Energetics and Mechanism of Alkyl Cleavage Transition States: Relative Gas-Phase Acidities of Alkanes

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Abstract: The product branching ratios from the infrared multiple-photon dissociation (IRMPD) of a series of tertiary alkoxides are examined and an overall order for the relative acidities of several alkyl groups is inferred. Comparison with the order of acidities derived from a similar silane system reveals an overall similarity, although small differences exist. A model system, the reaction of phenyltrimethylsilane plus hydroxide to give either benzene or methane, is studied more closely. Analysis of the energetics of the alkoxide system and the silane system using statistical reaction rate theory (RRK and RRKM) reveals differences between the mechanisms of decomposition for the systems. These discrepancies between the known, experimental product ratio and the energetics suggest that the transition state of pentacoordinate hydroxysilane anion decomposition has concerted, albeit polar character. Decomposition of the pentacoordinate adduct formed by the reaction of methoxide plus phenyltrimethylsilane is consistent with this suggestion. Caution should be used when inferring the relative acidities of alkyl groups from kinetic methods when assumptions of the decomposition mechanism have not been validated.

Introduction

Determination of the gas-phase acidities of weakly acidic compounds is a challenge. One especially interesting class of compounds is the simple alkanes, the acidities of which are mostly unknown. Inherent experimental limitations, such as difficulty in finding a strong enough base to deprotonate them and the lack of suitable reference standards, prevents the direct determination of their acidities by conventional methods. In most cases, the acidity is too small to measure directly and the lack of a useful compound whose acidity is known in the acidity range of interest precludes the measurement of these acidities by equilibrium experiments or bracketing experiments. Many of the conjugate bases of alkanes have negative electron binding energies, and therefore measurements of the abundances of those alkyl anions are impossible to obtain.[1]

In light of these difficulties, indirect methods are often employed, in which the relative rates of kinetic processes are correlated to equilibrium product ratios.[2,3] The product ratios from competing reactions from single-step, unimolecular decompositions of a common intermediate can be used to extract information about relative acidities. The most widely known of these methods is the kinetic method pioneered by Cooks,[4−6] where the relative acidity of two compounds is reflected in the product branching ratio of the decomposition of a proton-bound dimer. There is a log−linear relationship between the product branching ratio and the relative acidities.

Kinetic methods on various systems have been studied, such as proton abstraction from CH_3X ($X = P(CH_3)_2$, SCH_3, F, Cl, Br, or I) by Nibbering,[7] or the deprotonation of α-hydrogens from unsymmetrical ketones to determine kinetic versus thermodynamic control of regioselectivity by Squires[8] and to ascertain the effect of the various degrees of alkyl substitution on proton-transfer rates.[9] In the latter case, the product ratios from competitive bimolecular reactions were measured. Similarly, the decomposition of alcohol−alkoxide complexes has been investigated to measure the relative acidities of various alcohols. In most instances, these kinetic acidities correlate with acidities determined through other, more conventional methods, although there are several examples for which this is apparently not true, such as the acidities of α-hydrogens in unsymmetrical ketones.[8]

The product ratios of a unimolecular, two-step decomposition mechanism can also be compared. Properties of weakly bound alkyl anions that cannot be investigated directly by conventional methods can be indirectly ascertained from the product ratios from the infrared multiple-photon dissociation (IRMPD) of a common intermediate. We report here a study of the IRMPD of a series of tertiary alkoxide ions in which the various alkyl groups have been systematically varied. This involves a stepwise unimolecular decomposition,[10] giving a product branching ratio that reflects the relative acidities of the alkane fragments. The first step of the decomposition mechanism involves the formation of an anion−ketone complex, where the ketone effectively

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[1] These alkyl anions may be unbound and thus have negative electron affinities. It is also possible that these anions are (barely) thermodynamically stable, but have extremely short lifetimes. In this case, these anions would be indistinguishable from unbound species in our experiment.

[2] Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables*, 4th ed.; National Institute of Standards and Technology: Washington, DC, 1998; pp 1−1951.

[3] Farrar, J. M.; Saunders: W. H. *Techniques for the Study of Ion−Molecule Reactions*; Wiley: New York, 1988; Vol. 20.

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[6] Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279−1281.

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[8] Chyall, L. J.; Brickhouse, M. D.; Schnute, M. E.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 8681−8690.

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[10] Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 4053−4054.

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solvates the anion.[9,11] Anions where the electron is weakly bound are then stabilized by this interaction.

IRMPD has been employed to elucidate the mechanism of the unimolecular decomposition of tertiary alkoxide ions.[10,12] This method utilizes infrared photons to pump a compound with enough energy to exceed the dissociation threshold. Analysis of the ratios of the products formed reveals information about the associated fragments. The advantage of IRMPD involves the size of the incremental energy steps in the increase of the internal energy of a compound. The infrared photons in this study have energy of 3.0 kcal/mol. We therefore have a method by which we can excite a compound just beyond its dissociation threshold and subsequently monitor the fragmentation pattern.

DePuy and co-workers have investigated the decomposition of pentacoordinate hydroxysilane anions to derive information about the acidities of alkanes.[13,14] Comparison of the order of acidities from alkoxide decompositions to the order of acidities from a similar pentavalent hydroxysilane decomposition reveals interesting information about the mechanism of unimolecular decomposition in the two systems. Although the rough overall order of the alkane acidities is the same, there are some small differences. To understand the origin of these differences, we have analyzed both systems by statistical reaction rate theory. We have also explored the reactions of other ionic nucleophiles to further probe the mechanism in the silane system. We find that methoxide ion, which lacks an acidic proton, gives a very different ratio of products in this reaction.

