

Difluoro- and Dichlorodioxasilirane

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Received October 3, 1989

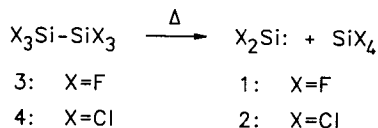
Key Words: Dioxasilirane / Silylene oxidation / Matrix isolation

The reaction of difluorosilylene and dichlorosilylene with molecular oxygen in Ar matrices has been investigated. Under the reaction conditions the silylenes proved to be of low thermal reactivity, and irradiation in the UV/VIS was necessary

to produce difluorodioxasilirane and dichlorodioxasilirane, respectively. The IR spectra have been assigned by isotopic labelling and by comparison with ab initio calculations.

Within the last few years dioxiranes have matured from rather exotic species isolable only under cryogenic conditions^{1,2} or requiring methods for the synthesis not available in most laboratories³⁻⁶ to powerful new oxidation reagents⁷⁻¹⁰. We therefore found it worthwhile to investigate the properties of sila analogues of these interesting compounds. The first dioxasilirane which has been characterized has been synthesized by direct reaction of dimethylsilylene and molecular oxygen (³O₂) in argon at cryogenic temperatures¹¹. To explore the scope of this reaction, we examined the oxidation of difluorosilylene (**1**) and dichlorosilylene (**2**).

The silylenes **1** and **2** were generated by flow pyrolysis (**3**: *T* = 850°C, **4**: *T* = 800°C) of hexafluorodisilane¹² (**3**) and hexachlorodisilane¹³ (**4**), respectively, and trapping the products in Ar at 10 K.



Comparison of the matrix IR data with the published data of **1**¹² and **2**¹³ showed that the silylenes [**1**: IR (Ar, 10 K): $\tilde{\nu}$ = 852.4, 842.5 cm⁻¹; **2**: IR (Ar, 10 K): $\tilde{\nu}$ = 512.0, 509.6, 501.4, 498.9 cm⁻¹] and the tetrahalosilanes were the major products.

Interestingly, no thermal reaction of **1** or **2** with ³O₂ was observed in the gas phase or in O₂-doped Ar matrices at low temperature (10–45 K). Even a large excess of ³O₂ in the pyrolysis zone did not lead to the formation of oxidation products, which demonstrates the low reactivity of **1** and **2** compared to dimethylsilylene¹¹. Due to this inertness, **1** and **2** can be isolated in pure O₂ matrices. Warming the O₂ matrices from 10 to 45 K produced no new compounds, although the formation of Si–O bonds is expected to be highly exothermic. IR bands of **1** and **2** exhibit shifts of several cm⁻¹ in O₂ compared to Ar, which may be explained by perturbations of the molecules in different matrices¹⁴. However, when **1** was isolated in O₂-doped Ar matrices with a comparatively low O₂ content (0.5–2.0% O₂), a splitting of the IR bands into two components ($\tilde{\nu}$ = 852.4, 842.5 and 856.2, 847.3 cm⁻¹) is observed. The appearance of a new set of bands at higher frequencies indicates the for-

mation of a complex between silylene **1** and molecular oxygen. Although the structure of this complex is unknown, the absence of line broadening implies a distinct structure.

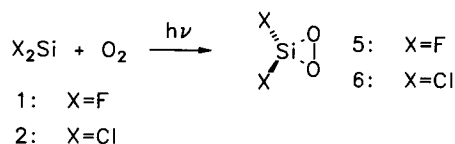
Irradiation of **1** or **2** in Ar/O₂ matrices with UV/VIS light produced new products **5** (Table 1) and **6** (Table 2), respectively, which proved to be completely stable towards short-wavelength UV light ($\lambda > 220$ nm). The photooxidation of **1** starts at 365 nm and the oxidation of **2** at 575 nm irradiation. In Ar matrices doped with 1% O₂, only the oxygen complex of **1** is converted into **5**, while in pure O₂ matrices complete conversion is observed.

Table 1. IR-spectroscopic data of **5**, matrix-isolated in O₂ at 10 K, and ab initio data of **5**, calculated at the HF/6-31G*/HF/6-31G* level (scaled by 0.93)

<i>v</i> ^{a)}	Matrix <i>I</i> ^{b)} Δ_1 ^{c)}	Δ_2 ^{d)}	<i>v</i> ^{a)}	6-31G* <i>I</i> ^{b)} Δ_1 ^{c)}	Δ_2 ^{d)}	Assign- ment ^{e)}
1155.2						
1153.5	1.0	-9.6	1120	1.0	-12.7	δ_s (Si–F)
1152.0						
1150.8						
1013.7	0.86	-0.5	967	0.87	-0.1	δ_{as} (Si–F)
862.7	0.02	- ^{f)}	800	0.12	-9.0	δ_s (Si–O)
			615	0.08	-13.7	δ (O–O)

^{a)} Wavelength in cm⁻¹. — ^{b)} Rel. intensity. — ^{c)} Isotopic shift if one ¹⁶O atom is replaced by ¹⁸O. — ^{d)} Isotopic shift if two ¹⁶O atoms are replaced by ¹⁸O. — ^{e)} Approximate description on the basis of observed isotopic shifts and the calculated mode vectors. — ^{f)} This weak peak of the mixed ¹⁶O¹⁸O isotopomer could not be observed.

