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Two Ways To Transfer a Proton. An ab Initio Study of the Identity Reaction of SiH_3^- + SiH_4 and Comparisons to the Reactions of AlH_3 and PH_3

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Summary: High-level ab initio calculations (G2+) indicate that, in the reaction of SiH_3^- + SiH_4, there are two, competitive mechanisms for proton transfer. Comparisons to the analogous reactions of PH_3 and AlH_3 are made.

Organosilanes have provided a rich gas-phase ion chemistry,[1] and in the present contribution, we report the theoretical prediction of an unconventional yet competitive mechanism for proton transfer in the title reaction. Silane is an unusual acid in that although it is a moderate gas-phase proton donor (ΔH_{acid} = 372.3 kcal/mol),[2] its Si–H bonds are polarized with excess density on hydrogen. That is, the hydrogens in SiH_4 are best described as hydride-like.[3] To complete a proton transfer, the Si–H bond must reverse its polarity in order to avoid an unfavorable electrostatic interaction.[4] Obviously this electron shift has an energetic cost, and recent theoretical as well as experimental work suggests that proton transfers in these "reverse-polarized" systems face unusually large barriers.[4–6] On the other hand, the charge distribution in SiH_4 is perfectly suited for nucleophilic attack at silicon, and many stable pentacoordinate siliconates are known.[7] In the present study, the identity reaction of SiH_3^- with SiH_4 is investigated and we report the unusual finding that nucleophilic attack at either hydrogen or silicon can competitively lead to proton transfer in this system.

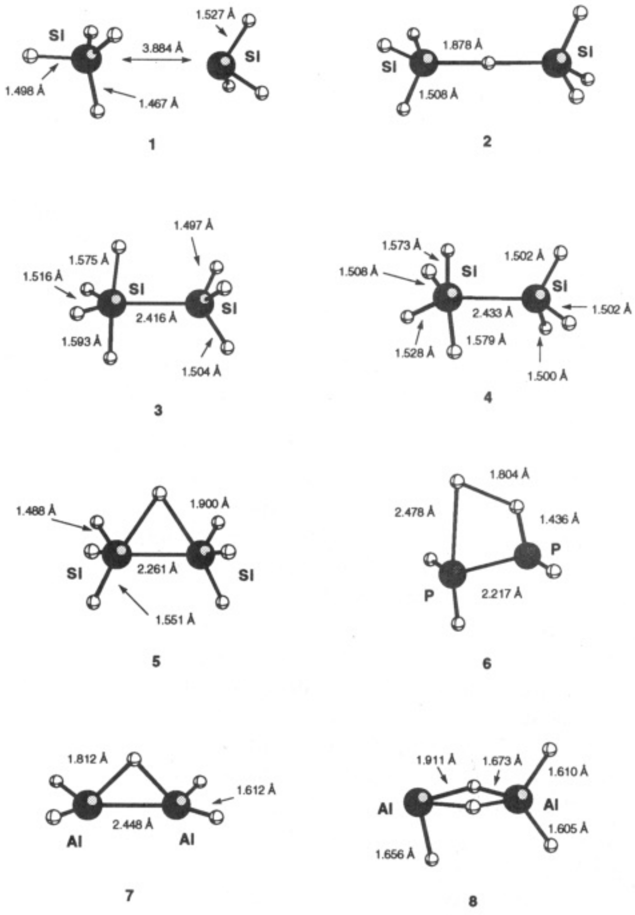

Figure 1. Optimized structures of complexes and transition states (MP2/6-31+G(d,p)).

For the reaction of SiH_3^- with SiH_4, the reactants, intermediates, and transition states were characterized at the G2+ level of theory (Figure 1).[4,8,9] When the silyl anion approaches silane, a weak ion–dipole complex, **1**, is formed where the SiH_3^- lone pair interacts with the backside of an Si–H bond. From the complex, attack at hydrogen leads to a conventional proton transfer transition state, **2**. The transition state has D_{3d} symmetry, has a single imaginary frequency, and is 12.3 kcal/mol less stable than the separated reactants at 298 K.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1993.

[1] For example, see: (a) Schwarz, H. In *The Chemistry of Functional Groups: The Chemsity of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 445–510. (b) DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1987**, *20*, 127. (c) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* **1986**, *5*, 2050, 2054. (d) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863. (e) Tumas, W.; Salomon, K. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2541.

[2] Proton affinities in the text are from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17* (Suppl. No. 1).

[3] Gronert, S.; Glaser, R.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 3111.

[4] Gronert, S. *J. Am. Chem. Soc.*, in press.

[5] Gronert, S. *J. Am. Chem. Soc.* **1991**, *113*, 6041.

[6] (a) DePuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 8650. (b) Gronert, S.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1991**, *113*, 4009.