Experimental Section

(a) Instrumentation. All experiments were carried out on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer consisting of an electromagnet (0.6 T), vacuum system, and 2.54 cm cubic trapped-ion analyzer cell, interfaced to an FTMS-2000 (IonSpec Corp., Irvine, CA) data acquisition system. The trapped-ion analyzer cell was modified for photochemical experiments using two IR transparent windows (Melles Griot, 50 mm diameter, 5 mm thick, zinc selenide coating) and replacing the back plate with a gold-coated copper mirror. All pressures were measured using a vacuum ionization gauge (Varian, model 844). Background pressures were typically 3×10^{-9} Torr and experiments were conducted under operating pressures of 1×10^{-7} to 5×10^{-7} Torr. Data acquisition consisted of at least 500 scans of a standard cycle of 1500 ms (limited by the laser repetition rate) with a 10 ms delay between laser pulse and detection. All data were collected within a few working days. Details of the Fourier transform instrumentation can be found elsewhere.[15]

Photochemical experiments were conducted with a Lumonics 103-2 CO_2 TEA laser operated multimode with the rear optic as a diffraction grating allowing line tunable output centered around the 9.6 and 10.6 μm transitions. Details of laser operation have been provided previously.[16] The laser intensity was attenuated using CaF_2 flats of varying thicknesses, and the laser spot size was fixed with a mechanical iris outside the analyzer cell. Laser power was measured using a Scientech Astral AD30 digital laser power meter with a Scientech AC25HDSPL 10.6 μm disk calorimeter. When the laser beam passed through the ICR cell twice, the effective fluence was twice the measured fluence. The actual fluence is calculated by dividing the energy per shot by the area of a beam spot (as measured on thermal paper).

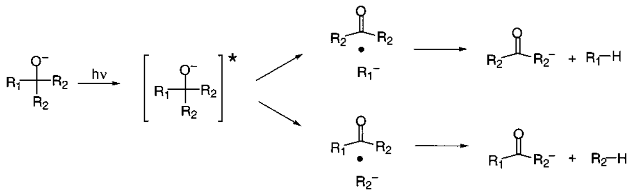

Figure 1. Mechanism of the IRMPD of an alkoxide.

(b)Materials. Nitrogen trifluoride was purchased from Ozark Mahoning and used without further purification. Methanol (99.8%), 2-methyl-2-pentanol (99%), 2,3-dimethyl-2-butanol (99%), 2,4-dimethyl-2-pentanol (99%), 2,3-dimethyl-2-pentanol (99%), and tetramethylsilane (99.9%) were purchased from Aldrich and used without further purification. Dimethyl peroxide was synthesized according to a literature procedure.[17]

The synthesized alcohols were prepared by standard Grignard reactions. The specific starting materials are described below. Each Grignard reaction was worked up by quenching with a saturated aqueous ammonium chloride solution. The alcohol was extracted from the aqueous layer with ether and dried over magnesium sulfate. The reaction mixture was then filtered and separated by either column chromatography or fractional distillation. The alcohol was further purified by preparative gas chromatography on a Hewlett-Packard 5790 gas chromatograph equipped with a thermal conductivity detector and a 1/4 in. diameter, 8 ft column (Alltech, OV-101 stationary phase on Chromosorb WHP solid support, 80/100 mesh, 10% load). The structures of the alcohols were confirmed by comparison of their NMR spectra with those reported in the literature. Each gave the appropriate M − 1 negative ion peak when reacting with F^- in the FT-ICR.

Alkylmagnesium Chloride (Bromide) + Carbonyl Compound. 2,2-Dimethyl-4-pentanol was prepared from methylmagnesium bromide and 3-methyl-2-pentanone (99% pure). 2-Methyl-2-hexanol was prepared from methylmagnesium bromide and 2-hexanone (98% pure). 5-Propyl-5-nonanol was prepared from *n*-propylmagnesium bromide and 5-nonanone (98% pure). 3-Isopropyl-2-methyl-3-heptanol was prepared from *n*-butylmagnesium bromide and 2,4-dimethyl-3-pentanone (98% pure). 2-Methyl-2-butanol was prepared from methylmagnesium bromide and 2-butanone (99% pure). 2,3,3-Trimethyl-2-butanol was prepared from methylmagnesium bromide and 3,3-dimethyl-2-butanone (pinacolone, 98% pure). 3-Ethyl-2-methyl-3-pentanol was prepared from ethylmagnesium bromide and 2-methyl-2-pentonone (99% pure). 3-Ethyl-2,2-dimethyl-3-pentanol was prepared from ethylmagnesium bromide and 2,2-dimethyl-3-pentanone (99% pure).

(c) Ion Formation. Primary negative ions were generated by the dissociated electron capture of appropriate precursors at pressures from 1×10^{-7} to 3×10^{-7} Torr. F^- was generated from NF_3 and CH_3O^- was generated from CH_3OOCH_3. The choice of a precursor for primary ion formation was determined by the acidity of the alcohol studied. Using the appropriate primary negative ion, the desired alkoxide ions were then formed by the deprotonation of the appropriate alcohol present at pressures from 3×10^{-7} and 1×10^{-6} Torr. The proton-transfer reaction was complete within 100−150 ms. All liquid samples were degassed prior to use with several freeze−pump−thaw cycles.

Results

The IRMPD of tertiary alkoxide compounds follows a two-step dissociation mechanism (Figure 1).[12] The first step is the fragmentation of an alkyl group to form an alkyl anion−ketone complex, followed by a facile, irreversible, proton transfer of the α-hydrogen of the ketone to the anion to form an alkane and an enolate ion. A series of tertiary alkoxide compounds

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[11] The hypersurface for the IRMPD of alkoxide anions crosses the transition state of the hypersurface for the bimolecular proton transfer between a ketone and an alkyl anion. By traversing the hypersurface for alkoxide decompositions, we are also accessing information about the transition state for this proton-transfer reaction.

[12] Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 2714−2722.

[13] DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051−4053.

[14] DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968−1973.

[15] Frieser, B. S. In *Techniques for the Study of Ion−Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley and Sons: New York, 1988; pp 61−118.

[16] Johnson, C. E.; Brauman, J. I. In *Techniques for the Study of Ion−Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley and Sons: New York, 1988; pp 563−589.

[17] Hanst, P. L.; Calvert, J. G. *J. Phys. Chem.* **1959**, *63*, 104.

