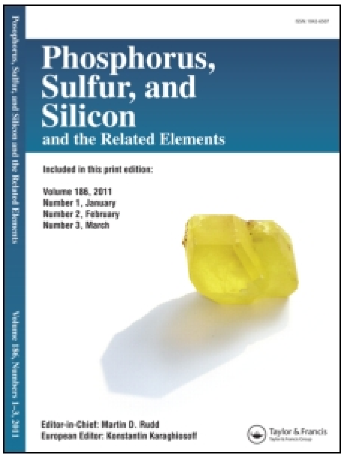

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Studies on the Thermodynamic and Kinetic Properties of the Reactions of Ti^+ with Sulfur Transfer Reagent SCO Along the C–S Bond Activation Branch at 200–1200K

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*Theoretical studies on the thermodynamic and kinetic properties of the reactions of Ti^+ with sulfur transfer reagent SCO via the C—S bond activation pathway have been carried on using DFT/B3LYP method, general statistical thermodynamics, and Eyring transition state theory with Wigner correction. The relevant reactions include reaction **1** ${}^4Ti^+ + {}^1SCO \rightarrow {}^4IM_1 \rightarrow {}^4TS_1 \rightarrow {}^4IM_2 \rightarrow {}^4TiS^+ + {}^1CO$, and reaction **2** ${}^4Ti^+ + {}^1SCO \rightarrow {}^4IM_1 \rightarrow CP \rightarrow {}^2IM_2 \rightarrow {}^2TiS^+ + {}^1CO$ in which the spin multiplicity changes from the quartet state to the doublet state in the crossing region. It is concluded that the increase of the temperature is favored to the reaction **1** process, since the equilibrium constants (K) rises from 0.566×10^{-9} at 200 K to 0.109×10^{0} at 1200 K, and the reaction rate constant (k) from $0.222 \times 10^{0}\ s^{-1}$ at 200 K to $0.540 \times 10^{11}\ s^{-1}$ at 1200 K. Moreover, reaction **1** is endothermic, and non-spontaneous in the way the entropy increases, while reaction **2** is exothermic and spontaneous in the way their entropy decreases. The reaction path **2** is the energetically favorable channel, and its thermodynamic data change not largely with the rise of temperature.*

Keywords C—S bond activation; sulfur transfer reagent SCO; thermodynamic and kinetic properties; titanium (I) ion

INTRODUCTION

The chemistry of transition metal sulfide systems has played an important role in the fields of catalysis, biochemistry, and material science

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recently, increased attention has been focused on the studies regarding their high selectivity.[1–4] In many investigations on transition metal sulfide, CS_2 and SCO (mono-oxygen substitute of CS_2) are the main sulfur transfer reagents, showing strong activity in their reactions with transition metal centers. There are a number of reaction types such as coordination, insertion, and so on, which were studied both experimentally and theoretically.[5] Jiang and Zhang[1] and Rue et al.[6] calculated and studied the reactions of V^+(Fe^+) and CS_2, and found it could go along in an insertion–elimination mechanism. As to the reactions of transition metal ion with another usual sulfur transfer reagent SCO, they would be more complicated because there are both a C—S bond and a C—O bond in the molecule, and the transition metal ions could attack the C—S bond as well as the C—O bond.

So far, the studies on the reactions of Ti$^+$ with SCO include the following: Kretzschmar et al. studied the bond-association energies of titanium sulfides experimentally and proposed the insertion–elimination mechanism.[7] Dai and Fan theoretically studied the potential energy surfaces for the reactions of Ti$^+$ with SCO by using DFT theory.[8] In the molecule SCO, the C—S bond energy is 3.14 eV, which is lower than the C—O bond energy (6.88 eV). This suggests that the C—S bond activation is energetically more favorable than that of the C—O bond energy. Consequently, the reactions involving the C—S bond activation received increased attention.

In our present work, a systematic theoretical study on the thermodynamic and kinetic properties of the reactions of titanium(I) ion with SCO along the C—S bond activation branch was carried out in detail on the basis of Dai and Fan's potential energy surfaces.[8] Our further theoretical study on these reactions will be useful for filling in the relevant information and making predictions for subsequent experimental research.

