Reaction of silylene with sulfur dioxide: some gas-phase kinetic and theoretical studies†

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Time-resolved kinetic studies of the reaction of silylene, SiH₂, with SO₂ have been carried out in the gas phase over the temperature range 297–609 K, using laser flash photolysis to generate and monitor SiH₂. The second order rate coefficients at 1.3 kPa (SF₆ bath gas) fitted the Arrhenius equation: $\log(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-10.10 \pm 0.06) + (3.46 \pm 0.45 \text{ kJ mol}^{-1})/RT \ln 10$ where the uncertainties are single standard deviations. The collisional efficiency is 71% at 298 K, and in kinetic terms the reaction most resembles those of SiH₂ with CH₃CHO and (CH₃)₂CO. Quantum chemical calculations at the G3 level suggest a mechanism occurring via addition of SiH₂ to one of the S=O double bonds leading to formation of the three-membered ring, thione-siloxirane which has a low energy barrier to ring expansion to yield the four-membered ring, 3-thia-2,4-dioxasiletane, the lowest energy adduct found on the potential energy (PE) surface. RRKM calculations, however, show that, if formed, this molecule would only be partially stabilised under the reaction conditions and the rate coefficients would be pressure dependent, in contrast with experimental findings. The G3 calculations reveal the complexity of possible intermediates and end products and taken together with the RRKM calculations indicate the most likely end products to be H₂SiO + SO (³Σ⁻). The reaction is compared and contrasted with that of SiH₂ + CO₂.

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Introduction

Silylenes are important intermediates in silicon hydride and organosilicon chemistry.^{1–3} Their characteristic reactions include insertions into Si–H, Si–OR and O–H bonds and π-type additions across C=C and C≡C bonds. Many of the fine details of the mechanisms of these reactions have been revealed by time-resolved kinetic studies employing direct monitoring of silylenes.^{4–8} In recent times, much attention has been devoted to the preparation and properties of large silylenes, stabilised either by bulky substituents, or by being built into N-heterocyclic rings or with N-heterocyclic adducts.⁹ Nevertheless there still remains a need to uncover further details of the behaviour of the smaller, more reactive silylenes to establish a reactivity baseline. In our laboratories we have undertaken gas-phase studies of the

prototype silylene, SiH₂.^{4–6} These investigations have shown, *inter alia*, that it reacts rapidly with many chemical species at close to collision rates. Amongst these are the reactions of SiH₂ with (CH₃)₂CO¹⁰ and CH₃CHO¹¹ which show that silylene addition to the C=O π-bond conforms to this pattern as well. Even the reaction of SiH₂ with CO is rapid at pressures sufficiently high to stabilize the silaketene product, H₂SiCO, although at normal experimental pressures (*ca.* 1.3 kPa) the reaction is quite slow.¹² We also investigated the reaction of silylene with CO₂ showing that the affinity of SiH₂ for the carbonyl bond extends even to the highly stable carbon dioxide molecule.¹³ However in this case the reaction is very slow with rate coefficients 10⁴–10⁵ smaller than collisional. This reaction also has a positive activation energy unlike those of most of the others. By means of quantum chemical calculations,¹³ we were able to trace the origin of the reaction bottleneck to the relatively high energy barrier for rearrangement of the initially formed H₂Si···O=C=O adduct.

Because of the unusual nature of its reaction with CO₂ we thought it would be worthwhile to extend our studies of SiH₂ to its reaction with SO₂. There has been no previous kinetic study of this reaction, so we have undertaken the first gas-phase investigation. As well as being a molecule of considerable atmospheric interest, SO₂ differs from CO₂ in being bent and having a somewhat weaker double bond. This should have significant consequences on the nature of the products and

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† Electronic supplementary information (ESI) available: It contains details of the microscopic reversibility relationship, and structures and enthalpies for the quantum chemical calculation of the reaction of SiH₂ with CO₂ to yield 3-sila-2,4-dioxo-cyclobutylidene and other species, at both G3 and G2 levels. See DOI: 10.1039/c3cp52189c

reactive intermediate species. We have therefore also carried out quantum chemical calculations of the potential energy surface for the reaction of $\text{SiH}_2 + \text{SO}_2$, to compare it with that for $\text{SiH}_2 + \text{CO}_2$, and also to try to elucidate potential products and reaction pathways.

Experimental

Equipment, chemicals and method

These have been described in detail previously^{4–6} and so only brief and essential details are provided here. SiH_2 was produced by the 193 nm flash photolysis of phenylsilane (PhSiH_3) using a Coherent Compex 100 exciplex laser. Photolysis pulses were fired into a variable temperature quartz reaction vessel with demountable windows, at right angles to its main axis. SiH_2 concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 argon ion laser and operating with Rhodamine 6G. The monitoring laser beam was multipassed between 32 and 40 times along the vessel axis, through the reaction zone, to give an effective path length of up to 1.6 m. A portion of the monitoring beam was split off before entering the vessel for reference purposes. The laser wavelength was set by reference to a known coincident transition in the visible spectrum of I_2 vapour and was checked at frequent intervals during the experiments. For SiH_2 detection, the monitoring laser was tuned to $17\,259.50\text{ cm}^{-1}$, corresponding to a known strong $^{\text{R}}\text{Q}_{0,0}(5)$ vibration-rotation transition¹⁴ in the $\tilde{A}^1\text{B}_1(0,2,0) \leftarrow \tilde{X}^1\text{A}_1(0,0,0)$ vibronic absorption band. Light signals were measured by a dual photodiode-differential amplifier combination and signal decays were stored in a transient recorder (Datalab DL910) interfaced to a BBC microcomputer. This was used to average the decays of between 5 and 20 photolysis laser shots (at a repetition rate of 0.5 or 1 Hz). The averaged decay traces were processed by fitting the data to an exponential form using a non-linear least squares package. This analysis provided the values for first-order rate coefficients, k_{obs} , for removal of SiH_2 in the presence of known partial pressures of substrate gas. Static gas mixtures were used and the optics were cleaned regularly.

