Theoretical Study on the Structures and Stability of Isomers and Complex of [Si, C, O, O] System

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A detailed singlet potential energy surface (PES) of [Si, C, O, O] system including a van der Waals (vdW) complex SiO···CO, eight isomers, and twelve transition states is investigated by MP2 and QCISD(T) (single-point) methods. At the final QCISD(T)/6-311+G(2df)//MP2/6-311G(d) level with zero-point energy included, the complex SiO···CO is found to be thermodynamically and kinetically the most stable species. Although eight isomers are located as local energy minima, they are rather unstable toward isomerization to the dissociation fragments or complex. For the reaction of silicon atoms with carbon dioxide, two competitive reaction channels are found, and the primary pathway, which leads to the products of SiO and CO fragments, is the direct oxygen-abstraction process from carbon dioxide by silicon atom with a 41.16 kJ/mol reaction barrier height. Our predications are in good agreement with previous experimental and theoretical studies.

Keywords potential energy surface, [Si, C, O, O] system, isomerization, stability

Introduction

[Si, C, O, O] system has attracted much attention in the fields of chemistry and materials[1-3] because of the following several causes. First, the interest is the potential importance in interstellar space. Heretofore, SiC, SiO and CO have been detected within the interstellar medium for many years, but no [Si, C, O, O] isomers were observed in the nebulae. For many Si-containing systems have been studied experimentally and theoretically,[4-8] and in view of the possible existence of the [Si, C, O, O] radical in interstellar space, we select the study in order to predict the isomer structures and their relative stability by means of theoretical methods. Second, silicon and some silicon-containing species are very significant in semiconduct and ceramic materials, and their interactions with CO_2 play an important role in the chemical vapor deposition (CVD). The reaction of silicon with CO_2 has been experimentally reported by Mick and Husain,[2,3] and in this paper we will predict the reaction mechanism by means of quantum chemistry methods. And last, [Si, C, O, O] system is isovalent to carbon monoxide dimer $(CO)_2$ and silicon monoxide dimer $(SiO)_2$. In this sense, [Si, C, O, O] system is a bridge between $(CO)_2$ and $(SiO)_2$ with intermediate physical properties. A large number of theoretical and experimental studies have dealt with the structures and spectroscopies of the dimer of CO.[9-14] These studies support the existence of a loosely bound van der Waals (vdW) dimer with a planar structure. But for dimer of SiO, many theoretical and experimental studies[15-19] support the assignment of a cyclic dimer in which the silicon and oxygen atoms are arranged alternately. No low-lying cyclic isomers in $(CO)_2$ and no vdW dimer in $(SiO)_2$ were located in corresponding potential energy surface. Then, some differences between the analogous $(CO)_2$ and $(SiO)_2$ radicals are expected to exist. Therefore, the studies on the potential energy surface of [Si, C, O, O] system are helpful not only for predicting the possible isomers and their relative stability but also for understanding the nature of the bonding in $(CO)_2$ and $(SiO)_2$.

Despite the potential importance, however, to our knowledge, there is only a literature report on the theoretical study of [Si, C, O, O] system by Zhang and co-worker.[1] Their study predicted a van der Waals complex SiO···CO as the most stable species on the singlet potential surface. Our goal in present work is to perform a theoretical computation on the potential energy surface of singlet [Si, C, O, O] system, and predict the possible isomers, their relative stability, and isomerizations.

Computational methods

All computations were carried out using the GAUSSIAN98 program package.[20] The geometries for all stationary points were optimized at the MP2/6-311G(d) level of theory[21,22] followed by the frequency analyses in order to charac-

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terize these calculated stationary points as minima or transition states. Moreover, single-point calculations were performed at QCISD(T)/6-311 + G(2df) level of theory[23,24] using the MP2/6-311G(d) optimized geometries. The zero-point vibrational energy (ZPVE) at MP2/6-311G(d) level was also included in the single-point energy. In order to confirm whether the obtained transition states connect with the right reactants and products, the intrinsic reaction coordinate (IRC)[25,26] calculations were performed at the MP2/6-311G(d) level of theory.

