One of the best methods is oxidation with dioxiranes, but this is a stoichiometric reaction that requires low temperatures, −20 to 0 °C.[10] Finding that hydrogen peroxide, catalyzed by MTO, is an effective reagent for this transformation, we began an exploration of the reaction and its mechanism. While this study was in progress, a report appeared that MTO catalyzes the selective conversion of silanes to silanols urea−hydrogen peroxide (UHP).[11] Nonetheless, we continued our studies of the kinetics and mechanism, which are reported herein, since those aspects had not been thoroughly addressed.

Experimental Section

The reagents were purchased, except tri-*n*-butylsilane-*d*, which was prepared following the literature procedure.[12] Solutions of MTO in CD_3CN were stored at 5 °C and used within 3 days. Varian VXR-300 and Bruker DRX-400 spectrometers were used to obtain ${}^1H$ and ${}^{13}C$ NMR spectra. Chemical shifts for both ${}^1H$ and ${}^{13}C$ were referenced to Me_4Si. The 400 MHz instrument was used for quantitative kinetic determinations, following loss of the silane resonance relative to an internal standard. For this purpose the very small concentration of CD_2HCN inevitably present in the CD_3CN solvent was used, since its intensity is constant and compa-

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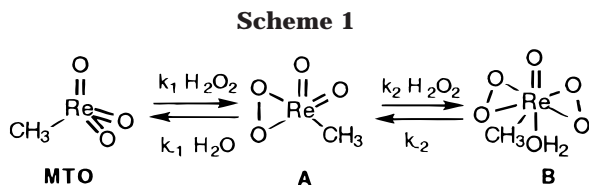(8) Espenson, J. H.; Zhu, Z.; Zauche, T. H. *J. Org. Chem.* **1999**, *64*, 1191.

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Scheme 1

rable in size to those of the solutes whose concentrations were being followed. The solvent for kinetics was 90:10 CD$_3$CN–H$_2$O, the water being added to maintain its activity constant in that the hydrogen peroxide is a 30% aqueous solution. The concentrations ranges were 10 mM R$_3$SiH, 200–800 mM H$_2$O$_2$, and 2–8 mM MTO. The temperature was controlled, usually at 25.0 ± 0.2 °C except for the determination of activation parameters. The kinetics data followed first-order kinetics, and the rate constant was determined from the intensity–time values by a nonlinear least-squares fit to the equation Int$_t$ = Int$_\infty$ + (Int$_0$ – Int$_\infty$) exp(–kt). In the sense of catalysis the amount of MTO is not particularly small compared to that of the substrate, but this remains the best method for exploring the kinetics of the overall catalytic reaction.

Products. A combination of ^{1}H NMR, ^{13}C NMR, and mass spectrometry was used to identify the reaction products, which are a mixture of the silanol, R$_3$SiOH, and the disiloxane, R$_3$SiOSiR$_3$. With time, the silanol decreases and the disiloxane increases such that it eventually is the only product detected. The method using solid UHP in place of the hydrogen peroxide, which primarily forms the silanol,[11] was used to verify the spectroscopic assignments. For this purpose 0.2 mmol silane was added to an NMR tube containing 6 μmol MTO and 0.5 mmol UHP in 1.0 mL CD$_3$CN. The tube was held at room temperature for several hours, whereupon the spectroscopic procedures were performed. The spectra are presented in the Supporting Information.

Computational Methods. Calculations for the transition state employ the GAMESS program.[13] Effective core potentials (ECPs) and valence basis sets (VBSs)[14] including polarization functions (d functions on main group elements and f functions on rhenium[13]) are used for heavy atoms and a –31G basis for H. The effective core potentials of Stevens et al.[14] (SBK) are derived from numerical Dirac–Hartree–Fock (DHF) calculations on atoms for all elements larger than neon and thus implicitly include the Darwin and mass–velocity relativistic effects. Spin–orbit coupling is averaged out in potential generation.[15] Geometries were optimized at the restricted Hartree–Fock (RHF) level for closed-shell singlets. Enthalpic data were determined using Møller–Plesset second-order perturbation theory (MP2) energies at RHF-optimized geometries with zero-point energy and temperature corrections (to 298.15 K).

Results

Kinetics. A considerable body of evidence points to the involvement of peroxorhenium intermediates in oxygen addition reactions.[1–5] These species are in equilibrium with MTO and hydrogen peroxide, as shown in Scheme 1. These equilibria are not instantaneously established, however, and species **A** and **B** remain at steady-state, not equilibrium, concentrations during the course of a kinetics experiment.

