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Theoretical study of the reaction of Ti^+ with SCO in gas phase

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Abstract

The quartet and doublet potential energy surfaces for the reaction of $Ti^+ + SCO$ have been calculated at the UQCISD(T)/6-311+G*//UB3LYP/6-311+G* level of theory. The present results show that the reaction mechanism is insertion–elimination mechanism both along the C–S and C–O bond activation branches, but the C–S bond activation is much more favorable than the C–O bond activation in energy. The minimum energy reaction path is found to involve the spin inversion in the reaction steps. Specifically, the reaction is most likely to proceed through the following steps: $^4Ti^+ + SCO \rightarrow {}^4IM1 \rightarrow CP1 \rightarrow {}^2IM2 \rightarrow {}^2TiS^+ + CO$. The overall reaction is calculated to be exothermic by 98.2 kJ/mol, which is in good agreement with the available experimental results.

Keywords: DFT theory; Potential energy surface; Transition-metal; SCO

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1. Introduction

Because the importance in the areas of catalysis [1–3], biochemistry [4,5], and material science [6], the thermochemistry of transition metal sulfide systems has been an active area for both experimental [8–13] and theoretical studies [16–36]. As important sulfur-transfer reagents, CS_2 and SCO have been shown to be very reactive toward transition-metal centers and can undergo a variety of reactions such as coordination, insertion, etc. [7]. Recently, Schwarz's and Amentrout's working groups have reported the experimental study of the reaction Ti^+ with SCO to obtain the accurate bond-dissociation energies of titanium sulfides by using Guided Ion Beam Mass Spectrometer [11]. In this reaction, TiS^+ and TiO^+ are found to be dominant products at the low energy condition, and they proposed the reaction could proceed in an insertion–elimination mechanism.

The previous theoretical studies of the reactivity of M^+ ($M = V^+$, Fe^+) toward CS_2 [16,17] provided that the reaction could proceed in an insertion–elimination mechanism. Because there are both C–S bond and C–O bond in SCO molecule, whereas only C–S bond exists in CS_2, so the reaction of M^+ with SCO may be more complicated than that with CS_2.

On the other hand, it is well known by now that transition-metal-mediated reactions very often occur on more than one adiabatic potential energy surface, denoted as "two state reactivity" (TSR) [37–41]. A number of reactions in organic, inorganic, and especially organometallic chemistry in which two states of different multiplicities are involved on the reaction pathway have been confirmed by experimental studies [42]. But experiments can not determine where the spin inversions occur, as well as the information of the energies and geometries at crossing points between the two different potential energy surfaces. So confirmation of the relevant mechanism needs the assistance of theory. The reaction mechanism provided by the previous theoretical studies of the reaction of M^+ ($M = Fe, Co$) with SCO is insertion–elimination mechanism along the C–S bond or C–O bond activation branch [20,21]. But these calculations did not discuss the TSR in detail. For the reactivity of Ti^+ toward SCO [11], although accurate thermochemical data have been provided by experimental

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study, the detailed information of the potential energy surface is still scarce. So we present here a theoretical study of the reactivity of Ti^+ with SCO to gain systematic insight into the mechanism of the reaction of first-row transition-metal ions with SCO. To better understand the spin inversion processes during the reaction, we determine the structures and energies of the crossing points between two PESs of different spin multiplicities on the reaction pathway. Our calculations lead to a generalized mechanism for the reaction of M^+ towards SCO in the gas phase.

2. Computational methods

All molecular geometries were optimized at UB3LYP/6-311+G* level [43–45]. This method is chosen in this study since the previous calibration calculations on transition-metal compounds have shown that this hybrid functional provides accurate results for the geometries and vibrational frequencies of systems containing transition-metal ions [46,47]. We inspected the values of $\langle S^2 \rangle$ for all species involved in the reaction of Ti^+ toward SCO, and found that the deviation of $\langle S^2 \rangle$ is less than 5%, which indicates that the spin contaminations were small in all of the calculations. The harmonic vibration analyses were performed at the same level of theory for all optimized stationary points to determine their characters (minimum or first-order saddle point) and to evaluate the zero-point vibrational energies (ZPEs). To verify whether the located transition states connect the expected minima, intrinsic reaction coordinate (IRC) calculations were carried out for each transition state at the same level [48–50]. To obtain accurate reaction enthalpies and barrier heights, we performed the UQCISD(T)/6-311+G* single-point calculations using the UB3LYP/6-311+G*-optimized geometries. All calculations in the present study were performed using the Gaussian 03 program [51].