Results and discussion

Structures of isomers and complex

The optimized geometry parameters of eight [Si, C, O, O] isomers and a vdW complex at MP2/6-311G(d) level of theory are shown in Fig. 1.

The species **1**, a vdW complex of SiO and CO, is found to be thermodynamically the most stable species on the singlet potential energy surface, and it is in good agreement with reported $(CO)_2$ complex in which two moieties form an angle between a T-shaped and a parallel configuration.[1] But many investigations indicated that Si_2O_2 has a rhombic structure in which the silicon and oxygen atoms are arranged alternately.[15-19] Species **1** is lower in energy than the dissociation fragments $SiO(^1\Sigma)$ + $CO(^1\Sigma)$ by 16.37 kJ/mol, while it lies 341.81 kJ/mol below $Si(^1D)$ + $CO_2(^1\Sigma)$. The result that indicates **1** a weak vdW species is in agreement with previous theoretical study by Zhang and co-worker.[1] When we tried to optimize a possible *trans*-SiOCO chainlike isomer, we obtained the second low-lying species **2**, which is a COSi three-membered ring planar structure, and is 127.99 kJ/mol higher in energy than the vdW species **1**. The SiO bond distance (0.17240 nm) in **2** is slightly longer than that in $HOSiH_3$ molecule (0.16556 nm at MP2/6-311G(d) level), thus it can be considered as a weak single bond. Furthermore, it is noted that the Si—C bond distance (0.18437 nm) in **2** is longer than that in H_2SiCH_2 (0.17107 nm at MP2/6-311G (d) level) and shorter than that in H_3SiCH_3 (0.18775 nm at MP2/6-311G(d) level), and while, we can regard the SiC bond in **2** as an intermediate between single and double bond. When we attempt to optimize a planar chainlike *cis*-SiOCO isomer, a SiOCO four-membered ring form with C_{2v} symmetry is located on the potential energy surface. But frequency analysis indicates an imaginary vibrational frequency (at 151.93 cm^{-1}), and the relaxation of C_{2v} symmetry leads to butterfly-form isomer **3** with $^1A'$ electronic state. The quasiplane isomer **3** with C_s symmetry has a SiOCO four-

