Pyrolytic, Kinetic, and Theoretical Studies on the Isomerization of Me2HSiCH2' to Me3Si'

Thomas J. Barton
Iowa State University, barton@ameslab.gov

Anthony Revis
Iowa State University

Iain M. T. Davidson
The University, Leicester

S. Ijadi-Maghsoodi
The University, Leicester

Kevin J. Hughes
The University, Leicester

See next page for additional authors
Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

Part of the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/253. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Pyrolytic, Kinetic, and Theoretical Studies on the Isomerization of Me2HSiCH2' to Me3Si'

Abstract
Evidence for the isomerization of 'CH2SiHMe2 to Me3Si' via a 1,2-migration of hydrogen has been obtained through pyrolytic studies of 4-(dimethylsilyl)-1-butene which decomposes through loss of the allyl radical to produce 'CH2SiHMe2• Rearrangement to Me3Si' was established by product analysis and trapping with methyl chloride. Kinetic analysis afforded a barrier of ca. 41 kcal/mol in excellent agreement with a calculated barrier of 42.6 kcal/mol achieved with fourth-order perturbation theory corrections (MP4) and addition of zero-point vibrational corrections.

Disciplines
Chemistry

Comments

Authors
Thomas J. Barton, Anthony Revis, Iain M. T. Davidson, S. Ijadi-Maghsoodi, Kevin J. Hughes, and Mark S. Gordon
sidered unambiguous experimental evidence for such a transfer of spin density onto the ligands.\(^{26}\) The absence of observable \(^{14}\)N superhyperfine coupling in the NH\(_3\)-bound form of the S\(_2\) state EPR spectrum, however, argues against a large change in the covalency of the Mn site due to ligation of NH\(_3\) molecules. In fact, ligand superhyperfine couplings are rarely resolved in Mn complexes having direct coordination of \(^{14}\)N atoms to Mn ions.\(^{25,27,28}\)

Alternatively, it is possible to account for a reduction in the observed hyperfine line spacing by invoking a change in the exchange couplings between the Mn ions in the Mn site, since the hyperfine coupling from each Mn ion in an exchange coupled Mn tetramer or Mn dimer complex is scaled by the projection of the individual ion’s spin angular momentum onto the total spin angular momentum.\(^{29}\) In Mn tetramer and also in Mn dimer complexes\(^{28}\) the largest term of the effective spin Hamiltonian is that of the ferromagnetic exchange\(^{30}\) is compatible with the known stoichiometry of Mn in the O\(_2\)-evolving complex\(^{1}\) and with the magnetic properties of the S\(_2\) state as previously described.\(^{12}\) Altering the size of the exchange coupling between the Mn ions can cause large changes in the \(^{55}\)Mn hyperfine coupling constants and in the magnetic properties observed. Work in our laboratory shows that altering the exchange coupling parameters for a \(^3\)Mn\(^{II}\)-Mn\(^{IV}\) tetramer complex can account for both the reduction of the hyperfine line spacing and the near-Curie law temperature dependence of the S\(_2\) state EPR spectrum in NH\(_4\)Cl-treated samples.\(^{30}\) Thus, we attribute the change in the observed spacing of the hyperfine lines in the EPR signal from the NH\(_3\)-bound form of the S\(_2\) state to a significant change in the exchange interactions between the Mn ions caused by the binding of one or more NH\(_3\) molecules.

The finding that the Mn site binds ligands in an EPR-detectable manner raises several new questions and possibilities concerning the structure of the Mn site and its coordination properties. Further studies are in progress to determine the number of exchangeable coordination sites on the Mn site and to determine the steric environment of the ligand-binding site(s). The results of this paper indicate that the S\(_2\) state multiline EPR spectrum will provide a spectroscopic probe sensitive to ligand exchange at the Mn site, which should greatly facilitate studies of the coordination chemistry involved in the mechanism of photosynthetic O\(_2\) evolution.