Compounds **5** and **6** have been assigned the structure of difluorodioxasilirane and dichlorodioxasilirane. This assignment is based on isotopic labelling experiments, comparison with the IR data of dimethyldioxasilirane¹¹, and ab initio calculations.



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Table 2. IR-spectroscopic data of **6**, matrix-isolated in O₂ at 10 K

$\nu^a)$	$I^b)$	$\Delta_1^c)$	$\Delta_2^d)$	Assignment ^{e)}
1054.4	1.0	-14.5	-30.9	δ_s (Si—O)
649.9	0.71	0	0	δ (Si—Cl)
647.0	0.63	0	0	δ (Si—Cl)
576.1	0.30	-11.1	21.1	δ (O—O)

^{a)} Wavelength in cm⁻¹. — ^{b)} Rel. intensity. — ^{c)} Isotopic shift if one ¹⁶O atom is replaced by ¹⁸O. — ^{d)} Isotopic shift if two ¹⁶O atoms are replaced by ¹⁸O. — ^{e)} Approximate description on the basis of observed isotopic shifts.

The symmetry of **5** and **6** can be established by isotopic labelling of the O atoms. ¹⁸O-labels are easily introduced by using ¹⁸O₂ or mixtures of ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ to react with the silylenes **1** and **2**¹¹⁾. Replacing one ¹⁶O atom in **5** by ¹⁸O shifts the strong band at $\tilde{\nu} = 1153$ cm⁻¹ (four peaks between 1155.2 and 1150.8 cm⁻¹) by 9.6 cm⁻¹ to lower frequencies while replacing both ¹⁶O atoms leads to a shift of 19.3 cm⁻¹ (Table 1). If a 1:2:1 mixture of ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ is used, a symmetrical triplet with the centre band having twice the intensity of the outer bands is observed (Figure 1). This proves the equivalence of the O atoms, as it is required for a molecule with C_{2v} symmetry. In a similar way it can be shown that the O atoms in **6** are also equivalent.

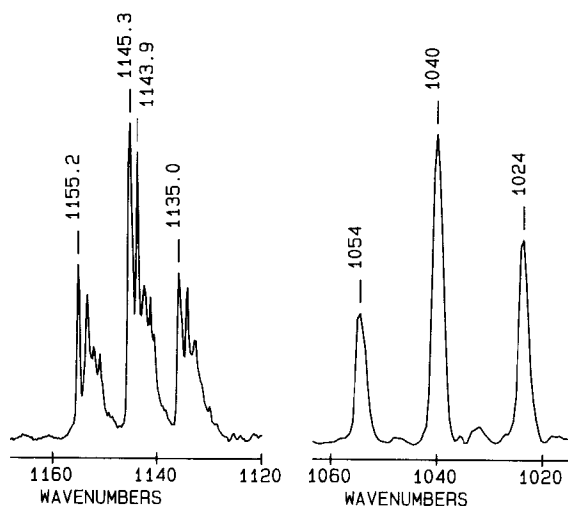
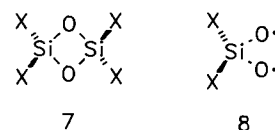


Figure 1. IR spectra (wavenumbers, cm⁻¹) showing a 1:2:1 mixture of ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ isotopomers of **5** (left) and **6** (right). Bands assigned to the ¹⁶O₂ isotopomers are at higher frequencies, bands assigned to the ¹⁸O₂ isotopomers at lower frequencies. The additional splitting of the bands of **5** into four components is caused by matrix site effects

Other possible structures with the same symmetry are the 1,3-disiladioxetane **7** and the bioxysilane **8**. The four-membered ring **7** is excluded by the chemistry of the formation of **5** and **6**. These compounds are formed under a variety of conditions (mixtures of Ar, Xe, and O₂ with 0.50–100% O₂) during the photolysis at 10 K, where the mobility of **1** and **2** is very low and the formation of

dimers has not been observed. The silylenes are highly diluted (only 500 ppm of **3** and **4** in the gas mixtures) and in the absence of O₂ completely stable towards UV irradiation. Thus it is very unlikely that products which require the proximity of two molecules **5** or **6** are formed.

Diradical **8** should have a very low barrier towards ring closure and is excluded by the assignment of a band attributed to the O—O stretching mode in **6** (Table 2). The corresponding vibration in **5** is too weak to be observed, but the observed vibrations are in good agreement with the ab initio calculation (Table 1).



Dimethyldioxasilirane is sensitive towards UV irradiation¹¹⁾ while **5** and **6** are completely stable. This difference is explained by the high stability of the Si—X bond (X = F, Cl) compared to the Si—C bond. The only possible photochemistry is the cleavage of the O—O bond to give diradical **8**. Because of the low migratory aptitude of X and the low thermodynamic stability of rearranged products the only intramolecular possibility to stabilize is ring closure to give back **5** or **6**.

This work was supported by the *Deutsche Forschungsgemeinschaft (SFB 247)* and the *Fonds der Chemischen Industrie*. We thank Prof. R. Gleiter for supporting this work. Calculations have been done with a CRAY-XMP 48 at the NSC in Linköping, Sweden.

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[321/89]