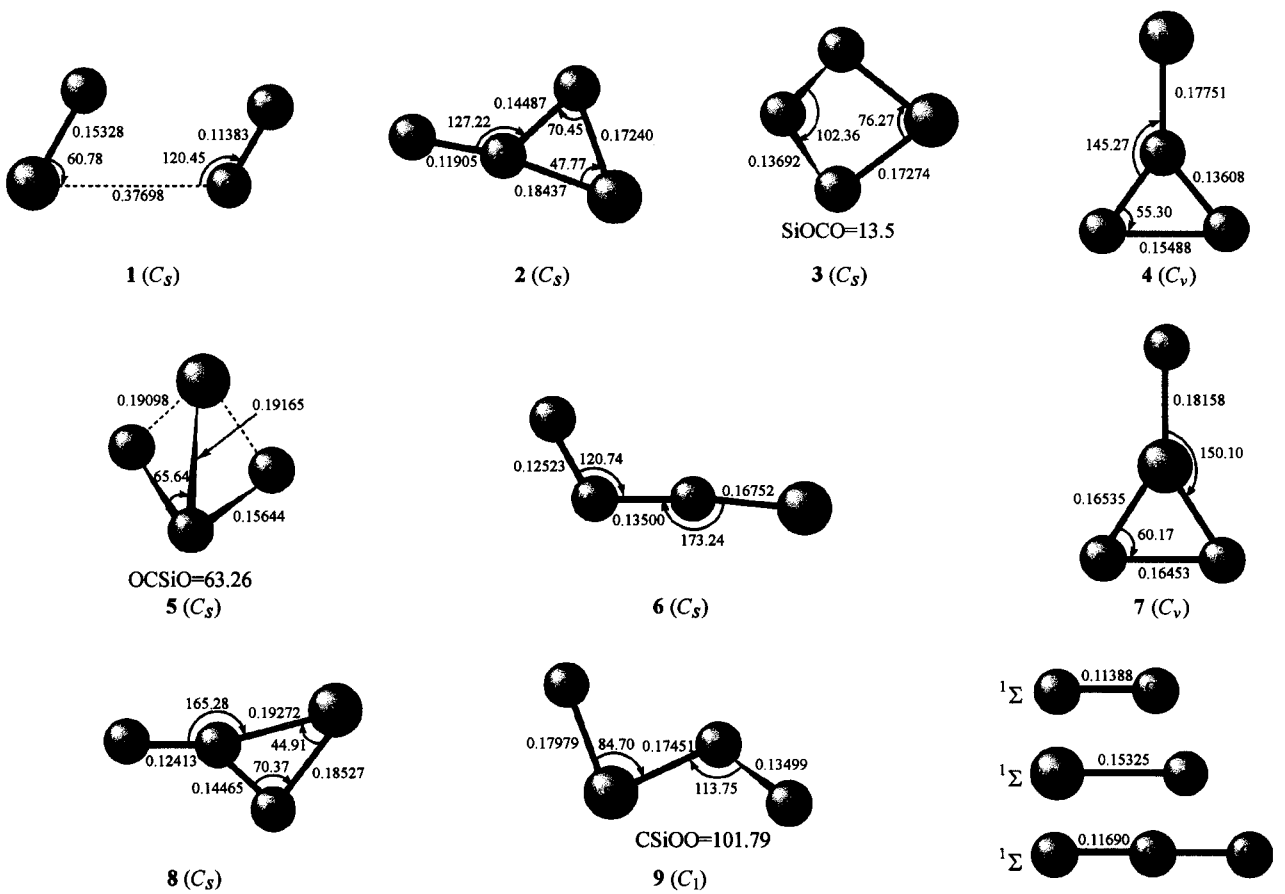

Fig. 1 Calculated structures of complex and isomers of [Si, C, O, O] system at MP2/6-311G(d) level of theory. Bond lengths are in nanometers, and bond angles in degrees.

membered ring, and the SiOCO dihedral angle is only 13.50°. In Si_2O_2 isomers, there is also a SiOSiO four-membered ring isomer, but it is planar. No isomer containing COCO four-membered ring was found in previous studies. Species **4** is a planar SiC(O)O isomer which has C_{2v} symmetry with exocyclic CSi bonding, and it is higher in energy than **1** by 645.10 kJ/mol. The Si—C bond distance in **4** is 0.17751 nm, which indicates that the Si—C bond is an intermediate between Si—C single and double bond. And thus, the species can not be regarded as a complex of Si and CO_2, but an isomer. Isomer **5** is 695.22 kJ/mol higher in energy than **1**, and it has a typical butterfly structure with C_s symmetry. The SiC and SiO bond lengths, which are 0.19165 nm and 0.19098 nm, respectively, are slightly longer than normal values. Similar butterfly-structure isomer was also found in $(SiO)_2$, but no such isomer was located on the potential energy surface of $(CO)_2$ in previous theoretical studies. Isomer **6** that has a SiCOO chainlike structure is higher in energy than **1** by 753.71 kJ/mol. In **6**, Si, C, and O atoms are almost co-linear, and the bond angle of OOC is 120.74°. When we again optimize the structure in which Si, C, O, and O are co-linear, we locate a stationary point, which has an imaginary vibrational frequency at 628.87 cm^{-1}. It indicates that the linear structure is a saddle point on the singlet potential energy surface. The relaxation of symmetry leads to bent form local minimum **6** with all real frequencies. No such CCOO or SiSiOO chainlike isomers were found in previous experimental and theoretical studies. The species **7** can be described as SiOO three-membered ring structure with C_{2v} symmetry and exocyclic SiC bonding. The difference between **7** and **4** is that the atom connecting with oxygen atoms is carbon in **4**, but it is silicon atom in **7**. Species **7** is higher in energy than **1** and **4** by 807.88 kJ/mol and 162.78 kJ/mol, respectively. The calculated results show that CO bonding in **4** is more favorable in energy than SiO bonding in **7**. The Si—C bond length is longer in **7** than that in **4** by 0.00407 nm. Furthermore, the SiC bond length in **7** is 0.18158 nm, as discussed in **2**, it is an intermediate between single and double bond. The species **8** with C_s symmetry is a SiCO three-membered ring form and is predicted to be local minimum on the potential energy surface with all real vibrational frequencies. Species **8** is higher in energy than **1** by 874.92 kJ/mol. The SiO and SiC bond lengths in SiCO three-membered ring of **8** are longer than those in **2** by 0.01032 nm and 0.00090 nm, respectively. Because the SiO bond distance is 0.19272 nm, which is somewhat longer than Si—O single bond length in $HOSiH_3$, the SiCO three-membered ring has a trend of ring-open process from SiO bond rupture. Isomer **9** containing a CSiOO chain has C_1 symmetry, and it is 982.73 kJ/mol higher in energy than isomer **1**. In a view of rather high energy, we did not work on its bonding further.