COMPUTATIONAL METHODS

We examined the influence of temperature on the reaction channels of Ti$^+$ with SCO along the C—O bond activation branch and their thermodynamic and kinetic characters over the temperature range of 200 K–1200 K, in the steps of 200 K, using the general statistical thermodynamics and Eyring transition state theory with Wigner correction. All computations of the thermodynamic and kinetic parameters (ΔH°, ΔG°, ΔS°, K, k, A) were obtained in the same way as in our previous works.[9,10] The required optimized geometries, harmonic vibration frequencies, and other relevant data were gotten at the UB3LYP/6-311+G* level, and were acquired by using the Gaussian 03 programs.[11]

RESULTS AND DISCUSSION

Figure 1 shows the potential energy diagram for the reactions of Ti^+ with SCO along the C—S bond activation branch calculated at the UB3LYP/6-311+G* level. The reaction channel **1** ($^4Ti^+ + ^1SCO \rightarrow ^4IM_1 \rightarrow ^4TS_{12} \rightarrow ^4IM_2 \rightarrow ^4TiS^+ + ^1CO$) could proceed in an insertion–elimination mechanism, and the reaction path $^2Ti^+ + ^1SCO \rightarrow ^2IM_2 \rightarrow ^2TiS^+ + ^1CO$ is a barrierless process. The optimized geometries of all relative species were also displayed in Figure 1. The reaction barrier of the ^{4}TS**1** (transition state **1**) is 12.8 kcal/mol, and its exoergic energy ΔE is 9.2 kcal/mol.

Alternatively, it is well known that every chemical reaction takes place at a certain temperature, so in order to obtain more information of the studied reactions, we used the general statistical thermodynamics and Eyring transition state theory with Wigner correction to make a further examination of the thermodynamic and kinetic properties of these reactions and the influence of temperature. First, we took

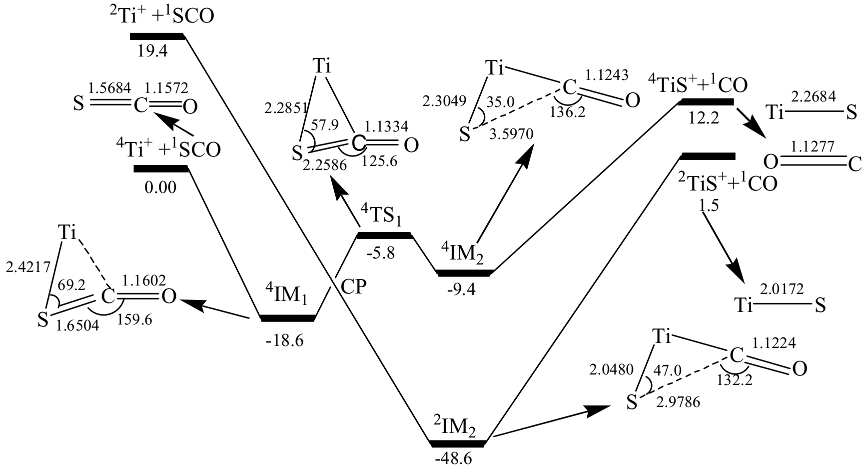

FIGURE 1 Potential energy diagram for the reaction steps of Ti^+ with SCO along the C—S bond activation branch calculated at the UB3LYP/6-311+G* level. Relative energies are given in kcal/mol. Geometric structures (bond lengths in Å and bond angles in deg.) of required species optimized at the UB3LYP/6-311+G* level of theory are also shown.

TABLE I The Thermodynamic Data for ^{4}IM$_1$, ^{4}TS$_1$, and ^{4}IM$_2$ in Reaction 1 over the Temperature Range of 200 K–1200 K[a]