Table 1. Enolate Ion Photoproduct Propensities from $R_1(R_2)_2CO^-$

compd no.	R_1	R_2	product channel	product yield (%)	ratio
1	*n*-Pr	Me	*n*-PrH	0	0.00
			MeH	100	
2	*s*-Bu	Me	*s*-BuH	0	0.00
			MeH	100	
3	neopentyl	Me	neopentane	100	
			MeH	0	
4	*n*-Bu	Me	*n*-BuH	15	0.35
			MeH	85	
5	*i*-Bu	Me	*i*-BuH	48	1.85
			MeH	52	
6	*n*-Bu	*n*-Pr	*n*-BuH	55	2.44
			n-PrH	45	
7	*n*-Bu	*i*-Pr	*n*-BuH	78	7.09
			i-PrH	22	
8	Et	Me	EtH	0	0
			MeH	100	
9	*i*-Pr	Me	*i*-PrH	0	0
			MeH	100	
10	*t*-Bu	Me	*t*-BuH	66	3.8
			MeH	34	
11	*i*-Pr	Et	*i*-PrH	45	1.6
			EtH	55	
12	*t*-Bu	Et	*t*-BuH	100	
			EtH	0	

was studied to compare the relative acidities of different alkyl groups. The tertiary alkoxides contained two of the same alkyl groups and one different alkyl group as a basis for the comparison.

The neutral photoproduct yields have been inferred from the enolate ion photoproduct propensities reported in Table 1. The ratios of the photoproduct yields are listed in the last column of Table 1 and have been statistically corrected to account for the number of alkyl substituents of each type on the substrate.

The photoproduct ratios have been determined from an average of several experiments, done over the course of several working days. Each experiment consisted of an average of at least 500 shots. The shot-to-shot reproducibility of the laser energy was within 10% of the measured power (as measured by the laser power meter). The daily variation in the measurement of these ratios was less than 10%.

Discussion

Alkoxides. The kinetic isotope effect in the IRMPD of tertiary butyl alkoxides has been previously investigated.[12] The method of activation involved IR radiation from a pulsed CO_2 laser, similar to our method of activation. There were two isotope effects observed in the dissociation: a large secondary isotope effect and a small primary isotope effect. The energy dependence (laser intensity dependence) of the two separate isotope effects was different, and it was concluded that the dissociation mechanism was not concerted, but consisted of two distinct steps. The secondary isotope effect arises from the cleavage of the carbonyl−methyl bond in a rate determining cleavage step and the primary isotope effect arises from the facile, exothermic proton transfer from the α-hydrogen of the ketone to the methyl anion within the intermediate ion−molecule complex.

In a similar experiment, Boering observed separate energy dependencies for the two isotope effects in *tert*-butoxide-d_6 anion.[18] The alkoxides were energetically activated by increasing their translational energy;[18−20] subsequent collision induced energy transfer to the vibrational modes of the alkoxide resulted in dissociation (CID). A small primary isotope effect and a large secondary isotope effect were observed, in agreement with Tumas's previous findings.

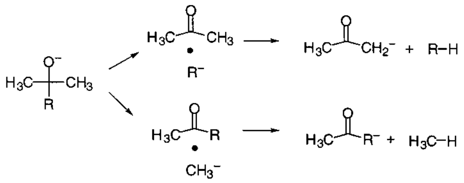

Figure 2. Mechanism of the IRMPD of 2-substituted 2-propoxide anions, R = H, Ph, CF_3.

Tumas determined the carbon−carbon bond cleavage to be heterolytic by investigating the product ratios from the competitive dissociation of a series of 2-substituted 2-propoxide anions, $R(CH_3)_2CO^-$, where R = H, Ph, CF_3 (Figure 2).[12] The dominant product channel follows the acidity of the leaving group rather than the R−C bond strength, showing that the cleavage is heterolytic. This mechanism is in accord with recent high-level ab initio calculations on the fragmentation pathways of the ethoxide anion.[21]

As an example, the only neutral photoproduct observed in the dissociation of 2-phenyl-2-propoxide ($Ph(CH_3)_2CO^-$, $C-CH_3$ cleavage versus C−Ph cleavage) was Ph−H (benzene). This is expected for a heterolytic mechanism, since loss of Ph^- is more favorable than loss of CH_3^- (the bond dissociation energy of Ph−H minus the electron affinity of $Ph^\bullet$ is smaller than the bond dissociation energy of CH_3-H minus the electron affinity of $CH_3^\bullet$). If the mechanism were homolytic, we would expect the methyl cleavage channel to dominate since the $C-CH_3$ bond is weaker than the C−Ph bond for homolytic cleavage.

The observed order of leaving group propensities (trifluromethyl anion > phenide > hydride > methyl anion) corresponds to the independently known order of acidities (trifluoromethane > benzene > hydrogen > methane). Since the carbon−carbon bond dissociation energies vary in the same way as the carbon−hydrogen bond dissociation energies, the product ratios from the IRMPD of the tertiary alkoxides correlate to the acidities of the corresponding alkanes.[22]

Model Calculation for the 2° Kinetic Isotope Effect on 2-Methyl-2-propoxide-*1,1,1*-d_3 Anion. More evidence for the elucidation of the alkoxide dissociation mechanism involves the IRMPD of 2-methyl-2-propoxide-*1,1,1*-d_3 anion investigated by Tumas et al.[23] They investigated the dependence of the branching ratio on the amount of energy in excess of the critical energy of the lower dissociation channel (in this case, the $C-CH_3$ cleavage) by using statistical reaction rate theory (RRKM).[24−26] The results of their model calculations show that

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[18] Boering, K. Ph.D. Dissertation, Stanford University, 1991.

[19] The alkoxide anions were activated by continuously accelerating and decelerating the ions and changing the phase of the rf driving signal by 180°. Subsequent collisions result in very low energy activation.

[20] Boering, K. A.; Rolfe, J.; Brauman, J. I. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 303−305.

[21] Chiu, S.-W.; Kai-Chung; Li, W.-K. *J. Phys. Chem. A* **1999**, *103*, 6003−6008.