Gas mixtures for photolysis were made up, containing between 0.19 and 0.5 Pa of PhSiH_3 , a few Pa of SO_2 and inert diluent (SF_6) at added pressures of between 0 and 13 kPa. For each series of experiments the pressures of SO_2 were in the range: 0–10.6 Pa. The majority of experiments were performed at a total pressure of 1.3 kPa. Pressures were measured by capacitance manometers (MKS, Baratron).

All gases used in this work were frozen at 77 K and pumped free of any vestiges of air prior to use. PhSiH_3 (99.9%) was obtained from Ventron-Alfa (Petrarch). SO_2 (99.9+%) was from Aldrich. Sulfur hexafluoride, SF_6 , (no GC-detectable impurities) was from Cambrian Gases.

Ab initio calculations

The electronic structure calculations were performed initially with the Gaussian 98 and subsequently the Gaussian 03 software packages.¹⁵ All structures were determined by energy minimization at the MP2 = full/6-31G(d) level. Transition state structures

were characterised as first order saddle points by calculation of the hessian matrix. Stable structures, corresponding to energy minima, were identified by possessing no negative eigenvalues of the Hessian, whilst transition states were identified by having one and only one negative eigenvalue. The standard Gaussian-3 (G3) compound method¹⁶ was employed to determine final energies for all local minima. For transition states the elements of the G3 method were used, viz.: optimization to TS at HF/6-31G(d), frequencies at HF/6-31G(d), optimization to TS at MP2 = full/6-31G(d), followed by four single point energy determinations at the MP2 = full/6-31G(d) geometry, viz.: QCISD(T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2 = full/G3 large, and the values were combined according to the G3 procedure.¹⁶ The identities of the transition state structures were verified by calculation of Intrinsic Reaction Co-ordinates¹⁷ (IRC) at the MP2 = full/6-31G(d) level. Reaction barriers were calculated as differences in G3 enthalpies at 298.15 K (quoted simply as ΔH in the tables and figures of results). Wavenumbers for harmonic vibrations, needed for Rice, Ramsperger, Kassel, Marcus (RRKM) calculations, were obtained by adjustment of the values given by the calculations, using correction factor, 0.893.¹⁸

Results

Kinetic measurements

It was independently verified during preliminary experiments that, in a given reaction mixture, k_{obs} values were not dependent on the exciplex laser energy or number of photolysis shots. This is especially important because SO_2 is known to absorb 193 nm radiation and undergo photodissociation.¹⁹ Because static gas mixtures were used, tests with up to 10 shots were carried out. The constancy of k_{obs} (5 shot averages) showed no effective depletion of reactants (especially of SO_2). The lack of dependence of k_{obs} on exciplex laser energy showed the unlikelihood of perturbation of the decay by additional reaction of SiH_2 with a photoproduct (such as SO). The sensitivity of detection of SiH_2 was high but decreased with increasing temperature. Therefore increasing quantities of precursor were required at higher temperatures. However, at any given temperature precursor pressures were kept fixed to ensure a constant (but always small) contribution to k_{obs} values.

A series of experiments was carried out at five temperatures in the range 297–609 K at total pressures of 1.3 kPa. At each temperature, a number of runs (at least seven) at different SO_2 partial pressures were carried out. The results of these experiments are shown in Fig. 1, which demonstrates the linear dependence of k_{obs} on $[\text{SO}_2]$, as expected for second-order kinetics. The second order rate coefficients, k , obtained by least-squares fitting to these plots, are given in Table 1. The error limits are single standard deviations. A few experiments at different total pressures up to 13 kPa (of added SF_6) were also carried out. In these experiments only two or three runs with different partial pressures of SO_2 were undertaken and second order kinetics was assumed. The rate coefficients from these experiments, inevitably with larger uncertainties, are also given in Table 1. It can be seen that there is a slight pressure dependence

Fig. 1 Second order plots for reaction of SiH_2 with SO_2 at various temperatures (indicated). Different symbols are used at the each temperature.

Table 1 Experimental second order rate coefficients^a for $\text{SiH}_2 + \text{SO}_2$

T/K	Pressure/kPa				
	0.13	0.40	1.3	4.0	13
297	2.53 ± 0.23	3.21 ± 0.26	3.15 ± 0.15	3.38 ± 0.33	3.66 ± 0.24
341	2.40 ± 0.17	2.50 ± 0.17	2.72 ± 0.09	2.92 ± 0.17	3.12 ± 0.68
409	1.85 ± 0.13	2.24 ± 0.23	2.22 ± 0.05	2.16 ± 0.13	2.93 ± 0.01
479	1.46 ± 0.03	1.61 ± 0.17	2.10 ± 0.07	1.92 ± 0.05	2.31 ± 0.06
609	1.12 ± 0.02	1.26 ± 0.09	1.47 ± 0.08	1.48 ± 0.06	1.57 ± 0.15

^a Units: $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

of the rate coefficients, although within the error limits, they are close to pressure independent.

An Arrhenius plot of k (at 1.3 kPa) is shown in Fig. 2. The data correspond to the following equation:

$$\log(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-10.10 \pm 0.06) + (3.46 \pm 0.45) \text{ kJ mol}^{-1}/RT \ln 10$$

Fig. 2 Arrhenius plot of rate coefficients for reaction of SiH_2 with SO_2 .

Fig. 3 Pressure dependence of second order rate coefficients for $\text{SiH}_2 + \text{SO}_2$ at different temperatures/K: $\circ$, 297; $\blacktriangle$, 341; $\square$, 409; $\bullet$, 479; $\triangle$, 609. Solid lines are RRKM theoretical fits at each temperature. NB 1 Torr = 133.2 Pa.