From calculated results, we can obtain the energetic ordering of the optimized [Si, C, O, O] local energy minima. Generally, the species with lower total energy has higher thermodynamical stability. At the single-point QCISD(T)/6-311+G(2df) level with zero-point energy correction, the thermodynamical stability order is **1** (0.00) > **2** (127.99) > **3** (168.14) > **4** (645.10) > **5** (695.22) > **6** (753.71) > **7** (807.88) > **8** (874.92) > **9** (983.73). The values in parentheses are relative energies in kJ/mol with reference to **1**. It is clear that **1** is thermodynamically the most stable species. Three-membered ring isomer **2** and butterfly-structure species **3** are also low-lying. The chainlike isomers **6** and **9**, three-membered ring isomers **4**, **7**, and **8**, and butterfly-structure species **5** are very high lying.

Kinetic stability and comparison with experiments

Let us turn to the kinetic stability of various [Si, C, O, O] species. Twelve transition states of [Si, C, O, O] system are obtained at MP2/6-311G(d) level of theory, and their structures are showed in Fig. 2. Their connections are checked by IRC calculations at MP2/6-311G(d) level. **TS*m*/*n*** denotes the transition states connecting the species ***m*** and ***n***. By means of the isomers, vdW species, dissociation fragments and transition states, a schematic potential energy surface is plotted in Fig. 3. For simplicity, the details of the obtained twelve transition states are omitted. The possible dissociation fragments SiO ($^1\Sigma$) + CO ($^1\Sigma$), Si (^{1}D) + CO_2 ($^1\Sigma$), and Si (^{3}P) + CO_2 ($^1\Sigma$) are also shown on the potential energy surface.

In fact, we can briefly discuss the kinetic stability of the obtained isomers in terms of the smallest isomerization or dissociation energies. From Fig. 3, we can see that all high-lying species can convert to the lowest-energy vdW **1** [or dissociation fragment SiO ($^1\Sigma$) + CO ($^1\Sigma$)] via one or more pathways. The lowest-lying vdW **1** is kinetically the most stable species with the smallest barrier 129.08 kJ/mol for **1**→**2** conversion. Thus, the lowest-lying vdW **1** is kinetically stable. The remaining isomers **2**, **3**, **4**, **5**, **6**, **7** and **8** may be considered as kinetically unstable towards isomerization or dissociation since the corresponding smallest barriers are just 1.09 (**2**→**1**), 24.83 (**3**→SiO + CO), 84.74 (**4**→Si + CO_2), 37.47 (**5**→**1**), 53.51 (**6**→**1**), 57.28 (**7**→**4**), and 23.15 (**8**→**6**) kJ/mol. For isomer **9**, it is somewhat abnormal in energy. Species **9** can isomerize into **4** via transition state **TS4/9** by a 4.44 kJ/mol isomerization barrier at MP2/6-311G(d) level with zero-point vibrational energy inclusion. But at QCISD(T)/6-311+G(2df)//MP2/6-311G(d) level with zero-point vibrational energy correction, **TS4/9** is 20.43 kJ/mol below isomer **9**. We believe that it is kinetically unstable isomer, and in view of the rather high energy (983.73 kJ/mol), we expect it to be of minor importance.