T/K	200	400	600	800	1000	1200
^{4}IM$_1$						
S_t	170.36	184.77	193.20	199.18	203.82	207.60
S_v	18.79	39.80	55.10	67.02	76.79	85.06
S_r	105.53	114.17	119.23	122.82	125.60	127.87
S_{total}	294.68	338.74	367.53	389.02	406.21	420.53
$C_{p,m}$	57.75	68.62	73.22	76.08	77.97	79.24
^{4}TS$_1$						
S_t	170.36	184.77	193.20	199.18	203.82	207.60
S_v	13.73	32.30	45.12	54.94	62.97	69.78
S_r	106.07	114.71	119.77	123.36	126.14	128.41
S_{total}	290.16	331.78	358.09	377.48	392.93	405.79
$C_{p,m}$	55.62	63.42	66.34	68.45	70.01	71.13
^{4}IM$_2$						
S_t	170.36	184.77	193.20	199.18	203.82	207.60
S_v	26.48	50.33	66.38	78.49	88.30	96.56
S_r	107.89	116.53	121.59	125.18	127.96	130.23
S_{total}	304.73	351.63	381.17	402.85	420.08	434.39
$C_{p,m}$	62.83	71.32	74.29	76.41	78.01	79.17

[a] S, $C_{p,m}$ are in units J/mol·K, J/mol·K, respectively.

reaction **1** as an example, and its variation of the thermodynamic data with temperature is given in Table I. From this data, we noted that translation entropies S_t of ^{4}IM$_1$, ^{4}TS**1**, and ^{4}IM$_2$ were equal. Such results could be readily understood if we consider that translation entropy S_t is a function of pressure, temperature, and molecular mass in statistical thermodynamics, and is in direct proportion to molecular mass. As to rotation entropy S_r, because of the difference in the spatial structures of the species involved, the configuration of ^{4}IM$_2$ is comparatively loose, while that of ^{4}TS$_1$ and ^{4}IM$_1$ are a little compact nonlinear, four-membered systems. Therefore, the order of these species is $S_r(^4IM_2) > S_r(^4TS_1) > S_r(^4IM_1)$, as are their moments of inertia. However, their vibration entropies S_v are in the order of $S_r(^4IM_2) > S_r(^4IM_1) > S_r(^4TS_1)$, which is in good agreement with the results obtained through quantum calculations, i.e., the larger the vibration frequencies, the smaller the vibration partition functions, and then the smaller the vibration entropies. As a result, the total entropies and equipressure molar heat capacities follow in the following order: $S_{total}(^4IM_2) > S_{total}(^4IM_1) > S_{total}(^4TS_1)$ and $C_{p,m}(^4IM_2) > C_{p,m}(^4IM_1) > C_{p,m}(^4TS_1)$. Moreover, these relative thermodynamic data

TABLE II The Thermodynamic and Kinetic Data for Reaction 1 Within the Temperature Range of 200 K–1200 K

T(K)	ΔH°	ΔG°	ΔS°	K	*k*	A
200	37.42	35.41	10.05	0.566×10^{-9}	0.222×10^{0}	0.657×10^{13}
400	38.21	33.05	12.89	0.483×10^{-4}	0.131×10^{7}	0.980×10^{13}
600	38.56	30.38	13.63	0.226×10^{-2}	0.260×10^{9}	0.109×10^{14}
800	38.69	27.63	13.83	0.157×10^{-1}	0.372×10^{10}	0.113×10^{14}
1000	38.73	24.86	13.86	0.503×10^{-1}	0.185×10^{11}	0.115×10^{14}
1200	38.72	22.09	13.86	0.109×10^{0}	0.540×10^{11}	0.115×10^{14}

ΔH°, ΔG°, and ΔS° are in units $\mathrm{KJ{\cdot}mol^{-1}}$, $\mathrm{KJ{\cdot}mol^{-1}}$, $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, respectively.

all increase with the increase of the temperature, and other reaction channels could also be discussed in the same way.

Table II showed the thermodynamic and kinetic data for reaction **1** within the temperature range of 200 K–1200 K. The entropy changes ΔS° are all positive at all temperatures, which means their entropy increases during the whole temperature scope. The enthalpy changes ΔH° and the Gibbs free energy changes ΔG° are positive too, so it is endothermic and non-spontaneous reaction over the whole temperature range of 200 K–1200 K.