[22] The difference between the $C-CH_3$ and $H-CH_3$ bond strengths can be compared to the difference between C−R and H−R bond strengths (where R is a carbon substituent). The difference in enthalpy between the formation of the two alkyl anions is $\Delta\Delta H^\circ = [\mathrm{BDE(C-R)} - \mathrm{BDE(C-CH_3)}] - [\mathrm{EA(R^\bullet)} - \mathrm{EA(CH_3^\bullet)}]$ and the difference in acidity between the two alkanes is $\Delta\Delta H^\circ = [\mathrm{BDE(H-R)} - \mathrm{BDE(H-CH_3)}] - [\mathrm{EA(R^\bullet)} - \mathrm{EA(CH_3^\bullet)}]$. The enthalpy differences are the same if the H−R and C−R bond dissociation energies vary in the same way. This correlation is completely valid if, given $R-R + H-H \rightarrow 2R-H$, ΔH° is independent of R.

[23] Tumas, W.; Foster, R. F.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 961−970.

[24] Forst, W. *Theory of Unimolecular Reactions*; Academic Press: New York, 1973.

[25] Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific Publications: Oxford, 1990.

the secondary deuterium isotope effect decreases rapidly with excess energy, in agreement with their experimental IRMPD results (both pulsed and continuous wave photochemical results). Since the magnitude of the primary isotope effect was independent of energy (intensity), they concluded that the two isotope effects originated in two separate transition states, thereby confirming the hypothesis of a multiple-step mechanism.

Tumas et al. also estimated the absolute rate constants for $C-CH_3$ cleavage. With an estimate of the mean pumping rate for the pulsed CO_2 laser (10^7 s^{-1}), they determined that under the low-pressure experimental conditions, dissociation occurred with 6−12 kcal/mol of excess energy (above the lower dissociation channel). They asserted that the distribution of energies at which dissociation occurred may be broad, but must have been in this energy regime. Our system is essentially identical and we believe that dissociation in our system occurs in this same energy regime, within a few photons above the critical energy.

Alkoxide Energetics. The method of activation, sequential absorption of IR photons from a CO_2 laser, introduces enough energy to dissociate an alkoxide ion, heterolytically breaking a carbon−carbon bond. The barrier for this bond cleavage has been estimated to be ~40 kcal/mol,[23] and since each infrared photon has an energy of about 3.0 kcal/mol, roughly 14 photons must be absorbed by each molecule to have enough energy to dissociate.

Since the rate of absorption of sequential photons for our system is on the same order as the rate of dissociation ($k \sim 10^6$ s^{-1})[23] and much slower than the rate of internal energy redistribution ($k \sim 10^{13}$ s^{-1}),[27] it is reasonable to expect that the internal energy of the molecules that dissociate is near the energy of the barrier for dissociation. This was confirmed experimentally by Tumas and co-workers who had measured kinetic isotope effects for both continuous wave (cw) and pulsed excitation methods for the dissociation of *tert*-butoxide. A large secondary kinetic isotope effect (KIE), associated with the first (rate limiting) step, was observed for both the cw and the pulsed experiments.

The KIE was smaller for the pulsed laser experiments than the cw laser experiments, implying that additional photons may be absorbed before dissociation occurs in the pulsed experiments.[23] We believe that in our pulsed laser experiments, we are not experiencing exclusively threshold behavior, but are one or two photons (3−6 kcal/mol) above the barrier. The dissociation of the alkoxides in this energy regime agrees with model statistical calculations done on the 2-methyl-2-propoxide-*1,1,1*-d_3 anion[23] discussed previously. At energies just above the barrier to dissociation, the kinetic isotope effect is largely dependent on the difference in zero point energies (ZPE). As internal energy increases, the sum of states for both channels increases rapidly and comparably and there is less dependence on the difference in ZPE's. Therefore, at energies significantly in excess of threshold, discrimination between the isotopes decreases and the KIE is smaller.

Similarly, Boering observed a dependence of the secondary KIE on the amount of excess energy. The secondary KIE was larger for lower excess kinetic energy excitation and decreased as the kinetic energy (the energy per collision) was increased.[18]

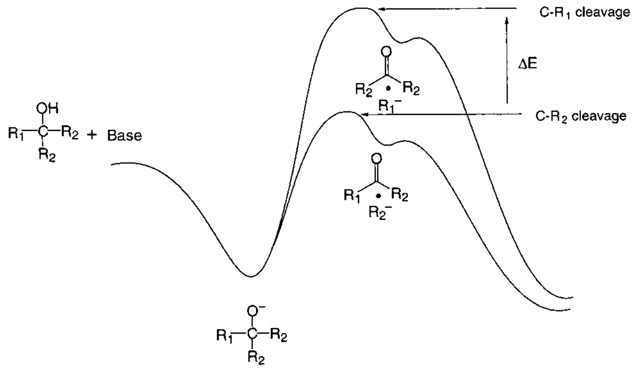

Figure 3. Potential surface for the dissociation of general alkoxide $R_1(R_2)_2CO^-$, where R_1 and R_2 are alkyl groups.

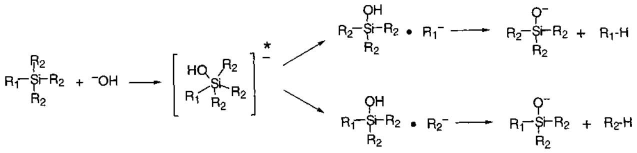

Figure 4. Mechanism for the reaction of hydroxide anion with a silane.

Alkoxide PE Surface and Mechanism. A potential energy surface for the dissociation of a general alkoxide $R_1(R_2)_2CO^-$, where R_1 and R_2 are alkyl groups, is shown in Figure 3. The mechanism of alkoxide dissociation is less clear for alkyl anions that have small (or possibly negative) electron affinities (EA's). The interaction between the neutral ketone and the alkyl anion in the intermediate complex provides 10−15 kcal/mol of stabilization, solvating the anion so that, in the complex, even ions with "negative" electron affinities are bound.[1] The amount of stabilization energy derived from this ion−dipole interaction is approximately the same for all of the complexes in our system and is therefore independent of the components in the complex. The difference in energy between two complexes is the same as the difference in energy between the corresponding unsolvated anions.