It is worth mentioning that although the cyclic isomer **2** and butterfly-structure isomer **3** are 517.11 and 476.69 kJ/mol lower in energy than the isomer **4**, they are rather unstable toward isomerization to the most stable vdW species **1** and SiO + CO fragments with only 1.09 and 24.85 kJ/mol, respectively, *i. e.*, they are kinetically more unstable than isomer **4**. Furthermore, the system [Si, C, O, O] has no

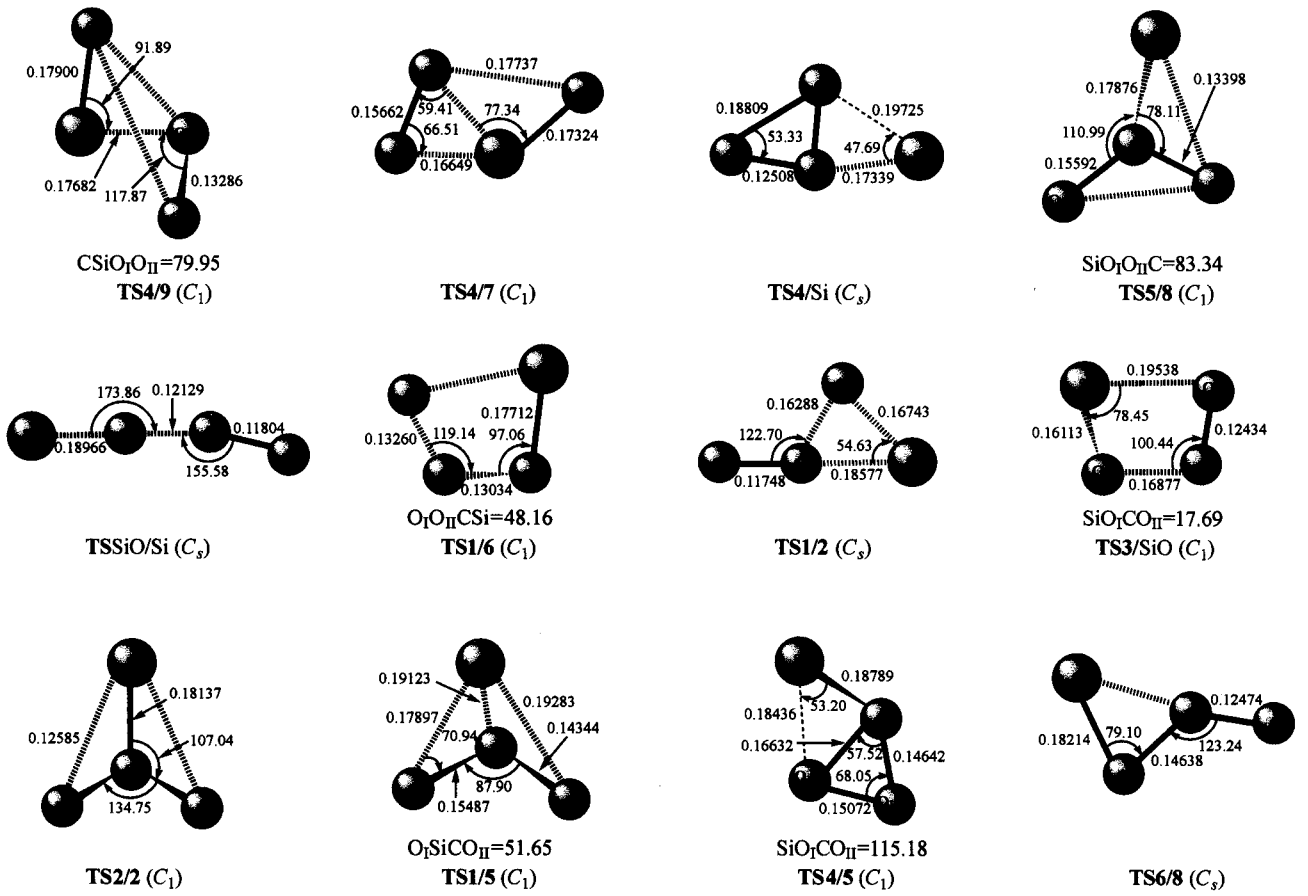

Fig. 2 Predicted structures of transition states of [Si, C, O, O] system at MP2/6-311G(d) level of theory. Bond lengths are in nanometers, and bond angles in degrees.

