Oxidation of Disilenes: Experimental and Theoretical Studies

Kirsten L. McKillopb, Robert Westb,*, Timothy Clark3, Heinz Hofmanna

a Computer Chemistry Center, University of Erlangen-Nürnberg, D-91052 Erlangen, Germany
b Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, USA

Dedicated to Prof. Dr. H. Schmidbaur on the occasion of his 60th birthday

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Disilenes

The oxidation of E-1,2-di-tert-butyl-1,2-dimesityldisilene (1) in benzene by gaseous dioxygen to give 2 and 3 has been studied at various temperatures and with rapid or slow addition of oxygen. The effect of various additives (amines, phosphines, THF) on the product distribution was also investigated. Ab initio MO calculations were carried out on the oxidation of \( \text{H}_2\text{Si} \equiv \text{SiH}_2 \) with triplet oxygen. These led to a proposed reaction mechanism for the oxidation of 1, in which the initial intermediate is a disileneperoxy biradical \( 6' \), which can close to give 2 or react with another molecule of disilene to give ultimately 3.

\[ \text{Mes} \cdots \text{Si} \equiv \text{Si} \cdots \text{Mes} \]

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Scheme 1. Calculated pathway for dioxygen oxidation of \( \text{H}_2\text{Si} \equiv \text{SiH}_2 \). Energies in kcal/mol.

Introduction

The oxidation of disilenes by oxygen of the air was one of the first reactions reported for disilenes [1]. For both tetramesityldisilene 1a and 1,2-di-tert-butyl-1,2-dimesityldisilene (1) the reaction has been shown to follow the pathway shown in Scheme 1 [2, 3]. The major initial product is the 1,2-dioxetane 2, 2a sometimes accompanied by smaller amounts of 1,2-disilaoxirane 3, 3a. The ultimate products of complete oxidation of these disilenes are the 1,3-cyclodisiloxanes 4, 4a formed by slow rearrangement of 2, 2a and by slow further oxidation of 3, 3a. Structures of all of the compounds in Scheme 1 have been established by X-ray crystallography. In addition, the oxidation of 1a has been shown to be stereospecific: E-1 reacts
with O₂, to give only E-2, E-3 and ultimately E-4, whereas a mixture of E and Z isomers of 1 oxidizes to give 2, 3, and 4 in the same isomeric ratios as in the starting material [3, 4].

The disilenes react very rapidly with triplet oxygen even at room temperature or below. In this they are very different from alkenes, which react with O₂ only under forcing conditions to afford 1,2-dioxetanes, products from dioxetane decomposition, or epoxides. At room temperature reaction takes place only for olefins having low-lying triplet states, for example cyclobutadienes or ketenes [5], or electron-rich olefins such as tetraaminoethylenes [6]. The reaction of ethylene with O₂ has been investigated by ab initio molecular orbital theory [7]. The first step is an endothermic addition of dioxygen to the olefin to give a trans triplet dimethyleneperoxy diradical intermediate, 5. Stretching of the O–O bond then takes place followed by concurrent closing of the oxirane ring and cleavage of the O–O bond to give oxirane and a triplet oxygen atom. The latter can then react with another oxygen atom to produce a second oxirane molecule.

Our study of the rearrangement of 3 to 4 was the subject of a recent publication [3]. In this paper, we report a preliminary study of the first step of the process, the reaction of 1 with O₂ to give 2 and 3. In an effort to gain additional information about the oxidation pathway, the oxidation of 1 was studied under a variety of conditions, including different temperatures, different rates of oxygen addition, and in the presence of various additives. To complement these experiments, theoretical calculations were carried out on the reaction of O₂ with the unsubstituted disilene, H₂Si=SiH₂.

### Results and Discussion

Results of the oxidation studies are listed in Table I. It was previously reported that oxidation of 1a at low temperature gave only the 1,2-disila-dioxetane 2a, while at higher temperatures a mixture of 2a and the disilaoxirane 3a was produced [2]. We find a similar temperature dependence in the oxidation of 1. At −65 °C only 2 could be detected after oxidation, but at any higher temperature 3 is also produced; traces of 3 were observed.