Fig. 3 shows the pressure dependence of k together with the results of RRKM calculations (see later), presented in a log-log plot for convenience.

Quantum chemical (*ab initio*) calculations

Apart from the reactant species, $\text{SiH}_2 + \text{SO}_2$, 17 other minima and 12 transition states (TS1–11) were found in these calculations. The minima comprised three molecular complexes ($\text{H}_2\text{Si} \cdots \text{OSO}$, $\text{H}_2\text{SiO} \cdots {}^1\text{SO}$ and $\text{H}_2\text{SiO} \cdots {}^3\text{SO}$),²⁰ three possible molecular product pairs ($\text{H}_2\text{SiO} + {}^1\text{SO}$, $\text{H}_2\text{SiO} + {}^3\text{SO}$ and $\text{SiO}_2 + \text{H}_2\text{S}$), four possible radical pairs ($\text{HSiO} + \text{HSO}$, $\text{HSiO} + \text{HOS}$, $\text{HSiOS} + \text{OH}$ and $\text{HOSi}=\text{O} + \text{SH}$) and 7 single molecular species (cyclo- $\text{H}_2\text{Si}(\text{=O})\text{O}$ –, cyclo- H_2SiOSO –, $\text{H}_2\text{SiOS}=\text{O}(\text{i})$, $\text{H}_2\text{SiOS}=\text{O}(\text{ii})$, $\text{HSiOS}(\text{H})=\text{O}$, HSiOSOH and cyclo- HSiOSHO –) two of which, thione-siloxirane (cyclo- $\text{H}_2\text{Si}(\text{=O})\text{O}$ –) and 3-thia-2,4-dioxasiletane (cyclo- H_2SiOSO –), three and four membered rings respectively, are potential molecular end products. The minima and transition states linking these species are shown on the PES in Fig. 4. Not included in the figure are $\text{HSiOS} + \text{OH}$ because it is too high in energy to be accessible and TS11, which is a transition state between two conformers of $\text{H}_2\text{SiO} \cdots {}^1\text{SO}$. The links from $\text{HSiOS}(\text{H})=\text{O}$ and HSiOSOH corresponding to dissociation pathways to $\text{HSiO} + \text{HSO}$ and $\text{HSiO} + \text{HOS}$ respectively, are only shown partially in order to avoid cluttering the diagram. These radical pairs are only marginally endothermic relative to $\text{SiH}_2 + \text{SO}_2$, and so are included in the surface. Total enthalpies (at 298 K) and enthalpy values for all structures

Fig. 4 Potential energy (enthalpy) surface for the reaction of $\text{SiH}_2 + \text{SO}_2$. All enthalpies are calculated at the G3 level and quoted at 298 K.

relative to $\text{SiH}_2 + \text{SO}_2$ are listed in Table 2. The structures of all these species are shown in Fig. 5–7.

G3 calculations were attempted on all species which appeared reasonable to us, although not all conceivable radical pairs (e.g. $\text{HSSi}=\text{O} + \text{OH}$) were considered. Moreover, pathways to some possible radical pairs (e.g. $\text{HOSi}=\text{O} + \text{SH}$), despite being exothermic with respect to reactants, were not considered because the bonding rearrangements required to produce them appear too complicated to be plausible. One exception to this, which illustrates this difficulty, was the stable product pair $\text{SiO}_2 + \text{H}_2\text{S}$. While these are the lowest energy products of the whole system, the pathway to them requires passage *via* TS8, with a positive enthalpy of 46 kJ mol^{-1} . If this pathway were to occur, the overall reaction would have a substantially positive activation energy.

The surface indicates that the reaction proceeds by the initial formation of the weakly bound $\text{H}_2\text{Si} \cdots \text{OSO}$ complex. Brief attempts were made to explore the possibility of formation of the $\text{Si} \cdots \text{S}$ bonded species, $\text{H}_2\text{Si} \cdots \text{S}(\text{O})=\text{O}$, but such a species could not be found. $\text{H}_2\text{Si} \cdots \text{OSO}$ reacts readily by a cyclisation process to the 3-membered thione-siloxirane ring *via* TS1. This ring exists in a fairly deep enthalpy well (-180 kJ mol^{-1}). Further reaction can now take place in three possible ways. The first, but least likely (due to its overall endothermicity), is a dissociation process into $\text{H}_2\text{Si}=\text{O} + {}^1\text{S}=\text{O}$ *via* TS9 and a weakly bound predissociation complex. The second and most likely is ring expansion to the 4-membered 3-thia-2,4-dioxasiletane ring, *via* TS2 (-96 kJ mol^{-1}). This 4-membered ring is the most stable single molecular species found in this system (with a relative enthalpy of -265 kJ mol^{-1}). Its formation appears to proceed only *via* the 3-membered ring. The third pathway which is endothermic but has a barrier, TS3 (-82 kJ mol^{-1}), only marginally higher than TS2, involves ring opening of the Si–S

Table 2 G3^a calculated total enthalpies, $H/\text{Hartree}$, and relative enthalpies, $\Delta H_{\text{rel}}/\text{kJ mol}^{-1}$, for stationary points of interest on the H_2SiSO_2 energy surface