The equilibrium constants (K) of reaction **1** increase sharply, for example, with the temperature increasing over the whole temperature range; K value of reaction **1** is 0.566×10^{-9} at 200 K, and it rises to 0.109×10^{0} at 1200 K. Figure 2 displays the plots of lgK–1/T and lg*k*–1/T (inset) for reaction **1** of quartet Ti^+ with SCO along the C—S bond activation branch. From this figure, we can see that this reaction is favored to proceed at high temperature.

In addition, we computed the kinetic parameters, the A factors and reaction rate constants *k*, in order to reveal the probabilities of these reactions and their temperature dependences. The rate constant expression can be written as:

$$k^{\mathrm{TST/W}} = g(k_{\mathrm{B}}\mathrm{T}/h)\exp(\Delta \mathrm{S}^{\neq}_{\mathrm{m}}/\mathrm{R} - \Delta \mathrm{H}^{\neq}_{\mathrm{m}}) \tag{1}$$

$$g = 1 + 1/24/(\mathrm{h}\nu^{\neq}/k_{\mathrm{B}}\mathrm{T})^2 \tag{2}$$

$$\mathrm{A} = \mathrm{g}(k_{\mathrm{B}}\mathrm{T}/h)\exp(\Delta \mathrm{S}^{\neq}_{\mathrm{m}}/\mathrm{R}) \tag{3}$$

where g is the factor corrected by Wigner; k_B and h are Bolztmann and Planck constants, respectively; R is the ideal gas constant; $\nu^{\neq}$ is the imaginary frequency of transition state; and $\Delta S^{\neq}_m$ and $\Delta H^{\neq}_m$ are standard entropy and enthalpy of activation for the system, respec-

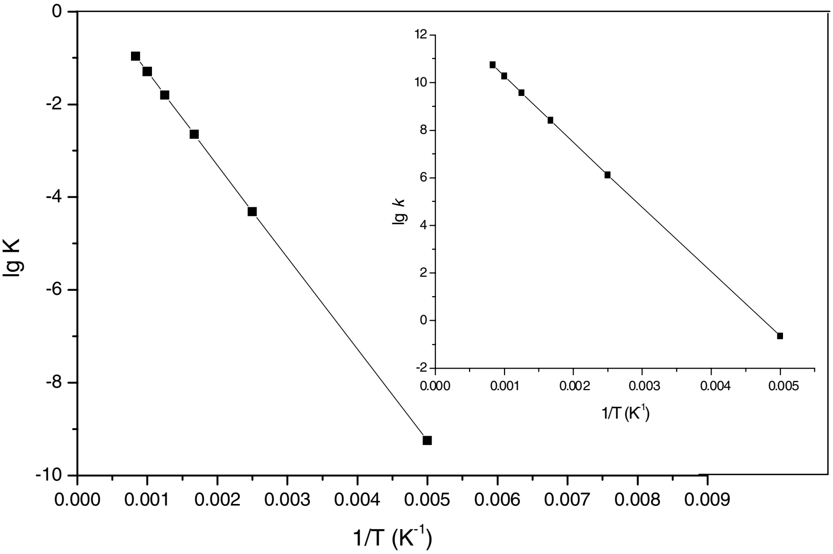

FIGURE 2 Plots of lgK–1/T and lg$k$–1/T (inset) for reaction **1** of quartet titanium (I) ion and SCO along the C—S bond activation branch.

tively. We found from Table II that lgA values of both steps are nearly equal to a certain value 13 and are temperature-independent, which indicates these reactions follow the Arrhenius equation. All reaction rate constants k increase sharply with increase of the temperature over the whole temperature range. For example, it rises from 0.222×10^0 s^{-1} at 200 K to 0.540×10^{11} s^{-1} at 1200 K. From Figure 2, we can clearly see that lg$k$ varies linearly with 1/T over 200–1200 K, and with increase in the temperature, the rate constants of this reaction increase rapidly.