### Table I. Ratios of 2 to 3 in the oxidation of disilene (1).

<table>
<thead>
<tr>
<th>Conditions for Oxidation</th>
<th>2/3</th>
<th>Time [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>+25 °C</td>
<td>2.6</td>
<td>15</td>
</tr>
<tr>
<td>−25 °C</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>−65 °C</td>
<td>&gt;50</td>
<td>190</td>
</tr>
<tr>
<td>Slow oxidation</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Ph₃P</td>
<td>14</td>
<td>30</td>
</tr>
<tr>
<td>Ph₃P, −25 °C</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Ph₃P, −65 °C</td>
<td>&gt;50</td>
<td></td>
</tr>
<tr>
<td>(PhO)₃P</td>
<td>2.5</td>
<td>35</td>
</tr>
<tr>
<td>THF as solvent</td>
<td>0.7</td>
<td>20</td>
</tr>
<tr>
<td>THF</td>
<td>1.0</td>
<td>15</td>
</tr>
<tr>
<td>DABCO</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>Et₃N</td>
<td>8.0</td>
<td>15</td>
</tr>
</tbody>
</table>

*At room temperature with 10 molar equiv. additive unless otherwise noted; b time required for decolorization of solution.*

### Table II. Total (Hartrees) and relative (kcal mol⁻¹, zero-point-energy corrected and relative to O₂ + anti-H₂Si=SiH₂ in parentheses) energies for triplet species.

<table>
<thead>
<tr>
<th>Species</th>
<th>HF/6–31G*</th>
<th>ZPE (NIMAG)</th>
<th>MP4sdtq/6–31G*</th>
<th>PMPsdtq/6–31G*</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>−149.61791</td>
<td>2.86</td>
<td>−149.95735</td>
<td>−149.95955</td>
</tr>
<tr>
<td>H₂Si=SiH₂</td>
<td>−580.07667</td>
<td>21.00</td>
<td>−580.27983</td>
<td>(−580.27983)</td>
</tr>
<tr>
<td>6a</td>
<td>−729.74424</td>
<td>26.04</td>
<td>−730.20975</td>
<td>−730.27117</td>
</tr>
<tr>
<td>6b</td>
<td>−729.74479</td>
<td>26.04</td>
<td>−730.26956</td>
<td>−730.17101</td>
</tr>
<tr>
<td>6c</td>
<td>−729.74153</td>
<td>25.89</td>
<td>−730.26602</td>
<td>−730.26745</td>
</tr>
<tr>
<td>6d</td>
<td>−729.74240</td>
<td>26.00</td>
<td>−730.26809</td>
<td>−730.26948</td>
</tr>
<tr>
<td>7</td>
<td>−1309.92261</td>
<td>50.04</td>
<td>−1310.65699</td>
<td>−1310.65776</td>
</tr>
</tbody>
</table>

* a ZPE = UHF/6–31G* calculated zero point energy (kcal mol⁻¹); NIMAG = number of imaginary vibrations (negative frequencies); b energy relative to O₂ + anti-H₂Si=SiH₂.
even when the oxidation was carried out at -60 °C. At 25 °C the ratio of 2 to 3 was 2.6:1. These results are consistent with formation of 2 and 3 from a common intermediate.

The rate of oxygen addition also affected the product distribution. Slow diffusion of oxygen above solution of 1a at 25 °C over a period of 8 h increased the proportion of 3 from 1:2.6 to 1:1.9.

**Theoretical calculations.** To find a likely reaction pathway, ab initio MO calculations were carried out at the UHF/6-31G* level [9] on the triplet potential energy surface for the reaction of 3O2 with the parent disilene, H2Si=SiH2. The first intermediate located for this process was the triplet disilene-peroxy biradical, 6. Since we were unable to locate a transition state on the way to 6, we believe that this initial step in the oxidation occurs without an activation barrier.

This addition is calculated to be exothermic by about 17.7 kcal mol⁻¹, as can be seen from the energies given in Table II. Biradical 6 exhibits a three-fold barrier around the Si–O bond. The anti conformer 6a is marginally (0.1 kcal mol⁻¹) more stable than the two enantiomeric gauche conformers 6b. The rotational transition states, 6c and 6d, lie 1.1 and 2.4 kcal mol⁻¹ higher in energy than 6a, respectively. Addition of 3O2 to disilene should therefore give an equilibrium mixture of about 35% 6a and 65% 6b.