Species	H (298 K)/Ha	$\Delta H_{\text{rel}}/\text{kJ mol}^{-1}$
$\text{SiH}_2 + \text{SO}_2$	−838.871430	0
$\text{H}_2\text{Si} \cdots \text{OSO}$ complex	−838.881596	−27
$\text{O}=\text{SiH}_2$	−838.940020	−180
$\text{H}_2\text{SiO}_2\text{S}$	−838.972484	−265
$\text{H}_2\text{SiOS}=\text{O}$ adduct(i)	−838.912578	−108
$\text{H}_2\text{SiOS}=\text{O}$ adduct(ii)	−838.911499	−105
$\text{HSiOS}(\text{H})=\text{O}$	−838.909122	−99
HSiOSOH	−838.913520	−111
$\text{HSiO}=\text{SH}$	−838.911133	−104
$\text{H}_2\text{SiO} \cdots \text{S}=\text{O}$ complex (singlet)	−838.879625	−22
$\text{H}_2\text{SiO} + {}^1\text{S}=\text{O}$	−838.864886	+17
$\text{H}_2\text{SiO} \cdots \text{S}=\text{O}$ complex (triplet)	−838.913721	−111
$\text{H}_2\text{SiO} + {}^3\text{S}=\text{O}$	−838.900142	−75
$\text{SiO}_2 + \text{H}_2\text{S}$	−838.979428	−284
$\text{HSi}=\text{O} + \text{HS}=\text{O}$	−838.862696	+23
$\text{HSi}=\text{O} + \text{HOS}$	−838.855714	+41
$\text{HSiOS} + \text{OH}$	−838.800711	+186
$\text{HOSi}=\text{O} + \text{SH}$	−838.931688	−158
TS1	−838.881213	−26
TS2	−838.908149	−96
TS3	−838.902757	−82
TS4a	−838.903787	−85
TS4b	−838.903742	−85
TS5	−838.897894	−69
TS6	−838.872222	−2
TS7	−838.899076	−73
TS8	−838.853934	+46
TS9	−838.861368	+26
TS10	−838.881197	−26
TS11	−838.876278	−13

^a Full expression: G3//MP2 = full/6-31G(d).

Fig. 5 Quantum chemical, MP2 = full/6-31G(d) calculated geometries of single molecular species on the $\text{SiH}_2 + \text{SO}_2$ potential energy surface. Bond lengths are in Å and angles in degrees.

bond to form a silylene sulfur dioxide adduct, $\text{H}_2\text{SiOS}=\text{O}(\text{i})$. This adduct and its conformational partner, $\text{H}_2\text{SiOS}=\text{O}(\text{ii})$, have the same molecular linkages as the initial complex, $\text{H}_2\text{Si}\cdots\text{OSO}$ but differ from it in having clearly defined Si-O and O-S single bonds which render both adducts more stable than the complex. $\text{H}_2\text{SiOS}=\text{O}(\text{i})$ and $\text{H}_2\text{SiOS}=\text{O}(\text{ii})$ only differ in enthalpy from one another by 3 kJ mol^{-1} and are readily interconverted by rotations around the single bonds *via* TS4a which lies only 23 kJ mol^{-1} above $\text{H}_2\text{SiOS}=\text{O}(\text{i})$. Another transition state, TS4b, was found with the same enthalpy value but with a linear Si-O-S configuration, indicating that interconversion *via* angle bending is also possible. Clearly the adducts are pretty labile species. In the light of these easy interconversions other possible conformers were searched for. None was found. It should be noted that possible routes from the initial complex directly to these adducts, which are exothermic, would appear to require only rather small changes in bond length and conformation. Nevertheless no such routes were found and the IRC pathway from TS1 to cyclo- $\text{H}_2\text{SiS}(\text{=O})\text{O}-$ was not diverted into either of the adducts.

It appears that adduct(i) can only be formed *via* the thione-siloxirane ring, and adduct(ii) only from adduct(i).

Since all the single molecular species reached thus far are substantially exothermic relative to reactants, $\text{SiH}_2 + \text{SO}_2$, further sequential processes across the reaction surface need to be considered. These may proceed from either the four-membered ring or one or both of the adducts. Pathways from 3-thia-2,4-dioxa-siletane are considered first. This has an endothermic route to $\text{H}_2\text{Si}=\text{O} + {}^1\text{S}=\text{O}$ *via* TS9 and the $\text{H}_2\text{Si}=\text{O}\cdots{}^1\text{S}=\text{O}$ predissociation complex. As well as $\text{H}_2\text{Si}=\text{O} + {}^1\text{S}=\text{O}$, TS9 lies above the reactant's enthalpy, making this pathway doubly unviable. An alternative decomposition route for 3-thia-2,4-dioxa-siletane, requires the double H-atom transfer from Si to S across the ring. The first step generates the new 4-membered ring, cyclo- $\text{HSiOSH}-$, (-104 kJ mol^{-1}) *via* TS7 (-73 kJ mol^{-1}), but the second step *via* TS8 ($+46 \text{ kJ mol}^{-1}$), is too high in enthalpy to permit this pathway leading to $\text{SiO}_2 + \text{H}_2\text{S}$, as mentioned above.

Starting from adducts (i) or (ii), dissociation to $\text{H}_2\text{SiO} + {}^1\text{SO}$ either directly or *via* the predissociation complex, might appear

Fig. 6 Quantum chemical, MP2 = full/6-31G(d) calculated geometries of small molecular fragment species on the $\text{SiH}_2 + \text{SO}_2$ potential energy surface. Bond lengths are in Å and angles in degrees.

as attractive possibilities. Although we searched for these, we could find no such pathways. Also searched for were potential transition states for direct formation of 3-thia-2,4-dioxasiletane from adducts (i) or (ii). Despite the apparent simplicity of a 1,4 Si to O ring closure, no such transition states were found. However pathways involving H-atom migration were found. From $\text{H}_2\text{SiOS}=\text{O}(\text{i})$, 1,3 H-migration from Si to S leads to $\text{HSiOS}(\text{H})=\text{O}$ *via* TS5 at an enthalpy 69 kJ mol^{-1} below that of the reactants and from $\text{H}_2\text{SiOS}=\text{O}(\text{ii})$, 1,4 H-migration from Si to O leads to HSiOSOH *via* TS6 at an enthalpy only 2 kJ mol^{-1} below that of the reactants. From a kinetic point of view, if H-migration is important at all, formation of $\text{HSiOS}(\text{H})=\text{O}$ would seem more likely. While these H-atom migrations are fairly close to thermoneutral, in fact HSiOSOH is 6 kJ mol^{-1} exothermic with respect to $\text{H}_2\text{SiOS}=\text{O}(\text{ii})$ while $\text{HSiOS}(\text{H})=\text{O}$ is 9 kJ mol^{-1} endothermic relative to $\text{H}_2\text{SiOS}=\text{O}(\text{i})$. It is worth noting that both these H-migration products are silylenes. A final question concerning these species is whether they possess plausible dissociation pathways. HSiOSOH might seem capable of breaking the