Conclusions

The effects of NH\(_3\) binding to the O\(_2\)-evolving complex are consistent with coordination of one or more NH\(_3\) molecules directly to the Mn site detectable in the S\(_2\) state by EPR spectroscopy. The novel S\(_2\) state EPR spectrum produced in the presence of NH\(_4\)Cl with illumination at 0 °C shows a near-Curie law temperature dependence which is significantly different from the temperature dependence of S\(_2\) state EPR signals observed in untreated samples, showing that the binding of NH\(_3\) significantly alters the exchange couplings between the Mn ions. Such a change in exchange couplings between Mn ions also accounts for the more than 20% reduction in hyperfine line spacing in the EPR spectrum of the NH\(_3\)-bound form of the S\(_2\) state relative to the hyperfine line spacing in the S\(_2\) state EPR spectrum observed in untreated samples. Because of the likelihood that NH\(_3\) binds in competition with H\(_2\)O to the substrate binding site of the O\(_2\)-evolving complex, causing inhibition of photosynthetic O\(_2\) evolution activity, our results indicate that the EPR-detectable Mn site is the H\(_2\)O-binding site. Since previous work strongly implicates this same Mn site in the process of accumulation of oxidation equivalents, it is probable that a single Mn site exists on the electron donor side of PSI, functioning both in the oxidation of bound H\(_2\)O molecules and in the storage of oxidation equivalents. The finding that the Mn site binds ligands in a EPR-detectable manner suggests new possibilities for the study of the coordination chemistry of the Mn site.

Acknowledgment

This work was supported by the National Institutes of Health (GM32715), the Chicago Community Trust/Searle Scholars Program, the Camille and Henry Dreyfus Foundation, and a National Science Foundation Graduate Fellowship to W.F.B.

Pyrolytic, Kinetic, and Theoretical Studies on the Isomerization of Me\(_2\)HSiCH\(_2\)\(^\cdot\) to Me\(_3\)Si\(^\cdot\)

Thomas J. Barton,*\(^1\) Anthony Revis,\(^1\) Iain M. T. Davidson,\(^2\) S. Ijadi-Maghsoodi,\(^3\) Kevin J. Hughes,\(^4\) and Mark S. Gordon*\(^5\)

*Contribution from the Departments of Chemistry, Iowa State University, Ames, Iowa 50011, The University, Leicester LE1 7RH, England, and North Dakota State University, Fargo, North Dakota 58105. Received September 19, 1985

Abstract: Evidence for the isomerization of 'CH\(_2\)SiMe\(_2\) to Me\(_3\)Si\(^\cdot\) via a 1,2-migration of hydrogen has been obtained through pyrolytic studies of 4-(dimethylsilyl)-1-butene which decomposes through loss of the allyl radical to produce 'CH\(_2\)SiHMMe\(_2\). Rearrangement to Me\(_3\)Si\(^\cdot\) was established by product analysis and trapping with methyl chloride. Kinetic analysis afforded a barrier of ca. 41 kcal/mol in excellent agreement with a calculated barrier of 42.6 kcal/mol achieved with fourth-order perturbation theory corrections (MP4) and addition of zero-point vibrational corrections.

Although silicon-centered radicals are significantly more stable than are nonresonance stabilized carbon-centered radicals, only two examples of rearrangement of R\(_2\)Si-R\(_2\) to R\(_2\)Si-\(^{13}\)C\(_2\);R have been reported, and both of these have silicon as the migrating group, R. The key step in the extensively studied isomerization of hexamethyldisilane involves a 1,2-silyl migration in I to produce

---

Isomerization of Me3HSiCH3 to Me3Si


Scheme I

Scheme II

silyl radical 2, and it has been shown that ring expansion of 3
proceeds through a 1,2-silyl shift from silicon to carbon in radical
4.3

In view of the numerous documented cases of 1,2-migrations
in all-carbon radicals, the absence of analogous isomerizations
(except for the above two cases) for α-silyl radicals is surprising.
For example, the 1,2-aryl shift from carbon to a carbon-centered
radical is well-known,4 but the analogous aryl shift from silicon
to carbon is not observed.5

Recently, the rearrangement of silyl-substituted, carbon-cen-
tered radicals has received attention due to the possibility6 that
this rearrangement could be involved in the thermal decomposition
of hydridosilacyclobutanes via the intermediacy of radical 5. Since
the hydrogen migration is an unprecedented reaction, we have
undertaken a collaborative effort to gain evidence about this
isomerization through the synthesis and gas-phase pyrolysis of
a suitable precursor of the model system, Me3HSi–CH2, kinetic
analysis, and theoretical calculations.

