

Theoretical Studies on the Abstraction Reaction of Atomic O (^3P) with Si_2H_6

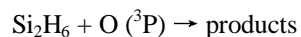
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Abstract: The hydrogen abstraction reaction of O (^3P) with Si_2H_6 has been studied theoretically. Two transition states of $^3\text{A}''$ and $^3\text{A}'$ symmetries have been located for this abstraction reaction. Geometries have been optimized at the UMP2 level with 6-311G+(d) basis set. G3MP2 has been used for the final single-point energy calculation. The rate constants have been calculated over a wide temperature range of 200~3000 K using canonical variational transition-state theory (CVT) with small curvature tunneling effect (SCT). The calculated CVT/SCT rate constants match well with the experimental value.

Keywords: O (^3P), disilane, *ab initio* calculation, variational transition state, rate constants.

Disilane is an important material in plasma chemical vapor deposition (CVD) and in semiconductor device process¹. The reaction of disilane with atomic oxygen is a likely initial step in systems where atomic oxygen is present, *e.g.* plasma enhanced CVD or photochemical vapor deposition (CVD) from $\text{Si}_2\text{H}_6/\text{N}_2\text{O}_3$ mixtures².



However, despite its importance, the kinetics work about this reaction was very limited. Only one experimental study is on record. In 1993, Taylor³ and his co-workers measured the rate constant of this reaction. The value is $(6.0 \pm 1.0) \times 10^{-12}$ ml molecule⁻¹ s⁻¹ at 295 K. To our best knowledge, little theoretical attention has paid to the reaction of O (^3P) with Si_2H_6 . We have initiated a theoretical study of the application of *ab initio* electronic calculations combined with the variational transition state theory for the hydrogen abstraction reaction of atomic O (^3P) with Si_2H_6 .

Computation Methods

Ab initio calculations have been carried out using Gaussian 94 programs. The geometries of the reactant, transition states and products have been optimized at the UMP2/6-311+G(d)

level. The vibrational frequencies have been calculated at the same level in order to determine the nature of different stationary points and the zero point energy (ZPE).

Although the geometrical parameters and the frequencies of various species can be determined satisfactorily at the UMP2/6-311+G(d) level, the energies obtained at this level may not be accurate enough for the subsequent kinetic calculations. Therefore, a reliable and inexpensive theory level, G3MP2⁴, was used in the energy calculation for the reaction of O with Si₂H₆. The rate constants were calculated using the variational transition state theory including the tunneling effects. All the kinetic calculations have been carried out using the POLYRATE 7.8 program.

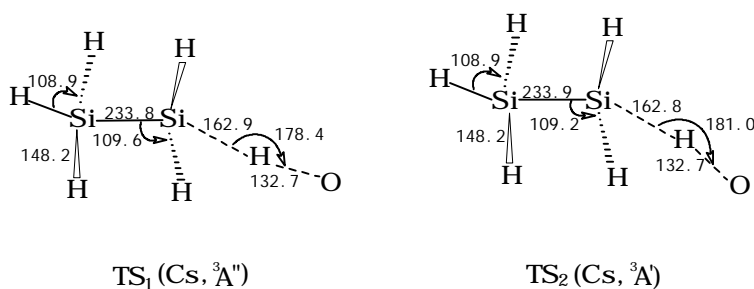
Result and Discussion

Reaction mechanism

The reactant disilane has two geometries: the staggered and the eclipsed. The energy of the eclipsed is 3.75 kJ/mol higher than that of the staggered at the G3MP2//UMP2/6-311+G(d) level. So in this paper the staggered configuration is regarded as the stationary geometry of disilane.

The hydrogen abstraction reaction of O (³P) with Si₂H₆ proceeds over two potential energy surfaces (PESs), ³A' + ³A'', generated by the Jahn-Teller effect. At UMP2/6-311+G(d) level, two transition states with ³A'' and ³A' symmetries were located whose geometrical structures are shown in **Figure 1**. Population analysis shows that the half-filled p-orbital of the ³A'' symmetry is in the SiSiHO plane and the half-filled p-orbital of the ³A' symmetry is perpendicular to this plane.

Figure 1 UMP2/6-311+G(d) optimized geometries for the transition states



Distance is in pm and angle is in degree.