relatively weak S–O bonds to yield either $\text{HSiO} + \text{SOH}$, or $\text{HSiOS} + \text{OH}$. Similarly $\text{HSiOS}(\text{H})=\text{O}$ could break its S–O bond to produce $\text{HSiO} + \text{HS}=\text{O}$. The calculations show that all these processes form product pairs which are endothermic with respect to the reactants, $\text{SiH}_2 + \text{SO}_2$, thus making them highly unlikely.

All of the above described pathways across this complex reaction landscape occur on the singlet state surface. But the ground state of sulfur monoxide, $\text{S}=\text{O}$ is $^3\Sigma^-$ (ref. 20) and the product pair $\text{H}_2\text{SiO} + ^3\text{SO}$, in contrast to $\text{H}_2\text{SiO} + ^1\text{SO}$, is exothermic with respect to reactants. Thus an attractive mechanistic pathway across this enthalpy surface would be one in which an intersystem crossing occurs at some stage before final formation of $\text{H}_2\text{SiO} + ^3\text{SO}$. Despite a brief search, we have not been able to identify such a pathway.

RRKM calculations

The pressure dependence of an association reaction corresponds exactly to that of the reverse unimolecular dissociation

Fig. 7 Quantum chemical, MP2 = full/6-31G(d) calculated geometries of transition states on the $\text{SiH}_2 + \text{SO}_2$ potential energy surface. Bond lengths are in Å and angles in degrees.

process providing there are no other perturbing reaction channels. Although the detailed quantum chemical calculations for $\text{SiH}_2 + \text{SO}_2$ suggest the possibility of several possible channels a strong candidate is the pathway leading to 3-thia-2,4-dioxasiletane (reaction (1)). Analogous association pathways leading to cyclic products exist for the reactions of SiH_2 with C_2H_2 ,²¹ C_2H_4 ,²² CH_3CHO ¹¹ and $(\text{CH}_3)_2\text{CO}$ ¹⁰ amongst others.⁶ These reactions all possess pressure dependent rate constants, but the extent of pressure dependence varies and depends on the particular molecular parameters of each reaction. Although any pressure dependence of the rate constants for $\text{SiH}_2 + \text{SO}_2$ is only very slight at most, the quantum chemical calculations provide

us with enough information to probe the question of whether such a pressure-dependence should be expected. We have therefore carried out RRKM calculations²³ on the unimolecular dissociation process of 3-thia-2,4-dioxasiletane *viz.*:

3-thia-2,4-dioxasiletane has never been isolated or studied experimentally and so we are reliant on the quantum chemical calculations to provide the necessary parameters for these calculations. This has been done as follows. First the likely Arrhenius *A* factors for these decomposition reactions were

Table 3 Standard entropy changes^a and decomposition A factors for 3-thia-2,4-dioxasiletane

Quantity	T/K				
	297	341	409	479	609
$\Delta S_{-1,1}^0$ ^{b,c}	162.9	161.9	159.8	157.3	152.9
$\log(A_{-1}/\text{s}^{-1})$	17.37	17.26	17.07	16.87	16.53

^a Pressure = 1 bar. ^b Units: J K⁻¹ mol⁻¹. ^c Modified from Qu. Chem. Calcns. (see text).

estimated (at each temperature) by use of the microscopic reversibility relationship, $\ln(A_{-1}/A_1) = \Delta S_{-1,1}^0/R$ where A_{-1} and A_1 are the decomposition and association A factors (*i.e.* A_{-1} is what is required and A_1 is the experimental value measured here) and $\Delta S_{-1,1}^0$ is the entropy change.²⁴ The values for $\Delta S_{-1,1}^0$ were obtained from the thermodynamic output of the theoretical calculations, although because of the approximations used in the procedure, they were corrected for the vibrational wavenumber factor (0.893). The entropy changes and calculated A factors are shown in Table 3. These were now used to assist in the assignment of vibrational wavenumbers for the transition state, based closely on those of the loose association complex, H₂Si...OSO, but modified by adjustment of the key transitional mode values leading to dissociation, using the standard Transition State Theory formula, $A = (ekT/h)\exp(\Delta S^\ddagger/R)$. Whether precise values of all vibrational wavenumbers are correct or not is not important provided the entropies of activation, *i.e.* values of $\Delta S^\ddagger$, are matched. The assignment of both molecule and transition state, for decomposition of 3-thia-2,4-dioxasiletane at 297 K, is shown in Table 4 which also includes the Lennard-Jones collision number value. The assignments at other temperatures are shown in Table 5. The value for the critical energy, E_0 , (259 kJ mol⁻¹) employed in these calculations was that given by the quantum chemical calculations (corresponding to $\Delta H = -265$ kJ mol⁻¹, Table 2). We have used a weak collisional (stepladder) model for collisional deactivation, because there is overwhelming evidence against the strong collision assumption.²⁵ The average energy removal parameter, $\langle \Delta E \rangle_{\text{down}}$ for SF₆ bath gas, was taken as 12.0 kJ mol⁻¹ (1000 cm⁻¹) as used previously for many such reactions.⁶ The results of these calculations are shown in Fig. 3 as pressure dependent “fall-off” curves

Table 4 Molecular and transition state parameters for RRKM calculations for decomposition of 3-thia-2,4-dioxasiletane at 297 K

