

Supplementary Information

Reaction of Silylene with Sulfur Dioxide: Some Gas-Phase Kinetic and Theoretical Studies

Rosa Becerra, J. Pat Cannady, Nicola Goldberg and Robin Walsh

Microscopic reversibility (conversion of units and standard states)

This equation links kinetic and thermodynamic quantities for reversible reactions. It is often written: $\ln(A_1/A_{-1}) = \Delta S_{1,-1}^\circ/R$. This hides the complexity that, whereas $\Delta S_{1,-1}^\circ$ is referenced to the pressure standard state of 1 bar, rate constants such as A_1 are measured in concentration units, viz. $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in this case.

The easiest way to deal with this problem is to correct $\Delta S_{1,-1}^\circ$ from 1 bar (called ΔS_p° below) to 1 mol dm^{-3} (called ΔS_c° below), via the equation^{1s}:

$$\Delta S_p^\circ = \Delta S_c^\circ + (\Delta n)R \times \ln R'T$$

where $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ and $R' = 0.08206 \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$.

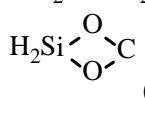
Note that the value of A_1 has to be converted from $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Further Quantum Chemical calculations for $\text{SiH}_2 + \text{CO}_2$

Both G3 and G2 calculations were carried out on this system: G3 for comparison with those for $\text{SiH}_2 + \text{SO}_2$ system (main paper) and G2 for consistency with earlier calculations^{2s} on the $\text{SiH}_2 + \text{CO}_2$ reaction. The results are shown in Table S1 (below). It can be seen that the ΔH_{rel} values differ by no more than 6 kJ mol^{-1} , indicating reasonable agreement between the two levels of calculation. The new structures, ie of species not found earlier, are shown in Fig. S1.

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Table S1 $G3^a$ and $G2^b$ calculated total enthalpies, H /hartree, and relative enthalpies, $\Delta H_{\text{rel}}/\text{kJ mol}^{-1}$, for stationary points of interest on the H_2SiCO_2 energy surface

Species	$G3^c$		$G2$	
	$H(298\text{ K})/\text{ha}$	$\Delta H_{\text{rel}}/\text{kJ mol}^{-1}$	$H(298\text{ K})/\text{ha}$	$\Delta H_{\text{rel}}/\text{kJ mol}^{-1}$
$\text{SiH}_2 + \text{CO}_2$	-478.950438	0	-478.521649 ^d	0
$\text{SiH}_2 \cdots \text{CO}_2$ (complex)	-478.955484	-13	-478.527461 ^d	-15
 (4-ring)	-478.976467	-68	-478.545523 ^c	-63
Siloxiranone (3-ring)	-478.980103	-78	-478.549586 ^d	-73
$\text{H}_2\text{SiO} \cdots \text{CO}$ (complex)	-478.985194	-91	-478.554958 ^d	-97
$\text{H}_2\text{SiO} + \text{CO}$	-478.979532	-76	-478.549824 ^d	-74
TS: $\text{SiH}_2 \cdots \text{CO}_2$ to 4-ring	-478.916769	+88	-478.487316 ^c	+90
TS: $\text{SiH}_2 \cdots \text{CO}_2$ to 3-ring	-478.946281	+11	-478.517211 ^d	+12
TS: 3-ring to $\text{H}_2\text{SiO} \cdots \text{CO}$	-478.974552	-63	-478.543277 ^d	-57

^a Full expression: $G3//\text{MP2}=\text{Full}/6-31\text{G}(\text{d})$ ^b Full expression: $G2//\text{MP2}=\text{Full}/6-31\text{G}(\text{d})$

^c This work ^d ref. 2s

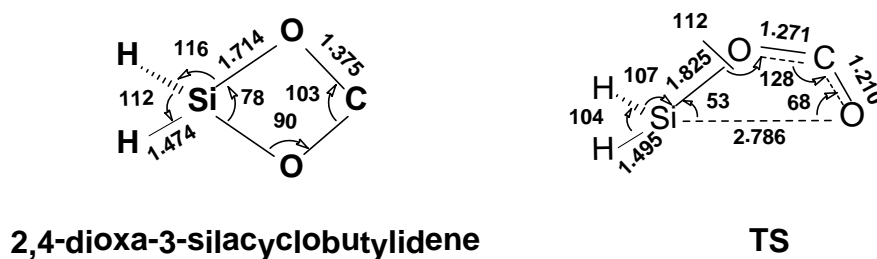


Fig. S1 Quantum Chemical $\text{MP2}=\text{Full}/6-31\text{G}(\text{d})$ calculated geometries of the cyclic four-membered ring product of reaction of $\text{SiH}_2 + \text{CO}_2$ and its transition state for formation. Selected distances are given in Å and angles in degrees.

Note: fuller details of previous calculations on the $\text{SiH}_2 + \text{CO}_2$ are given in reference 2s.

References

- (1s) S. W. Benson, *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976, pp 8, 9.
- (2s) R. Becerra, J. P. Cannady and R. Walsh, *J. Phys. Chem. A*, 2002, **106**, 4922.