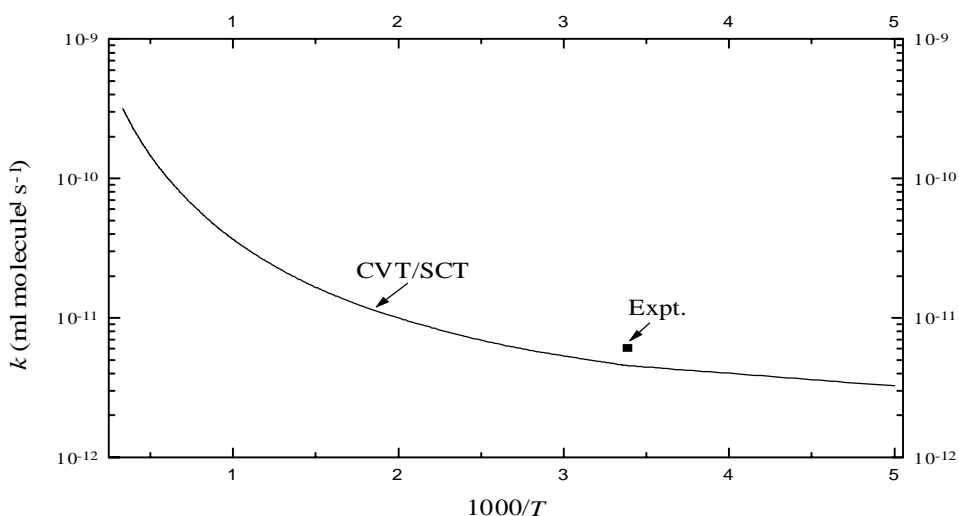
The two transition states have nearly identical geometries except for the orientation angle of Si-H-O. The O (3P) atom abstracts one of the H atoms of Si₂H₆ either from the *trans*-position via TS₁ on the $^3A''$ surface or from *cis*-position via TS₂ on the $^3A'$ surface. The breaking Si-H bonds are elongated by 9.8%, while the forming O-H bonds are longer than the equilibrium value of 97.00 pm by 36.8% for the transition states of $^3A''$ and $^3A'$ symmetries. Therefore, these two transition states are reactant-like, and the H abstraction reactions from Si₂H₆ by O atom via early transition states. The rather early character of these transition states is in accordance with the low reaction barriers and the high exothermicities of this reaction, and is in accordance with Hammond's postulate⁵. At the G3MP2 level, the potential barriers are 12.68 and 19.12 kJ/mol for the $^3A''$ and $^3A'$ surfaces, respectively.

At UMP2/6-311+G(d) level, both transition states have one and only have one imaginary frequency; the values of the imaginary frequencies are large, which implies that the quantum tunneling effect may be significant and may play an important role in the calculation of the rate constants.

The kinetic calculation

The kinetic natures for the $^3A''$ and $^3A'$ surfaces have been calculated independently. In order to calculate the rate constants, 30 points near the transition state region along MEP were selected ----15 points in the reactant zone and 15 points in the product zone.

Figure 2 Rate constants as function of the reciprocal of the temperature



(T) in the temperature range of 200~3000K for the whole reaction of O (3P) with Si₂H₆. the experimental value.

Figure 2 shows the total rate constant, which are obtained from the sum of the calculated CVT/SCT rate constants for the $^3A''$ and $^3A'$ surfaces, and the experimental values against the reciprocal of the temperature for the reaction of O (3P) with Si_2H_6 . It is obvious that the calculated CVT/SCT rate constants exhibit typical non-Arrhenius behavior. Therefore, a three-parameter formula is fitted in units of $mL\ molecule^{-1}\ s^{-1}$ as follows: $k(T) = 1.53 \times 10^{-17} T^{2.25} \exp(-834.32/T)$

Comparing the calculated value with the limited experimental result for the title reaction, it can be seen that the CVT/SCT rate constant is in good agreement with the experimental value at 295 K. This good agreement testifies that the hydrogen abstraction mechanism is reasonable for this reaction. No other addition product such as 3OSi_2H_6 structure, or insertion products such as 3H_3SiOSiH_3 or 3Si_2H_5OH , were located, so that at present *ab initio* theory supports abstraction as the main reaction mechanism in accord with the recommendation of Taylor³.

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