Results and Discussion

Flash Vacuum Pyrolytic Generation of α-Silyl Radicals. No
methods existed for the gas-phase thermal production of an α-silyl
radical so the homolytic cleavage of the carbon–allyl bond of
3-butenylsilanes was investigated. Published bond dissociation
energies1 indicated that the carbon–allyl bond in a 3-butenylsilane
should be ca. 15 kcal/mol weaker than the Si–C bond. Thus,
3-butenyltrimethylsilane (6) was synthesized and subjected to FVP
at 760 °C. Under these conditions, only 10% decomposition of
6 occurred to produce five major products which were identifiable
by GCMS comparison with authentic samples. The products were
tetramethylsilane, trimethylvinylsilane, ethyltrimethylsilane,
allytrimethylsilane (7), and 1,3-disilacyclobutane (8) in ratios of
c. 2:1:2:2:1. All of these products are readily explicable by
mechanisms (Scheme 1) initiated by the expected C–C bond
homolysis. The formation of 8 from 7 via the intermediacy of
Me3Si=CH2 is a well-established transformation.7 However,
under these conditions, the major route to this silene is probably
dissociation of Me3SiCH3 (–Me*).

Since the behavior of 6 appeared to establish decomposition of
butenylsilanes as the method for generation of α-silyl radicals,
3-butenyldimethylsilane (9) was synthesized and pyrolyzed (FVP)
at 840 °C. Only a 56% mass recovery was realized, but the

(6) Barton, T. J.; Burns, S. A.; Burns, G. T. Organometallics 1983, 2, 210. The results which we now report render this suggestion thermodynamically untenable.

Table I. Pyrolysis of 9 and 6 with Excess MeCl

<table>
<thead>
<tr>
<th>Me$_2$SiCl formation</th>
<th>total decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>silane</td>
<td>log $A$</td>
</tr>
<tr>
<td>9</td>
<td>15.5 ± 0.4</td>
</tr>
<tr>
<td>6</td>
<td>14.6 ± 0.4</td>
</tr>
</tbody>
</table>

pyrolyzate contained only two major products (in addition to 25% unreacted 9) which were isolated by preparative GC and identified as allyltrimethylsilane (7, 17%) and allyldimethylsilane (10, 4%). A trace of disilacyclobutane 8 (<1%) was detected by GC-MS, confirming the importance of bimolecular reactions in the pyrolysis of 9 via retroene elimination of propene followed by a silene/alkenylsilanes.\(^7\) In our earlier study of the decomposition of 9, MeCl formation total decomposition at a temperature range of 805 to 866 K. The Arrhenius parameters for the formation of Me$_2$SiCl are given in Table I. For comparison, also included is the copolymerization of MeCl and butenyltrimethylsilane 6, a system which a priori would have been expected to be a much more likely generator of Me$_2$Si$.^1$ It was gratifying to find that at 850 K 9 produces Me$_2$SiCl more than nine times more rapidly than does 6, where formation of Me$_2$SiCl constituted <10% of the total decomposition.

Table II. Arrhenius Parameters for Reactions in Scheme III

<table>
<thead>
<tr>
<th>reaction</th>
<th>log $A$</th>
<th>$E$, kcal/mol</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.5</td>
<td>68.4</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>13.5</td>
<td>varied</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
<td>$E_2 + 8.9$</td>
<td>from thermochemistry</td>
</tr>
<tr>
<td>5</td>
<td>9.5</td>
<td>14.3</td>
<td>adapted from b</td>
</tr>
<tr>
<td>6</td>
<td>8.1</td>
<td>7.2</td>
<td>c</td>
</tr>
<tr>
<td>7</td>
<td>8.5</td>
<td>9.6</td>
<td>d</td>
</tr>
<tr>
<td>8</td>
<td>8.0</td>
<td>9.1</td>
<td>adapted from e</td>
</tr>
<tr>
<td>9</td>
<td>9.3</td>
<td>17.9</td>
<td>b</td>
</tr>
<tr>
<td>10</td>
<td>7.6</td>
<td>4.1</td>
<td>same as reaction 4</td>
</tr>
<tr>
<td>11</td>
<td>10.1</td>
<td>47.9</td>
<td>this work (calculated by difference)</td>
</tr>
<tr>
<td>12</td>
<td>15.0</td>
<td>81.0</td>
<td>d</td>
</tr>
<tr>
<td>13</td>
<td>7.6</td>
<td>4.1</td>
<td>same as reaction 4</td>
</tr>
<tr>
<td>14</td>
<td>12.5</td>
<td>49.5</td>
<td>see text</td>
</tr>
<tr>
<td>15</td>
<td>8.1</td>
<td>7.2</td>
<td>c</td>
</tr>
<tr>
<td>16</td>
<td>fast</td>
<td></td>
<td>see text</td>
</tr>
<tr>
<td>17</td>
<td>8.5</td>
<td>9.6</td>
<td>d</td>
</tr>
</tbody>
</table>