The geometries of the isomeric species 6 are shown in Table III. There is little variation in the bond lengths on Si–O bond rotation, but the Si–O–O angle opens significantly at the two rotational transition states. The structures of 6 are, however, essentially those expected from a classical bonding model.

The Si–Si rotation barriers in triplet 6 were also investigated. The anti-Si–Si-rotation transition state 6c lies 12.4 kcal mol⁻¹ higher in energy than the corresponding minimum 6a, but the barrier for Si–Si rotation in the syn isomer 6b via transition state 6f is only 1.1 kcal mol⁻¹. The O–O bond in 6e is unusually long (1.349 Å) and the Si–Si–O angle is only 105.6°. The most significant geometry change, however, is the shortening of the Si–O bond from 1.711–1.710 Å in 6a–d and 6f to 1.692 Å in 6e.

These differences can be understood in terms of details of the bonding in 6a–6f. In 6a–6d, electron donation takes place from the ℏSi-Si orbital into the ℏSi-O orbital, lengthening the Si–O bond and stabilizing the structure. In 6f, a hyperconjugative interaction can occur between the Si–Si σ bond and the ℏSi-O antibonding orbital, with similar results. Both interactions are turned off in 6e, because of its near-planar structure. The intriguing result is that rotation about the Si–Si bond in the anti-adduct is less favorable than rotation about the Si–O bond but that Si–Si rotation can take place easily in the gauche conformer.

In the presence of excess disilene, addition of a second disilene molecule to 6a may take place to give triplet 7. This process also appears to take place with no barrier and is far more exothermic than the original addition of 3O2 to the disilene:

\[
6a + SiH_2 \rightarrow 7,
\]
\[
\Delta E = -64 \text{ kcal mol}^{-1} (\text{PMP4sdqt+ZPE})
\]

Structure 7 has C₂ symmetry. It is twisted by about 30° about the O–O bond, presumably to avoid lone-pair/lone-pair repulsions. The Si–O bonds are shorter than in the isomers of 6 (1.69 vs. 1.72 Å) and the O–O bond is considerably longer (1.42 vs. 1.32 Å). This suggests that cleavage of the O–O bond in 7 should be an easy process that would eventually lead to two disilaaoxirane molecules.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>2.334</td>
<td>1.711</td>
<td>1.326</td>
<td>108.0</td>
<td>111.2</td>
<td>180.0</td>
</tr>
<tr>
<td>6b</td>
<td>2.335</td>
<td>1.712</td>
<td>1.323</td>
<td>111.3</td>
<td>111.2</td>
<td>61.2</td>
</tr>
<tr>
<td>6c</td>
<td>2.336</td>
<td>1.715</td>
<td>1.320</td>
<td>1111.3</td>
<td>114.8</td>
<td>118.5</td>
</tr>
<tr>
<td>6d</td>
<td>2.335</td>
<td>1.716</td>
<td>1.318</td>
<td>112.9</td>
<td>115.6</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>2.338</td>
<td>1.686</td>
<td>1.424</td>
<td>106.7</td>
<td>107.3</td>
<td>179.2</td>
</tr>
</tbody>
</table>

*Si–O–O–Si dihedral angle = 151.8°.*

Table III. Geometrical parameters (bond lengths in Å, angles in °) for the triplet biradicals 6 and 7.
The calculations therefore suggest the mechanism for the formation of 1,2-disiladioxetane and disilaoxirane shown in Scheme 2. Inter-system crossing from 6b should lead to ring closure to form the dioxetane. However, addition of 6a to a further disilene is irreversible and should lead to oxirane formation via O–O bond cleavage. We cannot currently say whether this cleavage would occur in the triplet state or whether inter-system crossing to the singlet would be necessary for this stage of the reaction.