Parameter	Molecule	TS (297 K)
Wavenumbers/cm ⁻¹	2190(2) 1000 897 843 767 729 691 650 563 520 153	1976(2) 1401 1214 1009 529 90 70 65 60 35 —
A/s^{-1}		2.2×10^{17}
$E_0/\text{kJ mol}^{-1}$		259
$Z_{\text{LJ}}/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		4.25

Table 5 Temperature dependent transition state parameters for RRKM calculations for the decomposition of 3-thia-2,4-dioxasiletane

	T/K				
	297	341	409	479	609
TS wavenumbers/cm ⁻¹	90 70 65 60 35	90 85 70 68 38	100 95 85 85 42	120 110 95 90 49	140 130 125 105 61
$Z_{\text{LJ}}(\text{SF}_6)/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.25	4.34	4.47	4.60	4.83

where the calculated rate coefficients can be readily compared with the experimental values.

Discussion

General comments and rate constant comparisons

The main experimental purpose of this study was to measure the rate coefficients and their temperature dependence for the reaction of SiH₂ with SO₂. This has been accomplished. It is important to note that despite the known photodecomposition of SO₂ at 193 nm,¹⁹ under our conditions it was insufficient to interfere with the SiH₂ decay kinetics. There are no previous measurements of rate coefficients or Arrhenius parameters for this reaction. Other comparisons are, however, possible. Table 6 shows the Arrhenius parameters for this system alongside those of reactions of SiH₂ with other O-atom containing molecules, both organic and inorganic.^{10–13,26–33} It is assumed that in the reaction studied here, the Arrhenius parameters at 1.3 kPa are close enough to those at infinite pressure, to make no significant difference. Some of the other reactions are much more pressure dependent and where necessary rate coefficients have been extrapolated to obtain their true second order (infinite pressure) values. In these cases there is greater uncertainty associated with the Arrhenius parameters. In the examples listed there is some spread in values of A and E_a but most lie within fairly tight ranges: -10 to -12 for $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ and -1.6 to -6.2 for $(E_a/\text{kJ mol}^{-1})$. The significant exception to this is the reaction of SiH₂ + CO₂. The closest similarity of parameters occurs between those of the present study and the reactions with carbonyl compounds (apart from SiH₂ + CO₂). Another worthwhile

Table 6 Comparison of Arrhenius parameters for addition reactions of silylene to carbonyl and related species

Reactants	$\log A^a$	$E_a/\text{kJ mol}^{-1}$	Ref.
SiH ₂ + SO ₂	-10.10 ± 0.06	-3.45 ± 0.46	This work
SiH ₂ + CO ₂	-11.89 ± 0.13	$+16.4 \pm 1.2$	13
SiH ₂ + CO ^b	-9.99	-3.0	12
SiH ₂ + CH ₃ CHO ^b	-10.10 ± 0.06	-3.9 ± 0.5	11
SiH ₂ + (CH ₃) ₂ CO	-10.17 ± 0.04	-4.5 ± 0.3	10
SiH ₂ + O ₂	-11.08 ± 0.04	-1.57 ± 0.9	26
SiH ₂ + NO ^b	-11.66 ± 0.01	-6.20 ± 0.10	27
SiH ₂ + N ₂ O	-12.09 ± 0.04	-2.0 ± 0.3	28
SiH ₂ + THF ^b	-10.59 ± 0.10	-5.76 ± 0.65	29

^a Units: cm³ molecule⁻¹ s⁻¹. ^b Pressure dependent reaction; parameters obtained by extrapolation to infinite pressure.

Table 7 Comparison of Lennard-Jones collision efficiencies for reactions of SiH₂ with O-atom containing molecules at 298 K^a

Reactants	k^b	Z_{IJ}^b	Efficiency/%
SiH ₂ + SO ₂	3.15	4.41	71
SiH ₂ + CO ₂	$<4.2 \times 10^{-5}$	4.10	<0.00102
SiH ₂ + CO ^c	3.43	3.80	90
SiH ₂ + CH ₃ CHO ^c	4.0	5.39	74
SiH ₂ + (CH ₃) ₂ CO	4.2	5.54	76
SiH ₂ + O ₂	0.164	3.55	4.6
SiH ₂ + NO ^c	4.6	3.68	125
SiH ₂ + N ₂ O	0.019	4.12	0.46
SiH ₂ + THF ^c	2.8	5.2	45

^a For references see Table 6. ^b Units: 10^{-10} cm³ molecule⁻¹ s⁻¹. ^c Pressure dependent reaction; parameters obtained by extrapolation to infinite pressure.

comparison is that of the collision efficiencies of these reactions. Table 7 shows the 298 K values of the rate coefficients of these reactions and their calculated Lennard-Jones collision numbers. The ratios of these quantities give the collision efficiencies (expressed as percentages in the table). High efficiencies (70–90%) characterise both the current reaction³⁴ and those of reactions of SiH₂ with the carbonyl containing species (apart from CO₂). The reasons for the low value efficiencies have been discussed in detail in our earlier review⁶ and this is not repeated here. The high value efficiencies reflect the electrophilic nature of silylene combined with the easily accessibility lone pairs of electrons which result in a donor–acceptor interaction and facilitate the formation of an intermediate. One other factor which is important is that the resulting species must be capable of further reaction to an ultimately stable product (or products) without requiring a high (secondary) energy barrier.⁶ It is this latter limitation which causes the SiH₂ + CO₂ reaction to have an overall positive activation and low collisional efficiency. The reaction of SiH₂ with SO₂ is clearly different. The explanation for this is considered in the next section.