klnetics of the formation of this product were determined over a temperature range of 805 to 866 K. The Arrhenius parameters for the formation of Me$_2$SiCl are given in Table I. For comparison, also included is the copolymerization of MeCl and butenyltrimethylsilane 6, a system which a priori would have been expected to be a much more likely generator of Me$_2$Si$.^1$ It was gratifying to find that at 850 K 9 produces Me$_2$SiCl more than nine times more rapidly than does 6, where formation of Me$_2$SiCl constituted <10% of the total decomposition.

If it is assumed that the initially formed radical Me$_3$HSiCH$_2^+$ (11) isomerizes to Me$_2$SiH at a rate which is fast relative to the initial homolysis, then formation of Me$_2$SiCl is a measure of the latter. Indeed, the $A$ factor of 15.5 is quite reasonable for the homolysis to form the allyl radical.\(^10\) There is some uncertainty over bond dissociation energies in analogous hydrocarbons\(^11\) with current estimates of $D(C_2H_2C_2H_2)$ ranging from 81.7 to 86.2 kcal/mol. Furthermore, an a-silyl group appears to have some stabilizing effect.\(^12\) Accordingly, $E_{3e}$ for formation of Me$_2$SiCl from 9 is entirely consistent with C-C homolysis; thus, Route A of Scheme II is the only path to survive kinetic analysis. Since the allylic stabilization energy\(^10\) is ca. 14 kcal/mol, $E_{3e}$ for reaction 9 relates to a "normal" allyl-alkyl bond dissociation energy of (68.4 + 14) 82.4 kcal/mol.

For the isomerization reaction, Me$_3$HSiCH$_2^+$ $\rightarrow$ Me$_2$SiH, $\Delta H$ is simply $D(Si-H) - D(H-CH_2)=90.3 - 99.2 = -8.9$ kcal/mol. Harding\(^14\) has calculated that the analogous 1,2-H shift in CH$_2$CH$_2$H$_2$ has an $E_{3e}$ of 46 kcal/mol ($\Delta H = 0$). To the extent that Harding's results are an appropriate analogy for the isomerization of Me$_3$HSiCH$_2^+$, we would expect the $E_{3e}$ of our isomerization to be less than 46 kcal by ca. 9 kcal. We have tried to test this question experimentally and to obtain some estimate of the magnitude of the isomerization barrier. We hoped to monitor the isomerization by measuring the relative rates of formation of Me$_3$SiH and Me$_2$SiCl in pyrolysis with varying amounts of added MeCl, since Me$_2$HSiCH$_2^+$ should mainly abstract H while Me$_2$Si$^+$ mainly abstracts Cl. However, this approach failed since we find that neither Cl abstraction by the carbon radical nor H abstraction by Me$_2$Si$^+$ can be ignored.


\(^{(12)}\) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. J. Am. Chem. Soc. 1985, 107, 208. We are aware of the potential of this method to provide quantitative data on the ability of silicon to stabilize both a- and b-carbon-centered radicals and will report in detail our results on these questions in a subsequent paper.


Scheme III
Radical Reactions in the Pyrolysis of HMe₂Si~ with MeCl

other products

Competitive experiments with varying proportions of added MeCl and Et₂SiH₂ suffered from the same disadvantage, compounded by some decomposition to Et₂Si.