[7] For example, see: (a) Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889. (b) Gordon, M. S.; Burggraf, L. W.; Damrauer, R.; Davis, L. P. *J. Am. Chem. Soc.* **1988**, *110*, 6601. (c) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *Int. J. Quantum Chem.* **1992**, *44*, 691. (d) Apeloig, Y. In *The Chemistry of Functional Groups: The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 57–226. (e) Damrauer, R.; O'Connell, B.; Danahey, S. E. *Organometaillics* **1989**, *8*, 1167.

[8] Geometries are optimized at the MP2/6-31(+)G(d,p) level. Energies are calculated at the MP4/6-311+G(2df,p) level, and corrections are made for expanding the basis set (MP2/6-311+G(3df,2p)-MP2/6-311+G(2df,p)) and higher level correlation (QCISD(T)/6-311+G(d,p)-MP4/6-311+G-(d,p)). In the calculations of AlH_2^-, SiH_3^-, and PH_2^-, an additional set of hydrogen orbitals was placed at the position of the missing proton (counterpoise). Finally, the values are corrected for zero-point energies (scaled by 0.9) and converted to 298 K. For full details, see ref 4 as well as: Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

[9] Calculations were completed with Gaussian 92: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. H.; Foresman, J. B.; Johnson, B. D.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachar , K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92; Gaussian, Inc., Pittsburgh, PA, 1992.

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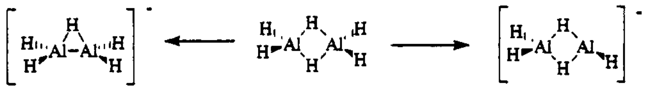
Alternatively, SiH_3^- could attack the silicon to give a pentacoordinate siliconate. Although the pentacoordinate complex with an axial silyl substituent is unstable and decomposes without a barrier to give **1**, the complex with an equatorial SiH_3 group, **3**, is a minimum on the potential energy surface. It is 1.7 kcal/mol less stable than **1**, and a small barrier (<1 kcal/mol) prevents dissociation. The dissociation involves transition state **4** and is essentially a pseudorotation process leading to the unstable axial SiH_3 complex. A brief study of the intrinsic reaction coordinate confirms that **4** links **1** to **3**. From **3**, an axial hydrogen can bridge the two silicons to give a C_{2v}-symmetric transition state, **5**, for exchange. The energy of transition state **5** is +7.2 kcal/mol with respect to the reactants. The process $\mathbf{1} \rightarrow \mathbf{4} \rightarrow \mathbf{3} \rightarrow \mathbf{5} \rightarrow \mathbf{3} \rightarrow \mathbf{4} \rightarrow \mathbf{1}$ effectively results in proton transfer, although the key transition state (**5**) is best described as a hydride transfer. The overall barrier is 5.1 kcal/mol lower than that of the conventional proton transfer; however, transition state **5** is far more ordered than **2**, and when entropy corrections are made at 298 K, the free energies of activation of the two processes are similar (18.3 and 18.0 kcal/mol for **2** and **5**, respectively).[10] *Proton transfer via nucleophilic attack at hydrogen or silicon should be competitive in* $SiH_3^- + SiH_4$.

Although only a small primary isotope effect is expected in **2**, the softening of the ancillary Si–H vibrations and bends in the transition state leads to the prediction of a significant isotope effect ($\Delta G^{\ddagger}(\mathbf{2}\text{-}d_7) - \Delta G^{\ddagger}(\mathbf{2}\text{-}d_0) = {\sim}1$ kcal/mol) in the reaction of SiD_3^- with SiD_4. In contrast, virtually no isotope effect ($\Delta G^{\ddagger}(\mathbf{5}\text{-}d_7) - \Delta G^{\ddagger}(\mathbf{5}\text{-}d_0) = {\sim}0$ kcal/mol) is predicted for the same reactants passing through transition state **5**, because here the Si–H vibrations and bends are relatively similar to those found in the reactants.[11] Therefore, the presence or the absence of an isotope effect in an appropriately labeled, polydeuterated system can be used experimentally to distinguish between the mechanisms. Unfortunately, the barrier for the parent system is above that typically accessible by gas-phase techniques,[12] but it is possible that derivatives could be amenable to experimental study.[13]

In the second row, silicon is unique in its ability to yield two pathways to proton transfer. Because phosphorus is more electronegative than silicon, the "reverse polarization" of the X–H bonds is less extensive in PH_3. In other words, the phosphorus is less electrophilic and the hydrogens have less hydride-like character. As a result, attack at hydrogen is favored and the proton transfer transition state is 1.4 kcal/mol more stable than the reactants.[4] In contrast, the potential energy surface for attack at phosphorus is repulsive and no hypervalent complexes could be found. In early gas-phase work, Beauchamp[14] reported that $PH_2^- + PH_3$ yields $P_2H_3^- + H_2$ in a relatively slow reaction. The transition state, **6**, for this process was located at the MP2/6-31+G(d,p) level. The reaction can be viewed as the concerted addition of PH_2^- to the phosphorus of PH_3 followed by loss of hydride and subsequent deprotonation of the PH_2 group to give H_2. In **6**, one of the P–H bonds in the PH_3 fragment is long (2.48 Å) and is in a position to interact with a hydrogen on the PH_2 fragment (H–H = 1.80 Å). With a relative energy of 30.7 kcal/mol, transition state **6** is much less stable than the reactants or the transition state for conventional proton transfer. On the basis of these results, the production of $P_2H_3^-$ from $PH_3 + PH_2^-$ should only be observable experimentally if the ions have excess vibrational or translational energy.