DePuy and co-workers observed a relationship between the product ratios and the gas-phase acidities of the alkanes in a silane system (Figure 4) where the strength of the Si−C bonds is also correlated with the C−H bond dissociation energies.[14] They assumed a linear relationship between relative acidities of two alkanes and the logarithm of their product ratios from the dissociation of a common pentacoordinate siliconate ion intermediate (Figure 4). Relationships such as these appear in many different systems.[5,13] Craig et al. and Klots showed by statistical reaction rate theory (RRK and RRKM theory[24,25]) that the branching ratios in activated systems follow a log−linear relationship.[28,29]

Silane PE Surface and Mechanism. By estimating the bond strengths from known energies and semiempirical calculations[30] we have constructed the energetics of the potential energy surface of the reaction of hydroxide ion with phenyltrimethylsilane (Figure 5). Specifically we have estimated the relative energies of the two reaction channels (methyl loss and phenyl loss) including the relative energies of the barriers.[31] Although heterolytic cleavage of the Si−C bond has a significant barrier, the energy of the incoming reactants (the hydroxide ion and neutral silane) is higher than this barrier and therefore the pentacoordinate adduct formed is chemically activated.[32]

Sheldon, Hayes, Bowie, and DePuy have suggested that the dissociation in the silane system follows a mechanistic route

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(26) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice-Hall: Englewood Cliffs, 1989.

(27) Lupo, D. W.; Quack, M. *Chem. Rev.* **1987**, *87*, 181−216.

(28) Craig, S. L.; Zhong, M.; Choo, B.; Brauman, J. I. *J. Phys. Chem.* **1997**, *101*, 19−24.

(29) Klots, C. E. *J. Phys. Chem.* **1995**, *99*, 1748−1753.

(30) Calculations were performed at the AM1 level using the semiempirical engine from MacSpartan Plus. *MacSpartan Plus*; Wavefunction, Inc.: Irvine, CA, 1996.

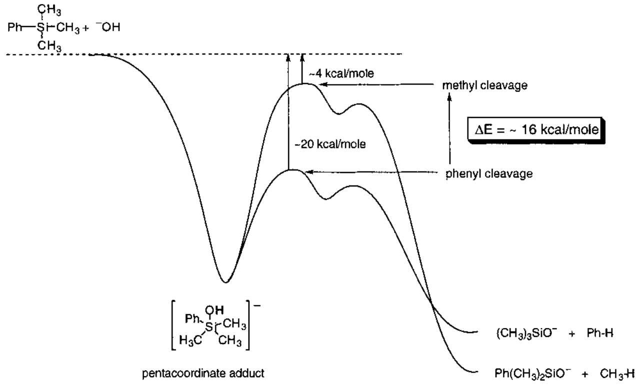

Figure 5. Potential surface for phenyl versus methyl cleavage in the silane system.

similar to that of the alkoxide mechanism (Figure 4).[33] The first step is a heterolytic Si−C bond cleavage to form a complex consisting of an alkyl anion and the corresponding silanol. The second step is a fast, facile proton transfer from the acidic hydroxyl proton to the alkyl anion. They suggested a carbanionic intermediate on the basis of model calculations on the dissociation of pentacoordinate siliconate anions and because the observed alkyl group loss was not in accord with known alkyl group radical stabilities. In certain instances, where the departing alkyl group is extremely basic, they suggested that partial proton transfer occurs before the Si−C bond has completely broken; this picture is supported by the ab initio calculations performed by Gordon and co-workers on the decomposition of the pentacoordinate tetramethylsilanol anion.[34] As in the alkoxide dissociation, the intermediate anion is presumably stabilized in the ion−dipole complex by about 10−15 kcal/mol. With this stabilization energy, weakly bound or possibly unbound carbanions are less likely to detach an electron.[14]

Comparison of Alkoxide and Silane Systems. A comparison of the alkyl leaving group propensities for the alkoxide and silane reactions reveals an overall similarity (Figure 6). The statistically corrected branching ratio is defined as the ratio of products observed between two alkyl cleavage channels after correcting for differences in the number of each alkyl group on the parent molecule before dissociation. We have confirmed several of the leaving group propensities of the silane system using our apparatus. There are, however, small differences among some of the alkyl groups.

The relative positions of the alkyl groups in Figure 6 are derived from the product ratios in Table 1. The position of neopentyl is established by the experimental neopentyl:methyl product ratio. We cannot measure the product ratio accurately enough to establish an absolute ratio quantitatively. Similarly, the position of *sec*-butyl is above that of *n*-butyl, but we were unable to anchor the position accurately since the branching ratio of *sec*-butyl:methyl was also unmeasurably large. Figure 6 also shows that the correlation of *sec*-butyl (dashed arrow) and of *n*-propyl crosses the methyl correlation line between the two systems. The complexation energy of the alkyl anion/ketone complex is assumed to be the same, regardless of the identity of the components in the complex.