The potential energy surface: comparisons with other systems

There has been no previous calculation of the potential energy surface for the SiH₂ + SO₂ reaction system with which to compare the results of the present work. However it is interesting to note that in the first step of the reaction the initial interaction of SiH₂ is with the O-rather than the S-atom. This contrasts with reactions of atoms (such as H) and radicals (such as OH and CH₃) where initial interaction at the S-atom appears to be favoured.³⁵ Of course SiH₂ has an empty p orbital rather than an unpaired electron, and so this comparison may not be particularly illuminating. Unfortunately there is no published study of the reaction ¹CH₂ + SO₂ with which to draw comparisons.

The energy surface found here shows a considerable complexity. It provides a lot of detailed information about possible intermediates in this reaction but it does not indicate a clearly defined mechanistic pathway. The main issue of contention seems to be whether the lowest enthalpy addition product *viz.* the four-membered ring, 3-thia-2,4-dioxasiletane is sufficiently stable to be the main reaction product. This is dealt with in the next section. Clearly the higher enthalpy three membered thione-siloxirane ring is not likely to be a final product, since

it is formed with considerable excess energy, well above the relatively low enthalpy transition state, TS2 (-96 kJ mol⁻¹), for isomerisation to the more stable 3-thia-2,4-dioxasiletane.

To provide some further insight we compare the surface to that for the reaction of SiH₂ + CO₂. Most of the species on the this latter surface have been calculated and published by us,¹³ but one essential species, 3-sila-2,4-dioxo-cyclobutylidene together with its transition state for formation, not identified previously, have been added here to enable a more illuminating comparison. Details of this are given in the ESI.† The essential parts of the two surfaces are shown in Fig. 8. It should be noted that loosely bound complexes have been omitted for simplification. This does not affect any conclusions. Several differences are worth pointing out. First the reaction of SiH₂ with SO₂ is barrierless, whereas that with CO₂ has two barriers, a low one to form the 3-membered siloxirane ring but a high one to form the 4-membered 3-sila-2,4-dioxo-cyclobutylidene ring. The latter process cannot compete, which shows why this product cannot be formed from SiH₂ + CO₂. In the SiH₂ + SO₂ reaction, probably the extra size and availability of d orbitals in the sulfur atom, make the bridging structure of the transition state for thione-siloxirane ring formation lower in energy than its carbon counterpart. In the sulfur case, the four-membered ring is not formed directly, but comes from the 3-membered ring. Such a pathway does not exist in the SiH₂ + CO₂ reaction, possibly because the dissociation process to SiH₂O + CO has such a low barrier, making other pathways uncompetitive. The direct pathway from SiH₂ + CO₂ to 3-sila-2,4-dioxo-cyclobutylidene probably owes its high barrier to the need to bend and break the highly stable π system of the C=O double bonds, and maybe also the lack of d orbital participation. The relative stabilities of π systems of the C=O and S=O double bonds can also be surmised as contributing to the significantly different exothermicities of formation of the 3-membered rings from their reactants, *viz.* siloxirane (-78 kJ mol⁻¹) compared to thione-siloxirane (-180 kJ mol⁻¹). For the 4-membered rings the exothermicity difference is even greater, *viz.* 3-sila-2,4-dioxo-cyclobutylidene (-68 kJ mol⁻¹) compared to 3-thia-2,4-dioxasiletane (-265 kJ mol⁻¹). As well as the loss of π -bonds which occurs on formation of these rings there is a formal valency change from 4 to 2 for the carbon or sulfur atoms involved. For sulfur, this is no problem: valence state 2 is its favoured state for bonding, but for carbon, valence state 2 is that of a carbene a rather unstable state of bonding (although the two bonded O-atoms doubtless contribute to its preferred existence as a singlet rather than triplet state). The final point to note concerns the dissociation products of the 3-membered rings. Both reactions produce silanone. In the carbon case this is accompanied by carbon monoxide with its stable triple bond, whereas in the sulfur case sulfur monoxide is only double bonded. Moreover if spin is conserved, sulfur monoxide is produced in an excited rather than its ground state. This accounts for the large difference in dissociation energies of these three membered rings.

As a further check on the accuracy of the calculations carried out here we have compared the computed thermochemistry of some of the overall processes forming possible end products

Fig. 8 Comparison of selected portions of the PE surfaces (G3 level) of $\text{SiH}_2 + \text{CO}_2$ and $\text{SiH}_2 + \text{SO}_2$.

with estimates made from previous work, part experimental, part theoretical. This is shown in Table 8. The literature estimates for ΔH^0 shown in this table are obtained by combining preferred values for ΔH_f^0 of the individual species, shown in Table 9 in the Appendix. Examination of Table 8 shows that the G3 values calculated here and the literature values differ by no more than 12 kJ mol^{-1} . The G3 method is reliable to within *ca.* $\pm 4 \text{ kJ mol}^{-1}$,¹⁶ and most values agree within combined uncertainty limits.

RRKM calculations and the reaction mechanism

It is quite clear from Fig. 3 that the RRKM calculated pressure dependence for reaction (1), based on the assumption that it should correspond to that of the decomposition process of 3-thia-2,4-dioxasiletane, reaction (1), is completely inconsistent with the experimental pressure dependence. The calculated pressure dependence implies that even if formed transiently,

3-thia-2,4-dioxasiletane would be too highly vibrationally excited to be stabilised to any extent, particularly at the lower pressures, and would mostly redissociate back to reactants. This rules out 3-thia-2,4-dioxasiletane as the stable reaction end product. It is worth pointing out that the difference between calculated and observed pressure dependences is so large that any minor uncertainties in the input parameters for the RRKM calculation would make no significant difference. This RRKM calculation also rules out the formation of thione-siloxirane as the final product, since, even if it were to have been stabilised to the extent that no isomerisation *via* TS2 to 3-thia-2,4-dioxasiletane had been possible, its energy well, at only 180 kJ mol^{-1} would not have allowed its stabilisation relative to redissociation back to reactants and so would have given rise to an even greater predicted pressure dependence than that calculated for 3-thia-2,4-dioxasiletane.