In AlH_3, the hydrogens are more hydride-like and the electrophilicity of the aluminum is enhanced by the presence of an empty valency. In the reaction of AlH_2^- with AlH_3,[15] a conventional proton transfer transition state cannot be located on the potential energy surface.[16] Instead, AlH_2^- attacks the aluminum of AlH_3 and directly forms a very stable complex with a bridging hydrogen, **7**.



7 **8**

The complex is 53 kcal/mol more stable than the reactants. The structure is similar to transition state **5**, but the open valency of aluminum favors the bridging hydrogen, and consequently, **7** is a minimum on the potential energy surface. The $Al_2H_5^-$ ion is the deprotonation product of dialane, and one could imagine that **7** is formed by the removal of a bridging hydrogen followed by Al–Al bond formation. The isomeric ion, **8**, formed by the removal of a terminal hydrogen is also a minimum on the potential energy surface but is 1.7 kcal/mol less stable at the G2+ level.[17]

Although the proton transfer behavior of the second-row systems varies considerably across this series, the proton affinities of the conjugate bases are relatively similar. At the G2+ level, the proton affinities are 373.1,[18] 373.0, and 368.0 kcal/mol for AlH_2^- ($^1A_1$), SiH_3^-, and PH_2^-, respectively. In a recent study,[4] this level of theory predicted proton affinities with an average deviation from experiment of only ±0.5 kcal/mol; therefore, it is anticipated that the present values are reasonably accurate. A small discrepancy is noted for PH_2^-. In equilibrium

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[10] Entropy corrections were calculated from the ab initio data by standard methods: Lewis, G. N.; Randall, M.; Pitzer, K. S.; Brewer, L. Thermodynamics; McGraw-Hill: New York, 1961.

[11] Tunneling may play a role in these proton transfers. Using a simple Wigner approach (Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. In *Theory of Chemical Reaction Dynamics*;Baer, M., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. IV), significant tunneling is expected in the conventional proton transfer (correction factor 2.9), but not in the alternative pathway (correction factor 1.2). However, to quantitatively assess the importance of tunneling, a full dynamics study is required. For example, see: Isaacson, A. D.; Wang, L.; Scheiner, S. *J. Phys. Chem.* **1993**, *97*, 1765.

[12] Barlow, S. E.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1988**, *110*, 7240.

[13] For conventional proton transfers, more acidic species give smaller gas-phase proton transfer barriers.[4] It is possible that a phenylsilane bearing an effective electron-withdrawing group (*i.e.* –CN) on the ring may be acidic enough for these measurements.

[14] Holtz, D.; Beauchamp, J. L.; Eyler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 7045.

[15] Only reactions of the singlet AlH_2^- anion are considered. The triplet is 18.7 kcal/mol less stable at the G2+ level.

[16] With geometry constraints, a conventional proton transfer structure can be located. It contains five imaginary frequencies and is over 75 kcal/mol less stable than **7**.

[17] Both ions have unusual geometries. Further studies, including electron density analysis, are underway and will be presented at a later time.

[18] In a previous paper, a value of 406.6 kcal/mol was reported for the 0 K proton affinity of AlH_2^-, but this value must be the result of a typographical error. At the same level of theory, we find a value of 373.5 kcal/mol: Pople, J. A.; Schleyer, P. v. R.; Kaneti, J.; Spitznagel, G. W. *Chem. Phys. Lett.* **1988**, *145*, 359.

[19] A proton affinity of 368.2 ± 0.5 kcal/mol can be calculated from the bond strength and electron affinity data in: Berkowitz, J.; Ellison, G. B.; Gutman, D. personal communication; *J. Phys. Chem.*, in press.

[20] Smith, B. J.; Radom, L. *J. Phys. Chem.* **1991**, *95*, 10549.

measurements,[2] a proton affinity of 370.9 kcal/mol has been reported for PH_2^-, but the G2+ calculations as well as other experimental results[19] predict a value near 368 kcal/mol. In addition, similar theoretical values have been reported by Gordon[7] *et al.* at the MP4/6-311++G(3df,-2pd) level and Radom *et al.* at the G2 level.[20] Therefore, it appears that the equilibrium-derived value is too large by ~3 kcal/mol.

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Supplementary Material Available: Listings giving optimized geometries for the various Si, P, and Al compounds discussed (6 pages). Ordering information is given on any current masthead page.

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