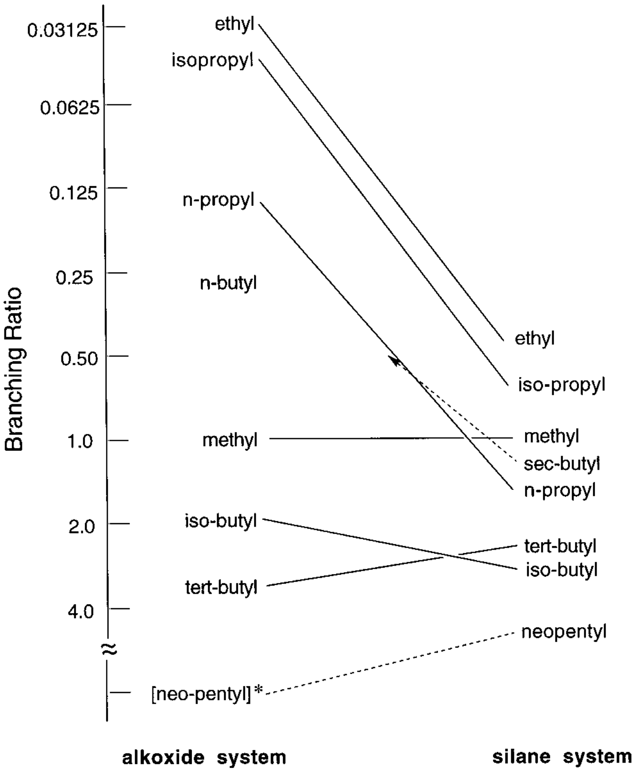

Figure 6. Comparison of the statistically corrected branching ratios in the silane and alkoxide systems. The position of *sec*-butyl is not shown in the alkoxide system, but it is higher than that of *n*-butyl (i.e., lies above *n*-butyl in the figure); see text. For [neo-pentyl]* the branching ratio of neopentyl:methyl is greater than 4.0; see text.

The product ratios depend not only on the nature of the leaving groups, but also on the method of activation. In comparing the alkoxide and the silane systems, the two methods of activation result in different internal energy profiles. In the silane system the chemically activated pentacoordinate siliconate anion intermediate has considerable excess internal energy due to the strength of the Si−O bond that is formed in the initial reaction step.[33] Infrared activation in the alkoxide system gives 6.0 kcal/mol (the energy of two IR photons) or less of excess internal energy.

The effect of the different energy activation schemes is evident by examining the range of product ratio values in both systems. The discrimination is much greater for the alkoxides than for the silane compounds. For example, the difference in the product ratio values between ethyl:methyl and neopentyl:methyl is 5.0 in the silane system and unmeasurably large in the alkoxide system. This difference in discrimination is due, in part, to the difference in the amount of excess energy above the alkyl cleavage transition states. Since the density of states increases rapidly with excess energy, for larger excess energies, discrimination for one cleavage channel over the other decreases and the product ratios decrease. Therefore, molecules with higher excess energy will have more similar ratios (i.e. the range of values for the product branching ratios will be smaller).[28]

Phe vs Me: Quantitative Comparison. Using statistical reaction rate theory, we can obtain a more quantitative picture of the relationship between the product branching ratios,

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(31) The difference in energy between the two transition states of the two cleavage channels was estimated as the difference in the heats of formation of $CH_3^- + Ph(CH_3)_2SiOH$ and $Ph^- + (CH_3)_3SiOH$. The values for the heats of formation were derived from specific thermochemical cycles or from additivity. Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246−252. Walsh, R. *The Chemistry of Organic Silicon Compounds*; John Wiley & Sons: New York, 1989.

(32) The magnitude of the excess energy was estimated using several thermochemical cycles. These estimates rely on relative energies of several similar compounds, and therefore we would expect errors due to these types of estimates to cancel.

(33) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H.; DePuy, C. H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 275−180.

(34) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056−3062.

mechanism, and energetics. We have chosen to investigate the leaving group propensities of phenyl versus methyl substituents in both systems.

The product in the IRMP dissociation of 2-phenyl-2-propoxide, $Ph(CH_3)_2CO^-$, is exclusively Ph−H (no CH_3−H elimination is observed). The difference in activation energy between the two dissociation channels is substantial enough that we cannot access the higher energy channel (methyl cleavage) with our method of activation. This complete discrimination for the phenyl cleavage channel is consistent with our interpretation of the energetics in our activation scheme.

The potential energy surface of the reaction of the addition of hydroxide ion to phenyltrimethylsilane is shown in Figure 5. Upon addition of hydroxide to phenyltrimethylsilane, a stable, negatively charged pentacoordinate adduct is formed.[33] Assuming that there is no unusual behavior associated with the bonding in the pentacoordinate adduct, we can estimate relative energies on this potential energy surface, including the energies of the transition states. If we assume that the transition state has essentially complete Si−C bond cleavage, the transition state resembles the products in the dissociation. We can then make the assumption that the energy of the transition state is equal to the energy of a complex composed of an alkyl anion (either methyl anion or phenyl anion) complexed with the corresponding trialkylsilanol and that the complexation energies of the two different complexes are the same.[35] It is important that the product branching ratios are related to the difference in energies of the two transition states (i.e. the relative energies) rather than the absolute energies. Errors associated with these assumptions should therefore systematically cancel.

The energy of the transition state of the methyl channel lies 16 kcal/mol above the energy of the transition state of the phenyl channel. We estimate the energy of the methyl cleavage channel to be 4 kcal/mol below the energy of the reactants and the energy of the phenyl cleavage channel to be 20 kcal/mol below the energy of the reactants.

DePuy has measured the ratio of phenyl cleavage to methyl cleavage in this silane system to be 40:1 and we have observed similar product ratios in our ICR.[36] We investigated these ratios by calculating the relative reaction rates as a function of excess energy using statistical reaction rate theory in both the alkoxide (2-phenyl-2-propoxide) and the silane (hydroxide + phenyltrimethylsilane) systems.

RRKM calculations were performed on the reaction of phenyltrimethylsilane with hydroxide anion.[37] With the barrier of the phenyl dissociation channel chosen as 20 kcal/mol and the barrier of the methyl dissociation as 36 kcal/mol, the calculations indicate essentially only phenyl cleavage. For the branching ratio to be within the same order of magnitude of the experimental ratio of 40:1, the energy difference between the methyl and phenyl cleavage transition state barriers (ΔE) would have to be less than 5 kcal/mol.