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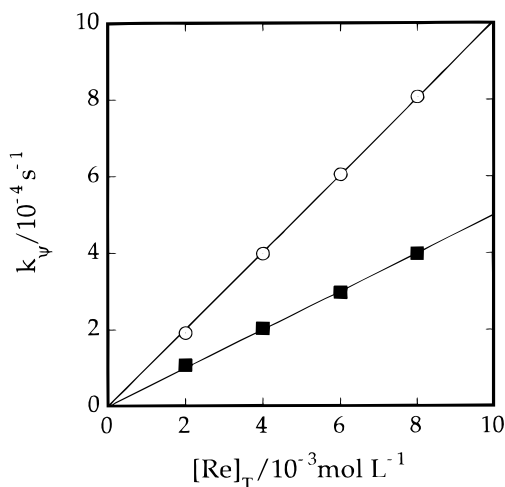
Figure 1. Pseudo-first-order rate constants for the oxidation of triisopropylsilane and dimethylphenylsilane by hydrogen peroxide as a function of the total concentration of the rhenium catalyst. Reactions were carried out in acetonitrile containing 10% water. Both sets of data are linear, with correlation coefficients > 0.999.

We have chosen to evaluate only the rate constant for the reactions between **B** and R$_3$Si–H, since numerous studies[3] have shown that the two follow in close parallel. As such, it is possible to devise experimental conditions to simplify the rate equation for the general case. To attain that limit, the peroxide concentration must be large enough that the equilibria in Scheme 1 are shifted entirely toward **B**. Also, the rate of step 2 must be sufficiently rapid in comparison to that of silane oxidation, which is realized by the use of high peroxide concentration and particularly by the use of a semi-aqueous medium, as the k_2 step in Scheme 1 is otherwise too sluggish to keep pace with the oxidation reaction.

Under these conditions, the rate of oxidation becomes

$$-\frac{d[R_3Si-H]}{dt} = \frac{d[R_3Si-OH]}{dt} = k_4[R_3Si-H][Re]_T \quad (1)$$

in which k_4 (in keeping with earlier notation) symbolizes the rate constant for the bimolecular reaction between **B** and R$_3$SiH. In any experiment, [Re]$_T$ remains constant. The experimental data, consisting of the intensity of the silane resonance as a function of time, thus follow first-order kinetics. A particularly important control experiment for the correctness of this simplified kinetic model is that the rate constant remain independent of the concentration of hydrogen peroxide. This was verified over the range 200–800 mM H$_2$O$_2$, but could not be expected to hold at low concentrations, which were therefore not employed in this study.

According to eq 1, the variation of the first-order rate constant, k_ψ, with catalyst concentration should define a straight line that passes through the origin. Data for two silanes, (i-Pr)$_3$SiH and PhMe$_2$SiH, are shown in Figure 1. The other compounds behave similarly. The slope of the plot of k_ψ against [Re]$_T$ provides the value of the second-order rate constant k_4. Table 1 presents the values for all of the silanes studied.

Activation Parameters. The variation of k_4 with temperature (0–50 °C) was evaluated for two com-

Table 1. Rate Constants for the MTO-Catalyzed Oxidation of Trialkylsilanes by Hydrogen Peroxide in Homogeneous Solution, ν_{Si-H} Stretching Frequencies, and the Products Obtained with Urea−Hydrogen Peroxide

reactant	$k_4{}^a$ (L mol^{-1} s^{-1})	ν_{Si-H} (cm^{-1})	product	% yield^b
Ph$_3$SiH	0.0217	2134.5	Ph$_3$SiOH	98
Ph$_2$MeSiH	0.0224	2132.0	Ph$_2$MeSiOH	95
PhMe$_2$SiH	0.050	2129.1	PhMe$_2$SiOH^c	82
t-BuMe$_2$SiH	0.100	2114.5	t-BuMe$_2$SiOH	94
i-Pr$_3$SiH	0.101	2097.9	i-Pr$_3$SiOH	98
Et$_3$SiH	0.103	2106.8	Et$_3$SiOH	94
EtMe$_2$SiH	0.110	2119.5	EtMe$_2$SiOH^c	80
n-Pr$_3$SiH	0.131	2108.5	Pr$_3$SiOH	97
n-Bu$_3$SiH	0.167	2107.6	Bu$_3$SiOH	97
(n-C$_6$H$_{13}$)$_3$SiH	0.171	2105.5	(n-C$_6$H$_{13}$)$_3$SiOH	96