**Mechanism of Oxidation of Disilenes**

With some additions, this pathway shown in Scheme 2 can account for the experimental observations on the oxidation of 1 (and 1a), through intermediates resembling 6 and 7 which we will label 6' and 7'. Since the oxidation products 2 and 3 are produced with retention of configuration, it is required that both 6' and 7' be relatively short-lived, although of course Si–Si bond rotation could be greatly slowed by steric hindrance in both intermediates. The strong temperature dependence of the formation of 3 implies a kinetic barrier to this reaction. Although no barrier was found in the calculated reaction of 6 with H2Si=SiH2, it is reasonable that there might be a significant barrier in the reaction of 6' with the highly hindered disilene 1. This pathway would also explain why no disilaoxirane is formed in the 3O2 oxidation of tetrakis (2,4,6-tri-iso-propylphenyl) disilene [4]; this disilene may be so hindered that approach of a second disilene molecule to the intermediate diradical is not possible.

The mechanism in Scheme 2 also accounts for the dependence of the product ratio on the rate of oxygen addition. When oxygen is admitted slowly the diradical 6' would be produced in the presence of a large excess of disilene molecules, which should favor the formation of 3.

We will now briefly consider, and dispose of, several alternative oxidation pathways and intermediates.

1. **Reaction of 3O2 with triplet-state disilene**

   This reaction would presumably be facile, but it is rendered unlikely by the high rate of the oxygen-disilene reaction, even at low temperatures. Although the triplet-state energy for disilenes is not known, the first singlet excited state lies about 3 ev above the ground state [10]. A reasonable estimate of the triplet state energy places it between 1 and 2 ev. Reaction of dioxygen with the triplet state disilene, in thermal equilibrium with the singlet ground state would therefore be slow. Moreover, disilenes 1 and 1a show no sign of other triplet-like reactions, at least below 100 °C.

2. **Perepoxide as an intermediate**

   Since perepoxides have often been invoked as intermediates in oxygen oxidation of olefins, we attempted to calculate a structure for the disilene perepoxide, both in the triplet and singlet state. All attempts to optimize a structure for the singlet perepoxide led directly to the 1,2-dioxetane; optimization of the triplet perepoxide led to O–O bond cleavage. We therefore believe that neither the triplet nor the singlet disilene perepoxides are minima on their respective potential energy surfaces. Perepoxides are therefore very unlikely to be intermediates in the dioxygen oxidation of disilenes.

3. **Singlet oxygen**

   Disilene 1 might catalyze the conversion of 3O2 to 1O2, which could then oxidize the disilene. One
item of evidence against this pathway is that the addition of large amounts of singlet oxygen-quenching agent, diazabicyclooctane, did not decrease the rate of the oxidation of 1 (vide infra).

Effect of additives on the oxidation of 1

The $^3$O$_2$ oxidation of 1 was carried out in the presence of various added compounds, with the results shown in Table I. Both triphenylphosphine and triphenylphosphite decreased the rate of oxidation; in the presence of either of these phosphines the rate of decolorization of the disilene was slowed by about a factor of 2. Triphenylphosphine also affected the product ratio, giving a much smaller amount of 3. Examination of the product mixtures showed that triphenylphosphine oxide was produced, in an amount equivalent to the (diminished) amount of 3 formed. The less basic phosphine, (PhO)$_2$P, slowed the oxidation but did not change the product ratio and did not become oxidized.

Amines, diazabicyclooctane (DABCO) and triethylamine, also increased the ratio of 2 to 3, but without markedly affecting the rate of oxidation. Addition of THF, on the other hand, decreased the 2:3 ratio to 1.0; when the reaction was carried out in pure THF, the ratio declined to 0.7.

Definite explanations for the effects of these various additives cannot be given at this time; at best we can suggest a few modes of action consistent with the experimental data in the context of the mechanism proposed in Scheme 2. The decrease in rate of decolorization of disilene in the presence of phosphines suggest that these molecules impede the first step of the process, perhaps by forming a complex with one of the reactants. NMR experiments gave no indication of complexation between Ph$_3$P and 1 [11], but the existence of a weak complex between Ph$_3$P and O$_2$ is well-established [12], and it is reasonable to suppose that (PhO)$_2$P forms a similar complex with dioxygen.