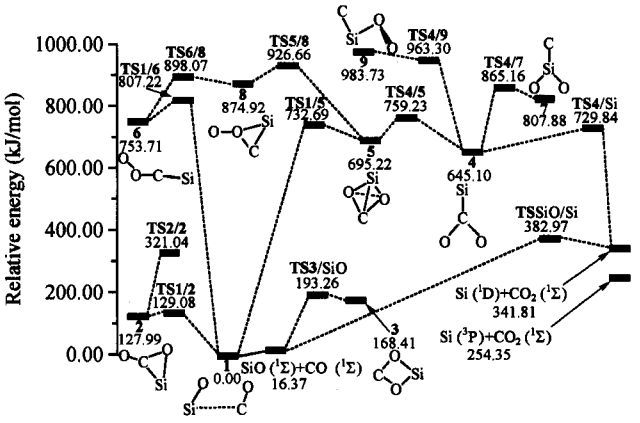

Fig. 3 Schematic potential energy surface of [Si, C, O, O] system at QCISD(T)/6-311+G(2df)//MP2/6-311G(d) level of theory with zero-point energy correction.

chainlike isomers that could be kinetically stabilized, although two chainlike forms are located as energy minima. It should be pointed out that transition state **TS4/7** is surprising in structure, but IRC calculations indicated that **TS4/7** connects actually species **4** with **7**. We have attempted to locate the O-shift transition state from **8** to **2** that is expected to have lower barrier. Yet, it does not succeed at the MP2/6-311G (d) level. We also expected to have a transition state that connects **4** with **2** via a simple interconversion with a lower barrier, but all attempts failed, and a large number of optimizations of the conversion transition state often lead to the saddle point **TS2/2**.

We discuss possible channels in the reaction of silicon atoms with carbon dioxide. The reaction of Si atoms with CO_2 was studied by means of Si atom absorption measurements in shock tube experiment by Mick and co-corker.[2] In fact, the reaction, Si (^{3}P) + CO_2 ($^1\Sigma$) $\longrightarrow$ SiO ($^1\Sigma$) + CO ($^1\Sigma$), is a spin-forbidden process. Calculated reaction enthalpy is about 237.98 kJ/mol at single-point QCISD(T)/6-311+G(2df) level, which is in good agreement with the experimental value 239.07 kJ/mol.[3] Based on the potential energy surface, we can see that there are two reaction channels from reactants silicon (^{1}D electronic state, and we do not discuss possible surface crossing processes) and carbon dioxide. One is direct reaction of silicon atoms with carbon dioxide via transition state **TS4/Si** by a 388.03 kJ/mol reaction barrier height, and this process will lead to the formation of isomer **4**. Another reaction channel is the direct abstraction process of oxygen atom from CO_2 molecule by Si atom via transition state **TSSiO/Si** with only 41.16 kJ/mol reaction barrier height, and the products are SiO and CO fragments followed by the formation of the vdW species **1**. The second pathway is more favorable in energy than the first channel. Thus, the predicted products in the reaction of silicon atoms with carbon dioxide by means of theoretical methods are

SiO + CO and vdW species **1**. This is in good agreement with Mick and Husain's experiments.[2,3] The fragments SiO + CO is slightly higher in energy than the vdW complex **1** by 16.37 kJ/mol, which indicates that the total energy of system reduces in the formation process of complex **1** by the interaction of SiO and CO.

Conclusions

(1) Potential energy surface of [Si, C, O, O] system is investigated at MP2/6-311G(d) and QCISD(T)/6-311 + G(2df)(single-point) levels. The vdW complex SiO···CO is predicted to be thermodynamically and kinetically the most stable species in [Si, C, O, O] system. No kinetically stable isomers of [Si, C, O, O] system are found, although eight isomers are located as energy minima on the singlet potential energy surface.

(2) The direct oxygen-abstraction reaction from carbon dioxide by silicon with 41.16 kJ/mol barrier is the primary channel in the reaction of silicon atoms with carbon dioxide.

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