In the Ti^++ SCO studied system, the energy of ground state Ti^+ (^4F) is lower than that of the excited state Ti^+ (^2F) by 19.4 kcal/mol at the UB3LYP/6-311+G* level, therefore, under the condition of low energy, the reaction between ground state $^4Ti^+$ and SCO is more favorable. So far, it is well known that a number of reactions in organic, inorganic, and organometallic chemistry, in which two states of different multiplicities are involved on the reaction path, have been verified in experimental studies.[12–14] The experimental results of Kretzschmar et al.[7] displayed that the dominant product of the reaction of Ti^+ with SCO is TiS^+ under low energy condition, and the energetically favorable channel is $Ti^+ + SCO \rightarrow TiS^+ + CO$. Because the ground

TABLE III The Thermodynamic Data for the Reaction 2 Within the Temperature Range of 200 K–1200 K

T(K)	200	400	600	800	1000	1200
ΔH°	−125.11	−124.79	−124.67	−124.68	−124.74	−124.82
ΔG°	−124.67	−124.37	−124.19	−124.03	−123.86	−123.67
ΔS°	−2.20	−1.05	−0.80	−0.82	−0.89	−0.95

ΔH°, ΔG°. and ΔS° are in units $KJ \cdot mol^{-1}$, $KJ \cdot mol^{-1}$, $J \cdot K^{-1} \cdot mol^{-1}$, respectively.

state of TiS^+ is $^2\Delta$, then the energetically favorable channel should be $^4Ti^+ + ^1SCO \rightarrow ^2TiS^+ + ^1CO$, which must proceed through intersystem quartet–doublet crossing. Dai and Fan found that the spin inversion might occur in this reacting system; the spin multiplicity should change from the quartet state to the doublet state in the crossing region and then move to the doublet potential energy surface as the reaction proceeds.[8] When SCO approaches the ground state $^4Ti^+$ from its sulfur side, there is an encounter complex and $^4IM_1$ is formed, its energy is lower than that of the reactants $^4Ti^+ +$ SCO by 18.6 kcal/mol. In reaction **2**, i.e., $^4Ti^+ + ^1SCO \rightarrow ^4IM_1 \rightarrow CP \rightarrow ^2IM_2 \rightarrow ^2TiS^+ + ^1CO$, the optimized structure of CP (crossing point) is r(C—S)1.7861Å, r(C—O)1.1651Å, r(Ti-S)2.2906Å, ∠SCO 145.0°, and ∠TiSC 64.9°. In order to obtain a better understanding of two reactions, further calculations of the thermodynamic data for reaction **2** with different environmental temperatures have been introduced in this work. As can be seen from Tables II and III, the enthalpy changes ΔH°, the Gibbs free energy changes ΔG°, and the entropy changes ΔS° of reaction **1** are all positive, while those values of reaction **2** are negative, which means reaction **1** is endothermic, and non-spontaneous in which the entropy increases, while reaction **2** is exothermic and spontaneous in which the entropy decreases. The reaction path **2** is the energetically favorable channel, and its thermodynamic data do not change much with the rise of temperature. For example, its enthalpy changes ΔH° is -125.11 $KJ \cdot mol^{-1}$ at 200 K and -124.82 $KJ \cdot mol^{-1}$ at 1200 K.

As the experimental data of this studied system are not well established, and the relative thermodynamic and kinetic parameters are insufficient and some are not available to our knowledge, our calculations could provide these important predictions and fill in the missing relative information in the research of transition metal sulfides chemistry.

CONCLUSIONS

From the investigations reported in this article, we can draw the conclusions based on the theoretical calculations as follows:

1. In reaction **1**, the total entropies and equipressure molar heat capacities occur in the following orders: $S_{total}(^4IM_2) > S_{total}(^4IM_1) > S_{total}(^4TS_1)$ and $C_{p,m}(^4IM_2) > C_{p,m}(^4IM_1) > C_{p,m}(^4TS_1)$. Moreover, these relative thermodynamic data all increase with the increase of the temperature.
2. The increase of the temperature is favored to this reaction process in reaction **1**, since the equilibrium constants (K) rises from 0.566×10^{-9} at 200 K to 0.109×10^{0} at 1200 K, and the reaction rate constant (*k*) from 0.222×10^{0} s^{-1} at 200 K to 0.540×10^{11} s^{-1} at 1200 K.
3. Reaction **1** is endothermic and non-spontaneous in which the entropy increases, while reaction **2** is exothermic and spontaneous in which the entropy decreases. The reaction path **2** is the energetically favorable channel, and its thermodynamic data do not change much with the rise of temperature.

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