These findings suggest a mechanism for this reaction in which an intermediate species is produced which cannot be stabilised but rather dissociates to yield the final products. If the three- or four-membered rings are formed at all they can only be in highly vibrational states which revert to the intermediate which can dissociate. Furthermore this intermediate must dissociate sufficiently rapidly to avoid collisional stabilisation, otherwise it would give rise to a pressure dependence. The very small effect observed experimentally does not suggest this (but see below). We have shown in these calculations: that product pairs, $\text{HSiO} + \text{HOS}$, $\text{HSiO} + \text{HSO}$, $\text{H}_2\text{Si}=\text{O} + {}^1\text{SO}$ can be ruled out because their formation is endothermic; that the product pair $\text{SiO}_2 + \text{H}_2\text{S}$ can be ruled out because its formation requires a positive enthalpy barrier; that formation

Table 8 Comparison of overall reaction enthalpies ($\Delta H^0/\text{kJ mol}^{-1}$) for end product formation in the $\text{SiH}_2 + \text{SO}_2$ reaction

Product	G3 enthalpy ^a	Literature ^b
$\text{H}_2\text{SiO} + {}^3\text{SO}$	-75	-69 ± 5
$\text{H}_2\text{SiO} + {}^1\text{SO}$	+17	$+7 \pm 5$
$\text{SiO}_2 + \text{H}_2\text{S}$	-284	-279 ± 9
$\text{HOSiO} + \text{SH}$	-158	-146 ± 7
$\text{HSiO} + \text{HSO}$	+23	$+31 \pm 15$
$\text{HSiO} + \text{HOS}$	+41	$+48 \pm 15$

^a See Table 2. ^b See Table 9 (Appendix) for ΔH_f^0 values and refs for each species.

Table 9 Enthalpies of formation, $\Delta H_f^\circ/\text{kJ mol}^{-1}$: values and sources

Species	ΔH_f° (298 K)	Ref.
SiH ₂	273 ± 2	38
SO ₂	−296.8 ± 0.2	39
H ₂ Si=O	−98 ± 8	40
	−98 ± 4	41
	−98.2	42
	−92 ± 20	38
	−98 ± 4	Preferred
HSi=O	36 ± 8	40
	30 ± 15	41
	28.8	42
	30 ± 15	Preferred
HOSi=O	−312.5 ± 6	41
	−313.5	42
	−313 ± 6	Preferred
SiO ₂	−282 ± 9	41
	−288	42
	−305.4 ± 33.5	39
	−282 ± 9	Preferred
³ SO	5.0 ± 1.3	39
¹ SO	81.0 ± 1.3	39
H ₂ S	−20.5 ± 0.8	39
SH	139.3 ± 5	39
	143 ± 3	43
	141.87 ± 0.52	44
	142.95 ± 0.78	45
	143.4 ± 1.9	46
	143 ± 2	Preferred
HOS	18 ± 15	43
	−21 ± 42	44
	−5.3 ± 2.3	46
	−5.3 ± 2.3	Preferred
HSO	−4 ± 3	43
	−4.8 ± 7.3	44
	−6.1 ± 2.9	45
	−22.6 ± 2.3	46
	−22.6 ± 2.3	Preferred

of HOSi=O + SH seems unlikely because of the required bonding reorganisation. This leaves H₂Si=O + ³SO as the only product pair both exothermic and with an apparently straightforward formation mechanism, although it requires an inter-system crossing to occur. Thus we suggest the following process as the best mechanistic description of this reaction:

The H₂SiOSO intermediate could be the initial complex but we believe that it is more likely a vibrationally excited version of the adduct (i), because (i) is more stable. Moreover this adduct has the characteristics of a diradical; it can be formally written H₂SiOŠ=O. This means that it has closely lying singlet and triplet states.³⁶ Although we have not been able to obtain details of the triplet surface here by calculation, it seems to us that adduct (i) is a likely species where the necessary intersystem crossing could occur. Of course we cannot rule out that intersystem crossing might occur during the dissociation³⁷ on the singlet surface at some intermediate stage of O–S bond lengthening, nor also that it might occur from the H₂Si=O...¹S=O complex itself, which is stable enough to be formed exothermically. Our experimental system does not allow us to detect either silanone or sulfur monoxide and so experimental confirmation of this mechanism must await further studies.

Conclusion

The reaction of silylene with sulfur dioxide in the gas phase is a fast process with no energy barrier, occurring at 71% of the maximum (collision) rate at 298 K. The rate coefficients show little or no pressure dependence. The G3 calculated potential energy surface shows the presence of two stable low-energy cyclic molecules, but the lack of pressure dependence, predicted by RRKM theory, shows that these are not the end products. The most suitable candidates for these are H₂SiO + ³SO. The reaction contrasts strongly with that of SiH₂ + CO₂, which is slow and has a positive activation energy. A comparison of the potential energy surfaces offers an explanation for these differences.

Appendix

Collected in Table 9 are the best literature values we have been able to find of ΔH_f° (298 K) for the potential end product species of reaction of SiH₂ and SO₂, as well as the reactants. These values were used to obtain the reaction enthalpies cited in Table 8 of this paper.

We have not ourselves evaluated the complete literature for each value but instead relied as far as possible on previous data evaluations.^{38–46} Where, in our opinion, these are sufficiently reliable we have chosen a single value. Where we were less certain we have cited several values and made the best choice we could. For the oxy-silicon species (H₂Si=O, HSi=O, HOSi=O and SiO₂) only theoretical values exist.^{38,40–42} There is a need for experimental values in this area, difficult though they may be to obtain. For the species HOS and HSO, we have taken the latest theoretical calculations of Nagy *et al.*⁴⁶ This paper attempts to evaluate previous literature, although there remain serious discrepancies between theory and experiment.

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