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DFT and ab initio theoretical study for the $CF_3S + CO$ reaction

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ABSTRACT

The potential energy surface for the reaction of CF_3S with CO is calculated at the G4//B3LYP/6–311++G(d,p) level of theory. The results show that F-abstraction and addition–elimination mechanisms are involved, and the latter one is dominant thermodynamically and kinetically. The dominant channel is the reactant addition to form CF_3SCO, and then decomposes to CF_3 + OCS. While the direct F-abstraction channel and CF_3SCO isomerization channel are not significant for the title reaction due to higher barriers involved. The comparisons among four reactions of CX_3Y + CO (X = H, F; and Y = O, S) are made to imply the similar and different properties and reactivities of the same family elements and the F- and S-substituted derivatives.

1. Introduction

The methoxy radical (CH_3O), which is an important intermediate in the photochemical oxidation of hydrocarbons in the atmosphere, might play a role in the conversion of NO to NO_2 in polluted urban atmosphere [1–4]. The methylthiyl radical, CH_3S, which is produced from the combustion of organic sulfur compounds and coals rich of sulfur, is also an important intermediate in the oxidative processes in the atmosphere [5–7]. Their F-substituted derivatives, CF_3O and CF_3S, also play important roles in the atmosphere. Therefore, the reactions of CH_3O, CF_3O and CH_3S with some oxidants such as O_2, O_3, NO_2, and NO have been investigated extensively [8–17]. However, a few reactions were reported if CF_3S reacting with radicals or small molecules. It is noted that the reactions of CH_3O, CF_3O and CH_3S with CO were investigated experimentally and theoretically [18–33]. In our work, the reaction CF_3S + CO was studied to reveal the reaction mechanisms, and show the differences and similarities of the CX_3Y + CO (X = H, F; and Y = O, S) reactions.

2. Computational methods

All the calculations were carried out using the GAUSSIAN 03 program package [34]. The geometries of reactant (R), products (P), intermediates (IM), and transition states (TS) were optimized using the B3LYP method in conjunction with the 6–311++G(d,p) basis set. Harmonic vibrational frequencies calculations were performed at the same levels of theory in order to determine the nature of the various stationary points, as well as zero-point-energy (ZPE) corrections. All the stationary points have been positively identified for minimum number of imaginary frequencies (NIMAG = 0) or transition state (NIMAG = 1). The transition states were verified by the intrinsic reaction coordinate (IRC) calculations to connect the designated reactants and products. In order to obtain more reliable relative energy of each stationary point on the potential energy surface (PES), single-point energy calculations have been performed by the higher level electron-correction G4 method [35].

For the G4 method, it is similar to other Gaussian-n methods. Only a brief description is given here. The geometry was optimized at the B3LYP/6–31G(2df,p) level, and single-point energy evaluations were performed at the CCSD/6–31G(d), MP4/6–31+G(d), MP4/6–31G(2df,p) and MP2/G3LargeXP levels of theory. Finally, the energy expression for G4 is given in:

$$E(\mathrm{G4}) = E(\mathrm{MP4/6\text{–}31{+}G(d)}) + E(\mathrm{MP4/6\text{–}31G(2df,p)}) + E(\mathrm{CCSD(T)/6\text{–}31G(d)}) - 2E(\mathrm{MP4/6\text{–}31G(d)}) + E(\mathrm{MP2/{+}G3LargeXP}) + E(\mathrm{MP2/6\text{–}31G(d)}) - E(\mathrm{MP2/6\text{–}31G(2df,p)}) - E(\mathrm{MP2/6\text{–}31 + G(d)}) + E(\mathrm{HF/limit}) - E(\mathrm{HF/G3LargeXP}) + E_{\mathrm{SO}} + E_{\mathrm{HLC}} + \mathrm{ZPE}$$

where

$$E(\mathrm{HF/limit}) = E(\mathrm{HF/aug\text{-}cc\text{-}pVnZ}) - B\exp(-\alpha n)\ (n = 4, 5).$$

The B3LYP method is proved to be an economic and accurate computational model for predicting electronic structure, and has been employed widely. Compared with other levels of theory, the B3LYP method was found to be sufficiently accurate for predicting

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reliable geometries of the stationary points, at the same time, it is not expensive computationally for scanning the potential energy surface. Also the calculations from another three methods prove the accuracy of B3LYP method. Moreover, B3LYP theory is able to suppress effectively the problem of spin contaminant.