^{a} In CD$_3$CN with MTO/30% H$_2$O$_2$. ^{b} Yield was measured in CD$_3$CN with MTO/urea−H$_2$O$_2$ and based on ^{1}H NMR or GC peak integrations. ^{c} In CDCl$_3$.

pounds, triethylsilane and tri-*n*-butylsilane. Analysis of the data was carried out by the Arrhenius and transition-state theory equations:

$$\ln\left(\frac{k_4}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$

giving these values:

	E_a (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
Et$_3$SiH	12.4(4)	11.8(4)	−22.6(1.6)
n-Bu$_3$SiH	13.0(1)	12.1(1)	−20.6(3)

Products. The yields of silanol obtained under these reaction condition lie in the range 80−98% for UHP, consistent with values recently reported.[11] Silanol yields are, however, much lower when hydrogen peroxide is used, where the disiloxane was predominant; over time, the disiloxane was obtained in nearly quantitative amount. A citation of the actual yield is not meaningful, since its concentration continues to increase until it is nearly the exclusive product. The substances with the smallest R groups, Me$_2$EtSiH and Me$_2$PhSiH, proved to be an exception, and a part of the silanol was lost to the disiloxane. We have traced the difference to the acid-catalyzed conversion

$$2R_3SiOH \xrightarrow{\text{cat. HX}} R_3SiOSiR_3 + H_2O \qquad (2)$$

The acid HX is in this case perrhenic acid, which is a known product of decomposition of MTO:[16]

$$CH_3ReO_3 + H_2O \rightarrow CH_4 + HReO_4 \qquad (3)$$

To confirm this assessment, independently prepared aqueous HReO$_4$ (10 mM) was added to 0.20 M Et$_3$SiOH in acetonitrile. After 1 h, nearly all the silanol had been converted to Et$_3$SiOSiEt$_3$. These data confirm the conclusion that UHP is much superior to H$_2$O$_2$ for silanol formation,[11] but this does not diminish the significance of the major thrust of this research, which is to define the reaction mechanism.

Kinetic Isotope Effect. To learn more about the elementary reaction of O atom insertion, kinetic data

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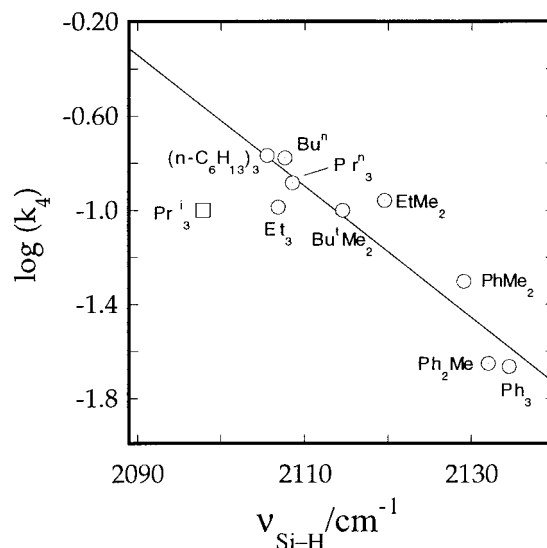
Figure 2. Rate constants k_4 for the oxidation of trialkylsilanes, on a logarithmic scale, shown as a function of the Si−H stretching frequency. With the deviant point for (*i*-Pr)$_3$SiH omitted, the correlation coefficient is 0.953.

were collected for the monodeuterio derivative, (*n*-Bu)$_3$Si−D. The value of k_4, in comparison with the same quantity for Bu$_3$Si−H, gave $k_H/k_D = 2.10 \pm 0.08$ at 0.0 °C.

Discussion

Our data have shown that the substituents on the silicon atom have a regular effect on the rate, depending on the direction in which they alter the electron density at the Si−H bond. From studies of silane oxidation, we find this order of reactivity: (*n*-C$_6$H$_{13}$)$_3$SiH > (*n*-Bu)$_3$SiH > (*n*-Pr)$_3$SiH > Et$_3$SiH.