The formation of Ph$_3$PO in an amount approximately equivalent to that of 3 suggests a competitive reaction occurring to a small extent, in which Ph$_3$P abstracts on oxygen atom from 6°, to give Ph$_3$PO and the disilaoxirane 3 [13]. The contrasting effects of the other additives on the product distribution could be explained in various ways. The details might be clarified by a full study of the kinetics of the oxidation, which we hope to carry out in the future.

Experimental Section

1,2-Di-tert-butyl-1,2-dimesityldisilene (1) was prepared by a standard procedure [12], the $^1$H and $^{29}$Si NMR spectra agreed with those of authentic material. Other reagents were purchased from Aldrich Chemical Co. Triphenylphosphine, triphenylphosphate, and triphenylboron were used directly. DABCO was sublimed under vacuum before use; triethylamine was stirred and refluxed over calcium hydride for 36 h and then distilled. Benzene and THF were dried and distilled from sodium metal immediately before use.

Oxidation reactions

An NMR tube was charged with 20 mg (0.050 mmol) of 1 and 0.5 ml of benzene. When other compounds were to be present, these were added in amounts of 0.50 mmol. (The reaction in THF as solvent was done in 0.5 ml of THF). The tube was immediately closed with a septum bearing a long needle reaching to the bottom of the tube and a shorter needle for exiting gases. Oxygen was bubbled through the solution at a standard rate of 0.1 ml/sec until the yellow color of the disilene was fully discharged. The tube was then purged with dry argon gas to remove excess oxygen.

Yields of 2 and 3 were determined from the integrated intensities of the tert-butyl peaks for these compounds in the $^1$H NMR spectrum except for the oxidation in the presence of Et$_3$N, where the ratio of $2:3$ was determined by integration of the peaks for the mesityl $meta$-protons. Each oxidation reaction was repeated three times; agreement between successive runs under the same conditions was $\pm 5\%$. The values reported in Table I are averages over the three determinations. The rate of decolorization of 1 was unchanged when the oxidation was carried out in the dark.

Slow oxidation

The slow oxidation experiments were done by closing the NMR tube with a septum bearing a needle attached to a calcium chloride drying tube. Allowing oxygen to diffuse into the tube through the needle, oxidation was stopped after 8 h, while there was still a slight yellow color due to unreacted disilene. The ratio of 1 to 2 to 3, was found by $^1$H NMR to be 0.3:1.9:1.0.
Over this time, considerable rearrangement of 2 to 4 took place. The sum of 2 and 4 was taken as the amount of 2 originally produced. (Oxygen oxidation of 3 to 4 does not compete with oxidation of 1).

Oxidation in the presence of phosphines

Standard conditions were employed. In the 25 °C reaction, triphenylphosphine oxide was detected by NMR: $^1$H, $^3$Si, $^29$Si, and $^31$P. Integration of the proton peaks at 7.7–7.8 ppm showed that Ph$_3$PO was present in an amount approximately equivalent to that of disilaaoxirane.

Molecular orbital calculations

All calculations used Gaussian 92 [15] on CRAY YMP 864, Convex C220/256 and Hewlett-Packard 9000/735 computers. The 6–31 G* basis set [9] was used throughout. Optimizations were carried out at the unrestricted Hartree-Fock (UHF) level and single-point energy calculations included a fourth order Møller-Plesset correction for electron correlation including single, double, triple, and quadruple excitations (MP4sdq(6–31 G*/*)/UHF(6–31 G*)). [16] MP4 calculations used the frozen core approximation. Stationary points were characterized by calculating the normal vibrations at UHF/6–31 G*. Energies discussed in the text are projected MP4 values [17] corrected by the UHF-zero-point energies.

Acknowledgements

This work was partially supported by a grant from the National Science Foundation. K. M. acknowledges a grant from the Dow Corning Corporation.

[11] The $^29$Si NMR of 1 in C$_6$D$_6$ solution was unchanged in the presence of excess Ph$_3$P. Similarly, the $^{31}$P NMR spectrum of a solution of Ph$_3$P was unchanged in the presence of excess 1.
[13] Reaction of Ph$_3$P with 2 to give 3 and Ph$_3$PO can be excluded. This reaction does take place but is many orders of magnitude slower than the formation of 3 in the oxidation of 1.