3. Results and discussion

The geometries of all reactants, products, possible intermediates (IM) and transition states (TS) involved in the reaction of CF_3S with CO are shown in Fig. 1. The potential energy surface of the title reaction at the G4 level is depicted in Fig. 2. Table 1 exhibits the relative energies and enthalpies (relative to the reactant of CF_3S + CO) at the B3LYP/6–311++G(d,p) and the G4 level. The G4 energy is used in discussion unless otherwise stated.

3.1. F-abstraction channel

The results show that the F-abstraction mechanism is involved in the title reaction.

One of the F atoms in CF_3S radical is abstracted by CO to product CF_2S + FCO, via the transition state TS1. In TS1, the broken C–F bond is elongated to be 2.142 Å, which is about 0.795 Å than the equilibrium length in the reactant CF_3S, and the new formed C–F bond is 1.934 Å, which is 0.587 Å longer than that in the product FCO. The angle of FCO is 119.6°, and about 7.9° larger than that in FCO. The angle of CFC is not linear, and takes the value of 157.4°. Therefore, TS1 is a product-like transition state and this abstraction channel proceeds via a late barrier, which is anticipated by the endothermicity (25.9 kcal/mol). The barrier of TS1 is rather high, which takes the value of 57.3 kcal/mol. With so tight barrier, obviously, it is difficult to occur at room temperature or typical atmospheric condition, even in the combustion progress.

3.2. The initial adduct

With the approaching of the C atom in CO to the S atom in CF_3S, the adduct CF_3SCO is generated. It is worth mentioning that CF_3SCO has two isomers according to different dihedral angle of CSCO, as labeled in Fig. 1, IM1 taking the value of 180°, and IM2 with the number of 0°. The calculations confirmed that the entrance reactions take place via transition states TS2 and TS3, respectively, to give out IM1 and IM2. As seen from Fig. 1, the newly formed C–S bond is as long as 2.419 and 2.275 Å, in TS2 and

