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**Preliminary communication**

# FEATURES OF THE $H_2SiO$ POTENTIAL ENERGY SURFACE. STABILIZATION OF A SILICON—OXYGEN DOUBLE BOND

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## Summary

In view of intense current interest in silicon—oxygen double bonds, the singlet potential energy surface of $H_2SiO$ has been explored through ab initio calculations, which is found to differ significantly from the $H_2CO$ potential energy surface. Also examined are the effects of fluorine substitution on the relative stabilities of $H_2SiO$ and its isomers.

For many years π-bonded silicon intermediates have attracted a great deal of attention in organosilicon chemistry [1]. Now that compounds containing silicon—carbon [2,3] or silicon—silicon [4,5] double bonds can be synthesized and isolated at room temperature, it is inevitable that considerable attention is directed toward the preparation of silicon—oxygen doubly bonded compounds, silanones. Although schemes for the synthesis of silanones have been devised, up to now only indirect evidence is available which suggests the transient existence [6]. We here report preliminary studies of the singlet potential energy surface of $H_2SiO$ and the effects of fluorine substitution on the silicon—oxygen double bond. The reactions considered are (1a) hydrogen elimination and (1b) isomerization to hydroxysilylene.

$$H_2SiO \rightarrow H_2 + SiO \tag{1a}$$

$$H_2SiO \rightarrow H\ddot{Si}OH \tag{1b}$$

In this work, stationary points on the potential energy surface were located with the 3-21G [7] SCF analytical gradient technique and were characterized by calculating routinely their harmonic vibrational frequencies. The harmonic fre-

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quencies obtained at this level were used to compute zero-point vibrational energies. Following the full optimization of stationary point geometries, additional single-point calculations were carried out with electron correlation incorporated through configuration interaction (CI) or third-order Møller-Plesset perturbation (MP3) theories [8], using the larger 6-31G** basis set [9], these being denoted by CI/6-31G**//3-21G or MP3/6-31G**//3-21G. In the correlation calculations, all single (S) and double (D) substitutions were included, with the restriction that the core-like orbitals (1*s*, 2*s* and 2*p* for Si, 1*s* for O and F in character) were excluded. The final CI energies were obtained by adding the Davidson correction [10] to allow for unlinked cluster quadruple correction (QC).

A schematic energy profile and transition state geometries for the reactions 1a and 1b are presented in Fig. 1. For comparison the analogous reactions 2a and 2b of $H_2CO$ were also calculated at the same level of theory and the results are included in the figure.

$$H_2CO \rightarrow H_2 + CO \tag{2a}$$

$$H_2CO \rightarrow H\ddot{C}OH \tag{2b}$$

Although our interest is at the characteristic comparison of $H_2SiO$ with $H_2CO$, the present energy values for $H_2CO$ are very close to those obtained previously with more sophisticated calculations [11—13].

Comparing $H_2SiO$ with $H_2CO$, the following similarities and differences are worth mentioning. (i) Both hydrogen elimination reactions 1a and 2a are slightly exothermic and undergo considerable energy barriers of 84.9 and 88.7 kcal/mol, respectively. The "widths" of the barriers, as characterized by the imaginary (re-

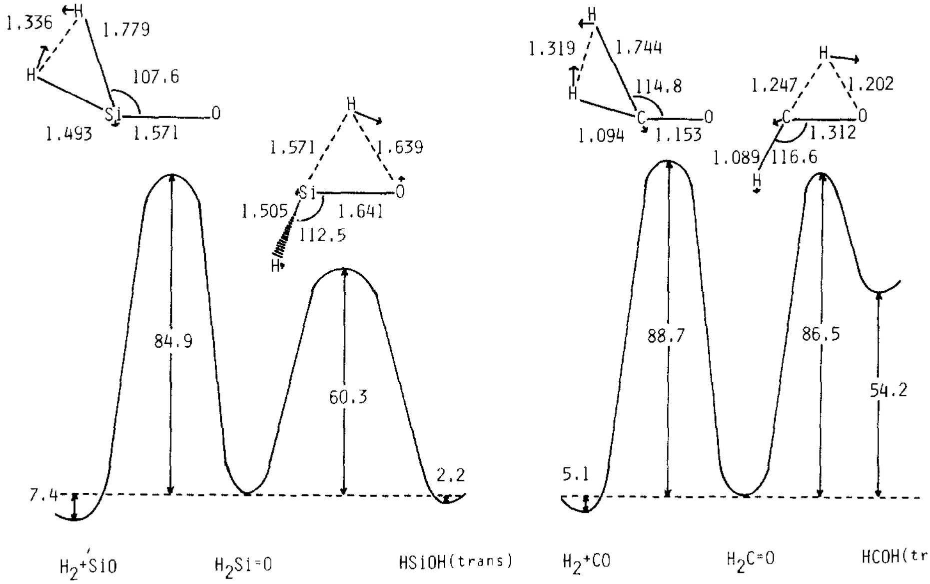

Fig. 1. Schematic energy profiles and transition state geometries for the hydrogen elimination and isomerization reactions of $H_2SiO$ and $H_2CO$. Relative energies in kcal/mol are CI(S+D+QC)/6-31G**// 3-21G values with zero-point correction. Geometries are in Ångstroms and degrees. The arrows indicate the displacement vector of reaction coordinates at transition states.