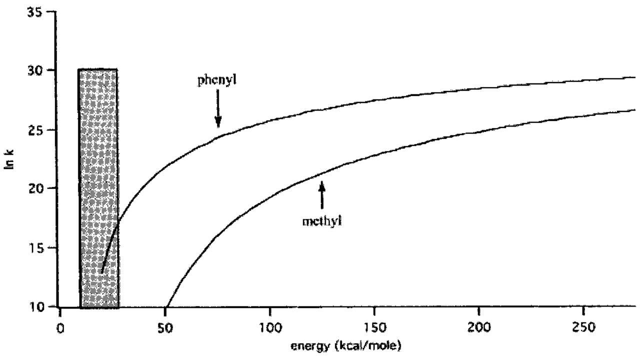

Figure 7. RRK results for the rate of methyl and phenyl cleavage as a function of energy for the alkoxide system.

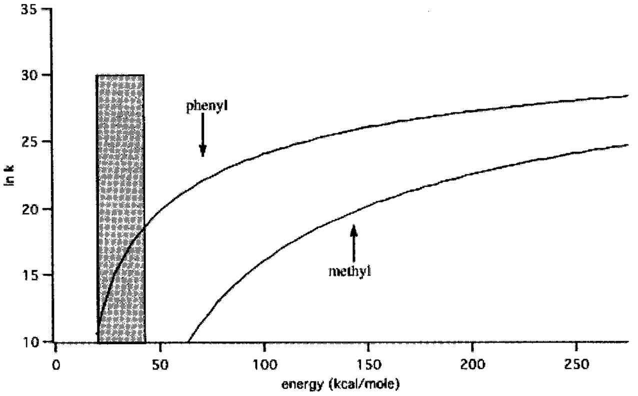

Figure 8. RRK results for the rate of methyl and phenyl cleavage as a function of energy for the silane system.

To investigate a wider range of excess energies, RRK calculations were performed on both the silane and alkoxide systems. Figures 7 and 8 show the relative rates of phenyl versus methyl cleavage for both systems. The energy distribution of the reactants is also indicated in each system. Note that the RRK calculations agree with the RRKM calculations done at the same energy. One quantum of energy was taken to be 1000 cm^{-1} (2.86 kcal/mol). For the silane system, the barriers of the phenyl and methyl dissociation channels were the same as in the RRKM calculations described above.

We can roughly estimate the amount of excess energy above the phenyl dissociation channel to be about 19 kcal/mol. [38] Given this amount of excess energy, RRKM calculations show that ΔE (Ph vs Me) would have to be less than 3 kcal/mol for the calculated branching ratio to be similar to the observed experimental ratio.

We have performed several RRKM calculations varying ΔE and the amount of excess energy. The relative rates are not especially sensitive to variations in the relative barrier heights or excess energy, but are somewhat sensitive to variations in ΔE. For excess energies less than 30 kcal/mol above the phenyl cleavage channel, the phenyl:methyl ratio is greater than 100 unless ΔE is less than 5 kcal/mol. For example, for 20 kcal/

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(35) The complexation energies of the two different complexes are not exactly the same, since the polarizability of the neutrals, trimethylsilanol and phenyldimethylsilanol, are different. We would expect the phenyldimethylsilanol to provide more stabilization in the ion−dipole complex because of the polarizability of the phenyl group. However, the incremental difference in stabilization energy is not significant and taking the complexation energies to be the same is suitable for our analysis.

(36) The values varied depending on our method of generating hydroxide, either by electron impact of N_2O or by electron impact on H_2O, but were still of the same magnitude. In all cases, both the phenyl and the methyl cleavage channel were observed with the phenyl channel more dominant.

(37) RRKM calculations were performed using a modified version of HYDRA. Wladkowski, B. D.; Lim, K. F.; Allen, W. D.; Brauman, J. I. *J. Am. Chem. Soc.* **1992**, *114*, 9136−9153. Frequencies were obtained from AM1 frequency calculations on geometry optimized (6-31G*) structures using Gaussian 94. Frisch, M. J. et al. *Gaussian 94*; Revision C3 ed.; Gaussian, Inc.: Pittsburgh, 1995.

(38) $\Delta H_f[SiPh(CH_3)_3] = -20.6$ kcal/mol, $\Delta H_f[Si(CH_3)_3OH] = -119.5$ kcal/mol, $\Delta H_f[OH^-] = -34.3$ kcal/mol, $\Delta H_f[Ph^-] = -55.8$ kcal/mol. The complexation energy between Ph^- and $Si(CH_3)_3OH$ was taken to be 10 kcal/mol. Walsh, R. *The Chemistry of Organic Silicon Compounds*; John Wiley & Sons: New York, 1989. Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables*, 4th ed.; National Institute of Standards and Technology: Washington, DC, 1998; pp 1−1951. Davico, G. E.; Bierbaum, V. M.; Depuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590.

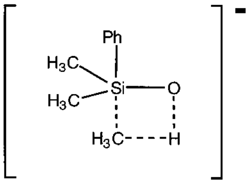

Figure 9. Methyl cleavage from a pentacoordinate siliconate anion with concerted character.

mol excess energy and a ΔE of 3 kcal/mol, the ratio is about 25. However, if we increase ΔE to 5 kcal/mol, the ratio is 151. Only in cases where ΔE is significantly small do we expect to see any of the methyl cleavage channel.

The most interesting information ascertained from these model calculations is the energy regime that corresponds to the observed experimental product ratios in the silane system (Figure 8). According to the model calculations, the amount of excess energy needed to achieve a product branching ratio of 40:1 is about 266 kcal/mol. Even if our estimate of ΔE is decreased by 3−4 kcal/mol, the amount of excess energy needed is still quite large, about 212 kcal/mol.

Possible Alternative Mechanism. The silane cleavage reactions, as noted initially by DePuy[39] and subsequently confirmed by Klass and co-workers,[40] are clearly anionic in character. The leaving group order follows the anionic stability and agrees well with the alkoxide results. In accord with their suggestions, our analysis of the energetics shows that a simple anionic cleavage is not plausible; complete bond breaking to give CH_3^- or Ph^- would lead to product ratios much farther from unity than is observed. Alternatively, the ΔE (phenyl to methyl energy difference) required is much smaller than expected for a fully anionic cleavage. Thus, either the Si−C bond is not fully broken or the departing group is protonated, or both. These characteristics require a concerted mechanism for the Si−C group cleavage transition state in the silane system.