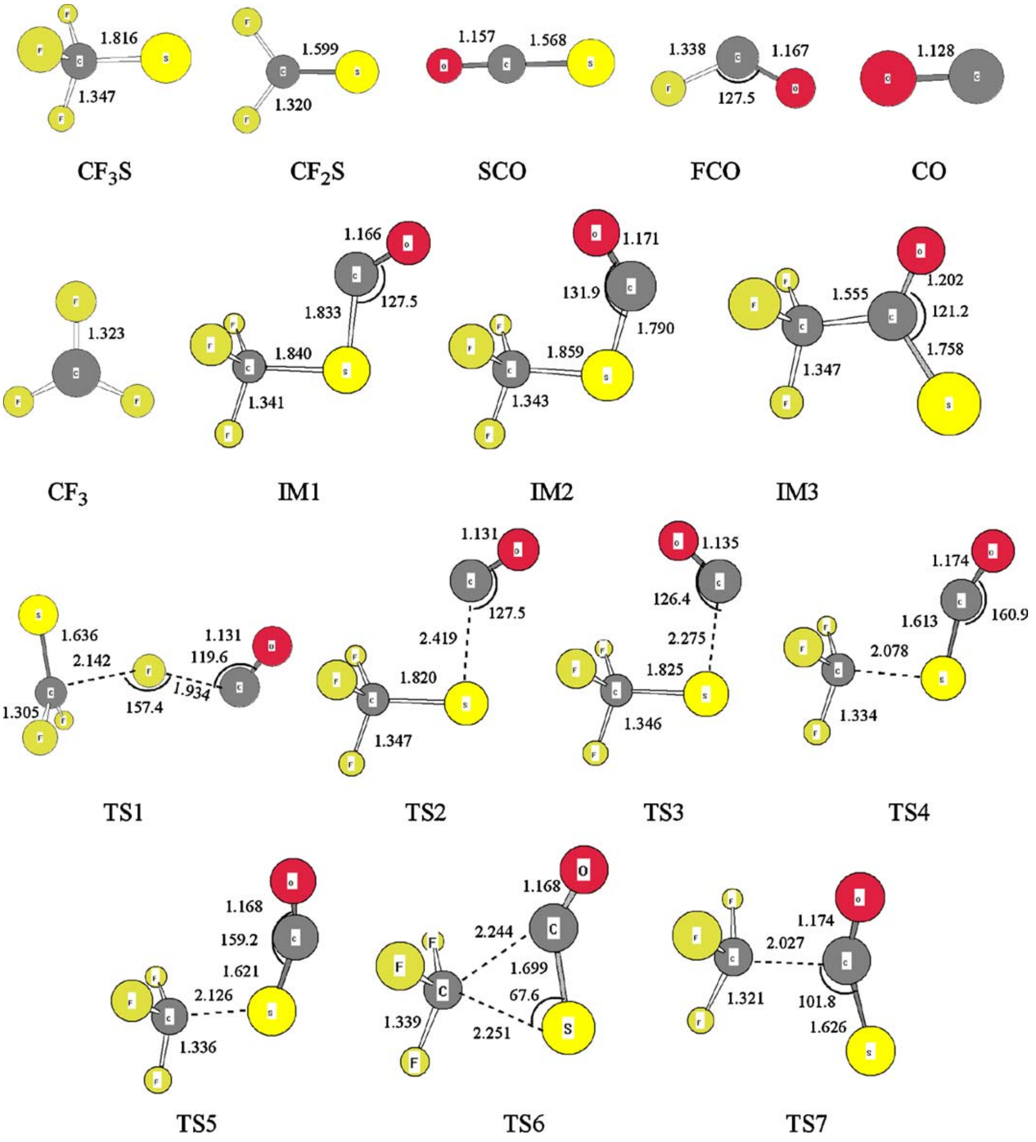

Fig. 1. The optimized geometries for the CF_3S + CO reaction at the B3LYP/6–311++G(d,p), levels. Bond distances are in angstrom and bond angles are in degrees.

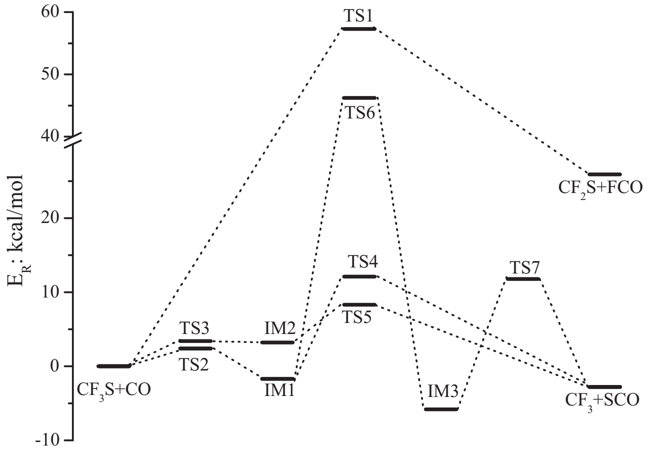

Fig. 2. The energetic reaction routes of the $CF_3S + CO$ reaction at the G4 level.

TS3, while other geometrical parameters are close to that in the reactant CF_3S. Therefore, both TS2 and TS3 are reactant-like products, and the initial adduct steps take place via early barriers. The barrier height for TS2 and TS3 is 2.4 and 3.4 kcal/mol, indicating that the addition reaction is easy to occur at room temperature. However, the energy of IM2 is higher than the initial reactants by 3.2 kcal/mol. On the other hand, IM1 is only 1.7 kcal/mol lower than the initial reactants. All suggests that CF_3SCO is not stable enough, and it might take place further isomerization or dissociation reactions.

3.3. Addition mechanisms

The first possible channel is the break of C–S bond in IM1 and IM2 to give out CF_3 + OCS surpassing transition states TS4 and TS5, respectively, as labeled in Fig. 1.

Starting from IM1 and IM2, the C–S bond connecting CH_3 and SCO groups is elongated to be 2.078 and 2.126 Å in TS4 and TS5, about 0.238 and 0.336 Å longer than the equilibrium distance in IM1 and IM2, respectively. Another C–S bond in SCO part is only 0.045 and 0.053 Å longer in TS4 and TS5 compared with it in the isolated SCO molecule. The energy of TS4 and TS5 locate on the 12.1 and 8.3 kcal/mol on the PES, and CF_3 + OCS is 2.8 kcal/mol lower than the initial reactants. Therefore, the channel from TS5 is more favorable with lower barrier height.

As said in the CH_3S + CO reaction, which we studied recently [33], the addition of multiple polarization functions has no significant affect on the $CH_3S + CO$ reaction. Therefore, we did not perform the calculations with larger basis set.

Table 1
the relative energy and enthalpy of all the species for the $CF_3S + CO$ reaction at the B3LYP/6–311++G(d,p) and G4 levels (unit: in kcal/mol).