action coordinates) vibrational frequencies of 2292i and 2212i cm$^{-1}$, were comparable to each other. The transition states for these reactions are planar with both hydrogens on the same side of the SiO or CO bond axis. (ii) For the isomerization of the doubly bonded to the divalent species, reaction 2b is 54.2 kcal/mol endothermic while reaction 1b is only 2.2 kcal/mol exothermic. This small energy difference between $H_2Si{=}O$ and HSiOH is a distinct feature of silicon compounds. As for the divalent species, both HSiOH and HCOH were calculated to be 0.3 and 4.4 kcal/mol more stable in the *trans* conformer than in the *cis* form. The energies required from the *trans* to the *cis* forms were 9.5 and 28.0 kcal/mol for HSiOH and HCOH, respectively. (iii) As shown in Fig. 1, the isomerization of $H_2SiO$ to HSiOH(*trans*) prefers a non-planar transition state with the HOSiH dihedral angle of 116.5°, while the corresponding reaction of $H_2CO$ proceeds via a planar transition state. The imaginary frequencies of 1912i and 2705i cm$^{-1}$ calculated for these transition states indicate that the former reaction gives rise to the larger "width" of the barrier than does the latter. The barrier height for the isomerization $H_2SiO \rightarrow$ HSiOH(*trans*) is 26.2 kcal/mol smaller than that for $H_2CO \rightarrow$ HCOH(*trans*), but still as large as 60.3 kcal/mol. These values suggest that $H_2SiO$ is sufficiently stable to isomerization.

In Fig. 2 are shown the effects of fluorine substitution on the relative stabilities of silanones and hydroxysilylenes. It should be noted that the relative stabilities of the doubly bonded and the divalent species are dramatically reversed when hydrogens were replaced by fluorines. The effect of difluoro substitution is of special interest since it strongly stabilizes silanone relative to hydroxysilylene.

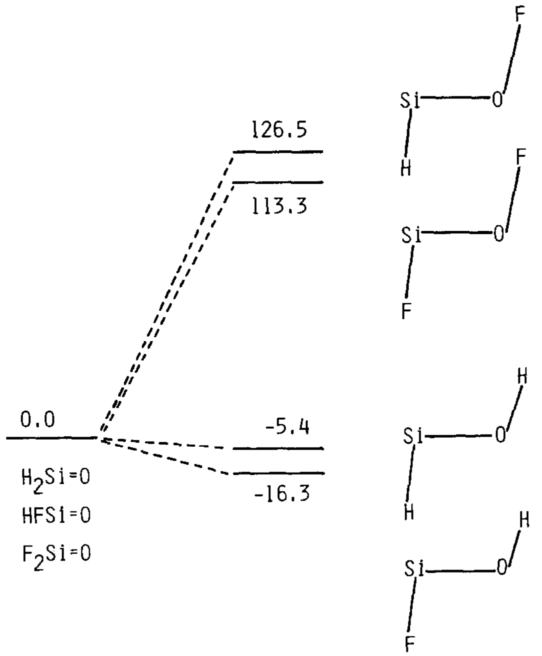

Fig. 2. Relative energies of silanones and hydroxysilylenes. Energies in kcal/mol are MP3(S+D)/6-31G$^{**}$// 3-21G values without zero-point correction.

In case of monofluoro substitution, HFSiO is more stable than HSiOF, but less stable than FSiOH. These effects of fluorine substitution are explained most probably in terms of the strength of the Si—F bonds. In addition, fluorine substitution causes the shortening of the silicon—oxygen double bond lengths (Å); 1.559 for $H_2SiO$, 1.542 for HFSiO and 1.534 for $F_2SiO$. Thus, it appears that fluorine substitution strengthens the Si=O double bond, as far as bond energy—bond length relationships are valid.

The present work predicts that silanone itself lies at the minimum of the potential energy surface and can be strongly stabilized in a thermodynamical sense with a proper choice of substituents. According to our preliminary calculations, however, silanone is even more reactive than are silene ($H_2Si{=}CH_2$) and disilene ($H_2Si{=}SiH_2$). In view of the interest in isolating a silicon—oxygen double bond, it is important to search for the substituents which reduce the high reactivity. A theoretical study along this line is in progress in our group.

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