

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

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Abstract

In order to elucidate the mechanism of reaction $\text{M}^+ + \text{SCO}$, both triplet and singlet potential energy surfaces (PESs) for the reaction of $\text{Sc}^+ + \text{SCO}$ have been theoretically investigated using the DFT (B3LYP/6-311+G*) level of theory. The geometries for reactants, intermediates, transition states and products were completely optimized. All the transition states were verified by the vibrational analysis and the intrinsic reaction coordinate calculations. The involving potential energy curve-crossing dramatically affects reaction mechanism, reaction rate has been discussed, and the crossing points (CPs) have been localized by the approach suggested by Yoshizawa et al. The present results show that the reaction mechanism are insertion–elimination mechanism both along the C–S and C–O bond activation branches, but the C–S bond activation is much more favorable in energy than the C–O bond activation. All theoretical results not only support the existing conclusions inferred from early experiment, but also complement the pathway and mechanism for this reaction. © 2006 Elsevier B.V. All rights reserved.

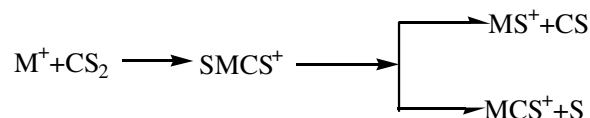
Keywords: DFT theory; Potential energy surface; Transition-metal; SCO

1. Introduction

The chemistry of transition-metal sulfides plays a very important role in catalysis, biochemistry, and material science [1]. In industrial areas, transition-metal sulfides are widely used in lubrication and catalysis [2,3]. In many biological systems, it has been found that sulfur coordination is necessary for the functioning of numerous biological transition-metal centers [4,5]. In addition, considerable attention has been focused on their higher selectivity [6]. CS_2 and SCO are important sulfur-transfer reagents, which have recently been considered as possible sulfur sources for preparing thin layers of semiconductor materials [7]. In fact, the thermochemistry of transition-metal sulfide systems has been an active area for both experimental and theoretical studies [8–20]. Recently, Amentroust's working group has examined the reaction of Sc^+ with SCO using Guided Ion Beam Mass Spec-

trometer [11], where metal sulfide bond energies were determined. In this reaction, ScS^+ and ScO^+ are found to be dominant products at the low energy condition, and they proposed the reaction could proceed in an insertion–elimination mechanism.

In the previous theoretical studies of the reactivity of M^+ ($\text{M} = \text{V}^+, \text{Fe}^+$) toward CS_2 [13,14], all experimentally observed results had been rationalized, and the reaction could proceed in an insertion–elimination mechanism described as follows:



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 . In addition, the C–S bond energy (3.74 eV) is

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lower than the C–O bond energy (6.88 eV) in SCO molecule [21], which indicates that the C–S bond is weaker than C–O bond, specifically, the activation of C–S bond is energetically much more favorable than that of the C–O bond activation.

On the other hand, the reactions catalyzed by organometallic systems may involve a change in the spin states and thus proceed via a non-adiabatic way on two or more potential energy surfaces [22–24], denoted as “two state reactivity” (TSR) [25], which has been confirmed by experimental studies. But experiments cannot 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^+ ($M = \text{Fe}, \text{Co}$) with SCO is insertion–elimination mechanism along the C–S bond or C–O bond activation branch [17,18]. But these calculations did not discuss the TSR in detail. For the reactivity of Sc^+ with SCO [8], although the experimental study has provided accurate thermochemical data, the detailed information of the potential energy surface is still scarce. To gain systematic insight into the mechanism of the reaction of first-row transition-metal ions with SCO, we present here a theoretical study of the reaction of Sc^+ with SCO. A possible reaction pathway and mechanism are proposed and the structures and energies of the stationary points involved in the reaction are examined and discussed. 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

Both the triplet and singlet PESs for the reaction Sc^+ with SCO have been considered in detail. All molecular geometries (reactants, intermediates, transition states and products) were fully optimized at UB3LYP/6-311+G* level [26–28]. 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 transitional metal ions [29,30]. We inspected the values of $\langle S^2 \rangle$ for all species involved in the reaction of Sc^+ toward SCO, and found that the deviation of $\langle S^2 \rangle$ is less than 3%, 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 [31,32]. All calculations in the present study were performed using the Gaussian 03 program [33].

3. Results and discussion

The optimized geometries of the stationary points and structures of the crossing points on the triplet and singlet PESs for the reaction of Sc^+ with SCO are depicted in Fig. 1. The potential energies curve-crossing diagrams between the triplet and singlet potential energy surfaces are drawn in Fig. 2. The relevant energies of various compounds in the reaction are listed in Table 1, and the profiles of the PES are shown in Fig. 3.

3.1. C–S bond activation (triplet PES)

The energy of ground state Sc^+ ($4s^1 3d^1$, 3D) is lower than the excited state ($4s^0 3d^2$, 1G) by 35.8 kcal/mol on the UB3LYP/6-311+G* level, so the reaction between ground state $\text{Sc}^+(^3D)$ and SCO is more favorable at low energy condition.

The reaction starts with the formation of the S-bound encounter complex $^3IM1(^3A'', C_s)$, which is 20.8 kcal/mol below the entrance channel $\text{Sc}^+(^3D)+\text{SCO}$. Starting from 3IM1 , it can rearrange to form 3IM2 , which undergoes a rupture of C–S bond via a transition state $^3TS_{12}$ that is only 5.6 kcal/mol above 3IM1 . As shown in Fig. 1, the distance between Sc and S in $^3TS_{12}$ is shortened by 0.092 Å. This fact indicates that the weak electrostatic interaction between Sc^+ and SCO has strengthened when it is converted into $^3TS_{12}$, and the Sc–S bond is nearly formed. The distance between Sc and C is shortened from 2.326 Å to 2.245 Å, which suggests that the Sc–C bond is forming. At the same time, the activated C–S bond is almost broken, and the bond length is elongated by 0.482 Å. The imaginary frequency of $^3TS_{12}$ is 272i cm^{-1} , and the normal mode corresponds to the rupture of C–S bond with the result of Sc^+ insert into C–S bond.

For the inserted intermediate 3IM2 , its ground state is $^3A'$ with C_s symmetry, which is 0.9 kcal/mol more stable than the encounter complex 3IM1 and 21.7 kcal/mol lower in energy than the reactants $^3\text{Sc}^+ + \text{SCO}$. As shown in Fig. 1, the C–S bond length in 3IM2 is elongated to 3.459 Å, which means this bond has ruptured thoroughly. The 3IM2 insertion species can dissociate without exit barrier to products $^3\text{ScS}^+ + ^1\text{CO}$ and $^3\text{ScCO}^+ + ^1\text{S}$, endothermic by 42.3 kcal/mol and 107.0 kcal/mol, respectively, so the energetically more favorable channel is to form the dissociation products of $^3\text{ScS}^+ + ^1\text{CO}$ through cleavage of Sc–C bond. The overall reaction for $\text{Sc}^+(^3D)+\text{SCO}(^1\Sigma) \rightarrow ^3\text{ScS}^+(^3\Pi) + ^1\text{CO}$ is calculated to be endothermic by 20.5 kcal/mol on UB3LYP/6-311+G* level.

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