Figure 9 depicts the methyl cleavage from a pentacoordinate siliconate anion as a concerted process with methyl cleavage and proton transfer from the oxygen occurring simultaneously; the oxygen bears a partial negative charge.[41] Quantum calculations confirm that this reaction is clearly more complicated than a simple cleavage. Previous ab initio calculations by Gordon and co-workers on the model system of the hydroxide plus tetramethylsilane indicate that carbon−silicon bond cleavage and carbon−hydrogen bond formation occur simultaneously, though there is still a substantial amount negative charge on the departing alkyl group in the transition state.[42] DePuy and co-workers have previously discussed the likelihood of a concerted mechanism in this cleavage, in light of these calculations.[14]

We have performed some illustrative quantum calculations at the AM1 level of theory on the reaction of hydroxide with phenyltrimethylsilane. We constrain the geometry of the hydroxyl group so that proton transfer to the exiting methyl group is prevented; the energy increases dramatically as the Si−C bond is stretched. However, if we allow the orientation of the hydroxyl group to relax, proton transfer from the hydroxyl group to the methyl group occurs concomitant with increasing carbon−silicon bond length. At no time does the methyl group bear a full negative charge. The energies calculated with this relaxed geometry increase toward a maxima when the Si−C bond is ∼3.5 Å and then decrease rapidly as the carbon−hydrogen bond forms. A constant, minimum value is reached at large Si−C bond lengths corresponding to the energy of separated products, methane and phenyldimethylsiloxide. We have identified several structures similar in energy with one imaginary frequency at the AM1 level of theory. These structures depict a concerted cleavage mechanism, corresponding to the transition state for methyl cleavage.

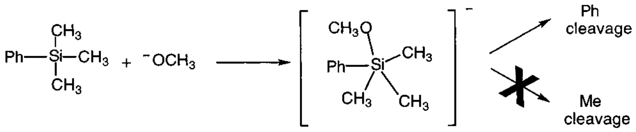

Figure 10. Reaction of methoxide plus phenyltrimethylsilane to form a pentacoordinate siliconate anion.

The validity of our AM1 calculations was confirmed by performing quantum calculations at the 6-31+G* level on a model system, the methyl cleavage channel in the decomposition of the tetramethylsiliconate anion. The Si−C bond length between the departing methyl group and the silicon center was increased incrementally from the equilibrium bond length. As the Si−C bond length is increased, the energy increases gradually, then decreases as the methyl anion is stabilized by the hydroxyl hydrogen. Similarly, the energy of the methyl cleavage channel was calculated where the departing methyl group was prohibited from interacting with the hydroxyl hydrogen. In this case, the energy increases rapidly, substantially above the energy of the concerted methyl cleavage. This energy profile for this reaction coordinate agrees well with our AM1 calculations, with the energy increasing toward a maximum value and then rapidly decreasing. Although a unique transition state structure was not identified, these calculations show that the methyl group does not leave as a “bare” anion, consistent with previous work[34] and with the results derived from our AM1 calculations.

A concerted process would have a critical energy for cleavage well below that required to make a simple anion. Consequently, there would be additional excess energy in the system which would also result in a product ratio closer to unity. In addition, for those cleavages that have concerted character, the critical energy differences would also be smaller.

Reactions with Other Nucleophiles. Our inferences about the loss of methane from phenyltrimethylsilanol anion clearly depend on the presence of the acidic O−H proton. Loss of any group from such a pentacoordinate silane anion would be very different if the O−H proton were absent. Consequently, we examined the reaction of methoxide ion with phenyltrimethylsilane.

The reaction of methoxide and phenyltrimethylsilane (Figure 10) produces an intermediate siliconate anion similar to that formed in the reaction of hydroxide and phenyltrimethylsilane. The two pentacoordinate intermediate anions should have similar excess energies, and they would presumably decompose by losing either a phenyl anion or a methyl anion. The significant difference between the two reactions is the lack of an acidic hydroxyl hydrogen in the methoxide reaction. Therefore, the pentacoordinate intermediate in the methoxide reaction cannot lose methyl anion through a concerted process such as that

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[39] DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012−5015.

[40] Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519−529.

[41] The polar Si−O and O−H bonds suggest a polar transition state where the Si−C bond cleavage is partially stabilized by the proton transfer, relieving some of the negative charge on the alkyl group, allowing part of the negative charge to reside on the oxygen. Studies on the pyrolysis of alkyl halides have shown that the elimination of H−X proceeds through a polar, concerted mechanism. Maccoll, A. *Chem. Rev.* **1969**, *69*, 33−60.

[42] Geometry calculations for this model reaction were performed at the 3-21G* SCF level. Energy differences were estimated by assuming correlation and polarization effects are additive. Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056−3062.

depicted in Figure 9. The expected methyl/phenyl product ratio should therefore be close to zero.

We indeed observe only phenyl loss in the reaction of methoxide plus phenyltrimethylsilane. This result is completely consistent with methyl loss occurring with concerted protonation of the departing methyl group. This result is also consistent with other experiments performed in our laboratory where we observe no methyl loss in the reaction of phenyltrimethylsilane with fluoride or cyanide.

We do not know the origin of the small differences found between the alkoxide and silane systems. Inasmuch as the silane cleavage reaction is concerted, it is possible that steric or dynamic effects could play a modest role.

Conclusion

Comparison of all of the leaving group propensities in the alkoxide and silane system (Figure 6) shows that while the major trends are common to both (Ph > H > CH_3) there are small but reproducible differences in the order of the alkyl groups (*tert*-butyl versus *iso*-butyl or *iso*-butyl versus *n*-propyl). Analysis of the energetics of the dissociation of phenyltrimethylsilanol anion using statistical reaction rate theory suggests that the methyl cleavage mechanism in the silane system is concerted in character and not purely anionic, in agreement with previous work on similar systems. This analysis is confirmed by the different quantitative behavior of the methoxide adduct. Determination of the relative acidities from a kinetic method can be misleading if assumptions about the mechanism are incorrect.

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