It is of interest to test whether the rate of the catalytic step is sensitive to the energy of the Si−H bond. Since the individual bond dissociation enthalpies are not known, we have taken as its measure the frequency of the Si−H stretching vibration.[17] Figure 2 displays the plot of log(k_4) against ν_{Si-H}. A linear relation was noted, save for one datum; the correlation coefficient from least-squares fitting is 0.93. (The deviant point is that for (*i*-Pr)$_3$SiH, which bears the bulkiest of the substituents.) The slope of the line is negative, signifying that those compounds with the smallest vibrational frequencies (and, therefore, the weakest Si−H bonds) react most rapidly. This is therefore consistent with a mechanism in which stretching of that bond plays a key role in the activation process. With the stronger Si−H bonds (those of higher frequency) the silanes have less reactivity.[18]

A linear free-energy relation (LFER) will also reveal information about the mechanism. The Hammett equation is not applicable, since the substituents are aliphatic. Thus we have used the Taft σ^* values, adding them together for each of the three R groups; this gives a quantity we designate as $\sum\sigma^*$, which is indicative of the total electronic environment of the silicon atom.[19] The plot of log(k_4) against $\sum\sigma^*$ is given in Figure 3. This

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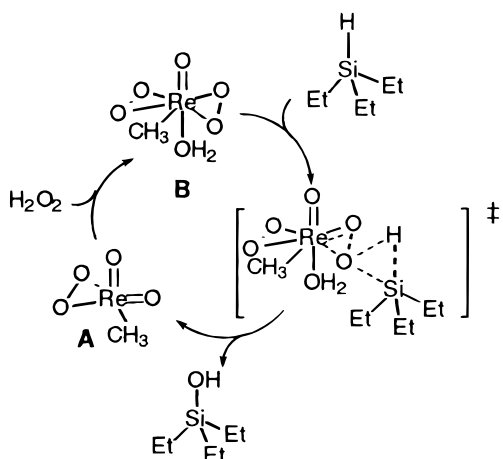(18) Spialter, L.; Swansiger, W. *J. Am. Chem. Soc.* **1968**, *90*, 2187.
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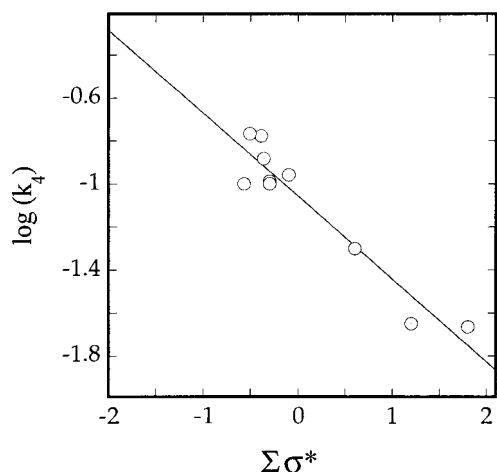
Figure 3. Correlation of the rate constants k_4, on a logarithmic scale, correlated with the Taft substituent constants. The correlation coefficient is 0.954.
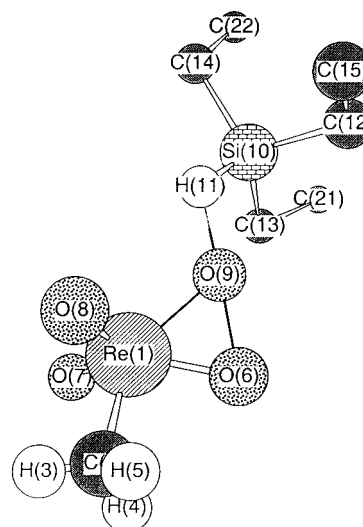
Scheme 2

Figure 4. Calculated geometry of the transition states for reactions of trialkylsilanes with the peroxorhenium compound **A**.

Table 2. Calculated Metrical Parameters for the Reaction of Triethylsilane with the Peroxorhenium Compound B

compound	bond	bond length (Å)	bond	bond length (Å)
$CH_3Re(O_2)O_2$ (**A**)	Re(1)−C(2)	2.131	Re(1)−O(8)	1.653
	Re(1)−O(6)	1.909	Re(1)−O(9)	1.880
	Re(1)−O(7)	1.653	O(6)−O(9)	1.395
$HSiEt_3$	Si(1)−H(2)	1.500	Si(1)−C(4)	1.904
	Si(1)−C(3)	1.904	Si(1)−C(5)	1.898
transition state	Re(1)−C(2)	2.122	Si(10)−H(11)	1.543
	Re(1)−O(6)	1.740	Si(10)−C(12)	1.891
	Re(1)−O(7)	1.663	Si(10)−C(13)	1.897
	Re(1)−O(8)	1.661	Si(10)−C(14)	1.898
	Re(1)−O(9)	2.144	Si(10)−O(9)	2.732
	O(6)−O(9)	1.817	O(9)−H(11)	1.532

relationship proves to be linear; its slope gives the reaction constant as −0.39. The negative value implies that the silicon atom becomes less negative or more positive in the activated complex. The hydrogen bonded to silicon is hydridic and is likely the site of attack by an electrophile. In this case, the electrophile is a peroxo oxygen atom, polarized by coordination to Re(VII).