Species	G4		B3LYP/6–311++G(d,p)	
	ΔE	ΔH	ΔE	ΔH
$CF_3S + CO$	0	0	0	0
$CF_2S + FCO$	25.9	25.9	20.0	19.8
$CF_3 + SCO$	−2.8	−2.8	−6.9	−7.3
IM1	−1.7	−2.3	−1.7	−2.3
IM2	3.2	0.7	3.6	1.2
IM3	−5.8	−6.3	−6.7	−7.5
TS1	57.3	56.7	41.4	41.7
TS2	2.4	1.8	7.9	7.9
TS3	3.4	2.8	3.3	2.9
TS4	12.1	11.5	10.0	8.8
TS5	8.3	7.7	5.0	4.4
TS6	46.2	45.7	41.7	41.0
TS7	11.8	11.2	7. 3	5.9

The second pathway is the isomerization of IM1. With the approaching of the C atom in CO group to the C atom in CH_3 group, the C–S bond is broken and the C–C bond is formed at the same time. The transition state involved is TS6, which is a three-member-ring structure, the broken C–S bond is stretched to be 2.251 Å, and the formed C–C bond is 2.244 Å. Here it should be noted that the C–S bond length in SCO group is 1.669 Å, and it is shorter than the equilibrium distance in reactant and product IM3. With tension of three-member-ring, it is understood that TS6 is a tight barrier locating on the point of 46.2 kcal/mol on the PES. And the IRC calculations confirmed that IM3 is the right product, −5.8 kcal/mol, and it is the most stable species on the PES. In IM3, the C–C bond is 1.555 Å, which is "normal single" C–C bond, and the C–S bond is also single bond with the value of 1.758 Å. After IM3 is formed, the C–C bond can rupture to give out CF_3 + OCS via transition state TS7. The broken C–C bond is elongated by 30.3% compared with that in IM3, and the two parts connecting by the broken C–C bond are close to that in the final product. The barrier height of TS7 is 17.6 kcal/mol, and TS7 is 11.8 kcal/mol higher than the initial reactants. With higher barrier heights, this channel is more difficult to take place compared with the dissociation channels.

Although many attempts were made, other channels involving the isomerization of intermediates (IM1, IM2 and IM3) are failed.

From the channels stated above, it could be concluded that the most favorable channel is the addition of initial reactants to CF_3SCO, and then dissociate to CF_3 + OCS thermodynamically and kinetically. The abstraction channel and IM1 isomerization channel play no important role for the title reaction especially at the room temperature or typical atmospheric condition.

3.4. Comparisons among $CX_3Y + CO$ (X = H, F; and Y = O, S) reactions

It is very important to compare the PES feature of the CF_3S + CO reaction with that of analogous reactions CH_3O + CO, CH_3S + CO and CF_3S + CO, and the three reactions were studied experimentally and theoretically already [18–33]. Although the methods used are different, the comparisons will give some interesting similarities and differences and imply the properties of the same family elements.

First, the comparisons of theoretical results indicate that all reactions undergo a direct abstraction channel, i.e. $CX_3Y + CO \rightarrow$ transition state $\rightarrow CX_2Y + XCO$ (X = H, F; and Y = O, S). And the abstraction channel is not the dominant channel with high barrier. The barrier height increases with the order of CH_3O, CF_3O, CH_3S and CF_3S.

Second, the addition channels to form adducts CX_3YCO (X = H, F; and Y = O, S) are similar via a low barrier for all reactions except the CF_3O + CO reaction, in Xu's report there is no barrier involved in the entrance. But the dissociation channels from CX_3YCO to the final products $CX_2 + YCO$ (X = H, F; and Y = O, S) are similar for all. And it should be mentioned that Xu's study suggesting this dissociation step does not proceed directly from trans-CF_3OCO. Third, the isomerization channels are found all reactions expect the CF_3O + CO reaction, in which Xu did not investigate it at all. However, only one isomerization channel is determined via a three-member-ring transition state in the CF_3S + CO reaction, and it is also confirmed to take place in the CH_3Y + CO (Y = O, S) reactions. As for the CH_3O + CO and CH_3S + CO reactions, there is four-member-ring transition state involved in another isomerization channel.

On the other hand, a four-centered-ring transition state is found to give out CF_2O + FCO starting from the initial adduct CF_3OCO. But this kind transition state is not located for another three reactions.

All the similarities and differences imply the similar and different properties and reactivities of the same family elements and the F- and S-substituted derivatives.

4. Conclusions

In this paper, the mechanisms of the $CH_3S + CO$ are investigated employing DFT and ab initio methods. The results show that F-abstraction and addition–elimination mechanisms are involved, and the latter one is dominant thermodynamically and kinetically. The dominant channel is the reactant addition to form CF_3SCO, and then decomposes to $CF_3 + OCS$. While the direct F-abstraction channel and CF_3SCO isomerization channel is not significant for the title reaction due to higher barriers involved. The comparisons among four reactions of $CX_3Y + CO$ ($X = H$, F; and $Y = O$, S) are made to imply the similar and different properties and reactivities of the same family elements and the F- and S-substituted derivatives.

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