The most useful results were obtained simply by measuring the ratio of Me₃SiCl formed to 9 decomposed in pyrolyses of 9 with added MeCl. The effect of added MeCl was to inhibit the bimolecular reactions of 9 in Scheme II, thus reducing the rate constants for decomposition of 9 by about one-third. The results in Table I for formation of Me₃SiCl and for total decomposition of 9 in the presence of a 10-fold excess of MeCl gave values of the ratio (R) of Me₃SiCl formed to 9 decomposed ranging from R = 0.354 at 805 K to R = 0.556 at 866 K. The dependence of R on the size of the isomerization barrier was calculated by numerical integration of Scheme III (Table II). In principle, Me₃SiCl is not a unique measure of reaction 4, and hence of the concentration of Me₃Si radicals, because Me₃SiCl is also known to be formed by radical-induced rearrangement of HMe₂SiCH₂Cl, observed as a minor product in our experiments (unimolecular dissociation by reaction 12 was negligibly slow, even at 866 K). To ensure that this rearrangement did not invalidate our conclusions, we included the following in Scheme III: (i) reaction 13; (ii) the reaction sequence 15-17, with reaction 16 assumed to be so fast as to be quantitative; and (iii) the overall reaction 14 with no assumptions as to mechanism, the Arrhenius parameters for which were directly measured by pyrolyzing HMe₂SiCH₂Cl [synthesized by LiAIH₄ reduction of ClMe₂SiCH₂Cl (Cambrian Chemicals)] in our LPP and SFR apparatus. The calculated results at 866 K, where the experimental value of R was greatest, are illustrated in Figure 1. The experimental results at 805 K could be simulated equally well. From the sensitivity of R to values of E₂ greater than 40 kcal/mol, we found that the best overall agreement with experiment was obtained with E₂ ~ 41 kcal/mol. Under these conditions, 99.9% of the Me₃SiCl came from reaction 4, even though the alternative routes to Me₃SiCl must be overestimated; reaction 16 may not be fast, while reaction 14 almost certainly subsumes contributions from reactions 13 and 15-17. Because these reactions are so minor, it does not matter that other reactions of comparable rate, such as radical additions, have been omitted from Scheme III.

We conclude that E₂ is greater than 40 and less than 44 kcal/mol, probably ca. 41 kcal/mol.

Theoretical Calculations

Preliminary predictions of the structures of the radicals CH₃SiH₂⁺ and SiH₂CH₂⁺ and the transition state connecting them (within C₂ symmetry) were carried out at the SCF level with the 3-21G basis set. For each structure, the second derivative matrix has the appropriate number of negative eigenvalues (zero for the two isomers and one for the transition state). At this level of computation, the methyl radical is found to be planar at the carbon end, while the silyl radical is predicted to be pyramidal with an

internal rotation barrier of just 1 kcal/mol. The effect on this barrier of improving the basis set to 6-31G*\(^8\) is negligible.

The structures of SiH\(_3\)CH\(_2\)Staggered CH\(_3\)SiH\(_2\) and the transition state, refined with the 6-31G* basis set,\(^9\) are in excellent agreement with the experimental estimates of 8.9 and 41 kcal/mol noted above.

Further support for this is provided by the larger atomic spin density on carbon than on silicon at the transition state.

The peak areas and response factors were obtained on either a gas chromatograph. The work at North Dakota University by the National Science Foundation is gratefully acknowledged. Thomas J. Barton and Anthony Revis are grateful to Dow Corning Corp. for support of Anthony Revis with a Dow Corning Predoctoral Minority Fellowship.

Acknowledgment. The support of this work by Iowa State University by the National Science Foundation is gratefully acknowledged. The support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the National Science Foundation (CHE-8309948). The computer time made available by the North Dakota State University Computer Center is gratefully acknowledged.

Réserve No. 6, 763-13-3; 7, 762-72-1; 9, 18163-02-5; 11, 34377-79-2; SiH\(_3\)CH\(_2\)Si; 51220-22-5; CH\(_2\)SiH\(_2\); 24669-75-8; 4-bromo-1-buten, 5162-44-7; chlorodimethylsilane, 1066-35-9; 1-bromoo-3-buten, 5162-44-7; trimethylchlorosilane, 75-77-4.


(20) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, D. J.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82; Carnegie-Mellon University, Pittsburgh, PA, 1983.