We postulate, therefore, that **B** attacks in the rate-controlling step and that the Si−H bond is partially broken, accompanying partial insertion of oxygen. Consistent with that, the kinetic isotope effect (kie) of 2.1 for $(n\text{-Bu})_3Si(H,D)$ shows that a primary isotope effect exists. This value is in the range for two other reactions in which insertion into the Si−H bond takes place: $(n\text{-Bu})_3SiH$ with kie = 1.23 for the insertion of dichlorocarbene[20] and Et_3SiH with kie = 2.6 for the insertion reaction with dioxirane.[10] Therefore, as for the carbene insertions, an oxene insertion mechanism is proposed for the oxidation of the trialkylsilanes by the peroxorhenium compound **B**. The structures involved are shown in Scheme 2. The activation parameters support this model, the negative value of $\Delta S^\ddagger$ being consistent with a bimolecular reaction and the relatively modest value of $\Delta H^\ddagger$ indicating the compensating factors of bond making and bond breaking in the insertion process.

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Further information about the detailed mechanism comes from the calculation of the structure and energetics of the transition state. These calculations were carried out for Et_3SiH, and **A** was used instead of **B** to simplify the calculation; as explained earlier, this substitution will not have a significant effect. Results gleaned from several publications on a variety of systems have been summarized;[3] the values of k for reactions of **A** and **B** are nearly always within a factor of 3 of one another. Data are collected in Table 2. The calculated structure of the transition state is shown in Figure 4. The partial insertion of the oxygen atom into the Si−H bond is evident. The calculation shows that these bonds are longer than in the reagents, Si(10)−H(11), Re(1)−O(9), and O(6)−O(9), whereas the Re(1)−O(6) bond is shorter because the rhenium oxygen multiple bond will be restored after the reaction. The charge distributions on the peroxide oxygens O(6) and O(9) of **A** are less negative than those of the oxo oxygens O(7) and O(8), explaining why the peroxo oxygen is the one that attacks the Si−H bond electrophically. In the transition state the charge distribution on peroxo oxygen O(9) becomes more positive during the reaction, consistent with electrophilic attack on the Si−H bond. However oxo oxygen O(6) is more negative, as it is in the process of changing back into a Re=O double bond. The activation energy is 27.5 kcal mol^{-1} from the

Table 3. Calculated Mulliken Charge Distribution

compound	atom	charge distribution	atom	charge distribution
CH_3ReO_3	Re(1)	1.597	H(5)	0.167
	C(2)	−0.111	O(6)	−0.662
	H(3)	0.167	O(7)	−0.662
	H(4)	0.167	O(8)	−0.662
$CH_3Re(O_2)O_2$	Re(1)	1.479	H(5)	0.160
	C(2)	−0.025	O(6)	−0.334
	H(3)	0.166	O(7)	−0.622
	H(4)	0.160	O(8)	−0.622
			O(9)	−0.362
$HSiEt_3$	Si(10)	0.162	C(14)	−0.281
	H(11)	−0.056	C(15)	−0.137
	C(12)	−0.268	C(16)	−0.140
	C(13)	−0.256	C(17)	−0.152
transition state	Re(1)	1.511	Si(10)	0.078
	C(2)	−0.047	H(11)	−0.021
	H(3)	0.157	C(12)	−0.253
	H(4)	0.160	C(13)	−0.243
	H(5)	0.162	C(14)	−0.250
	O(6)	−0.597	C(15)	−0.163
	O(7)	−0.632	C(21)	−0.141
	O(8)	−0.622	C(22)	−0.149
	O(9)	−0.317		

calculation, more than double the experimental value obtained in aqueous CD_3CN. The calculated Mulliken charge densities are given in Table 3. From them, one can see that the transition state has more polar centers than the triethylsilane. The charge on Si in the reactant is +0.162, whereas in the transition state it is +0.078; thus Si is clearly more negative (less positive) in the activated complex, by 0.1 electron. In Et_3SiH, the largest charge is −0.27. In the transition state, Re is +1.5 and the three O's are very negative, ca. −0.6. This will attract more polar solvent molecules in the solution. The surrounding solvent molecules around will stabilize the transition state in solution, decreasing the transition-state energy level and the activation energy barrier in the solvent.

Supporting Information Available: Tables of NMR and mass spectrometric data for trialkylsilanols. This material is available free of charge via the Internet at http://pubs.acs.org.

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