3. Results and discussion

The quartet and doublet PESs for the reaction of Ti^+ with SCO have been considered in detail. The optimized geometries of the stationary points and structures of the crossing points are depicted in Fig. 1. The potential energies curve-crossing diagrams between the quartet and doublet potential energy surfaces are drawn in Figs. 2 and 3. The theoretical and experimental bond dissociation energies of some species are compared in Table 1. The relevant energies and harmonic vibrational frequencies of various compounds in the reaction are listed in Tables 2 and 3, respectively, and the profiles of the PES are shown in Fig. 4.

3.1. Evaluation of the computational accuracy

We have first calculated the bond dissociation energies (BDE) for several species involved in the reaction of $Ti^+ + SCO$ system at the UB3LYP/6-311+G* and the UQCISD(T)/6-311+G*//UB3LYP/6-311+G* level of theory respectively, to evaluate the reliability of the chosen method. As shown in Table 1, where some available experimental values are also listed for comparison. By comparing these theoretical values with experimental findings, we found that UQCISD(T)/6-311+G* //UB3LYP/6-311+G* method gave relatively smaller absolute errors than UB3LYP/6-311+G* method, most of the theoretical values are in agreement with experimental findings, the discrepancies of relative energies are between 0.1 and 0.4 eV for all species. In addition, our main goals are to examine the detailed mechanism of the reaction and obtain the relative energy levels of the species involved in the present work, so the theoretical level chosen in this work is reliable of describing the features of the PES of $Ti^+ + SCO$.

3.2. C–S bond activation (quartet PES)

The reaction starts with the formation of the S-bound encounter complex ^{4}IM1 ($^4A''$, C_S), which is 86.7 kJ/mol below the entrance channel $Ti^+(^4F) + SCO$. Starting from ^{4}IM1, it can rearrange to form ^{4}IM2, which undergoes a rupture of C–S bond via a transition state $^4TS_{12}$ that is 29.8 kJ/mol above ^{4}IM1. As shown in Fig. 1, the distance between Ti and S in $^4TS_{12}$ is shortened by 0.1383 Å. This fact indicates that the weak electrostatic interaction between Ti^+ and SCO has strengthened when it is converted into $^4TS_{12}$, and the Ti–S bond is nearly formed. The distance between Ti and C is shortened from 2.4020 to 2.2004 Å, which suggests that the Ti–C bond is forming. At the same time, the activated C–S bond is almost broken, and the bond length is elongated by 0.6105 Å. The imaginary frequency of $^4TS_{12}$ is 465i cm^{-1}, and the normal mode corresponds to the rupture of C–S bond and the formations of Ti–S and Ti–C bonds.

For the inserted intermediate ^{4}IM2, its ground state is $^4A'$ with C_S symmetry, which is 1.7 kJ/mol above the encounter complex ^{4}IM1 and 85.0 kJ/mol lower in energy than the reactants $^4Ti^+$ + SCO, As shown in Fig. 1, the C–S bond length in ^{4}IM2 is elongated to 3.5970 Å, which means this bond has ruptured thoroughly. The ^{4}IM2 insertion species can dissociate without exit barrier to products $^4TiS^+ + {}^1CO$ and $^2TiCO^+ + {}^3S$, endothermic by 74.0 and 329.0 kJ/mol, respectively. Obviously, the energetically more favorable channel is to form the dissociation products of $^4TiS^+ + {}^1CO$ through cleavage of Ti–C bond. The overall reaction for $Ti^+(^4F) + SCO(^1\Sigma) \rightarrow {}^4TiS^+(^4\Sigma) + {}^1CO$ is calculated to be exothermic by 11.0 kJ/mol on UQCISD(T)/6-311+G*//UB3LYP/6-311+G* level.

3.3. C–S bond activation (doublet PES)

Next let us turn to the doublet PES, as depicted in Fig. 4(a). Different from that of quartet path, the first step of the reaction on the doublet path is the formation of the inserted complex ^{2}IM2 ($^2A''$, C_S) directly, exoergic by 278.2 kJ/mol, which is a barrierless process. This result