Density Functional Studies of the C—F Bond Activation of CF_3 Radical by Bare Co^+

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The C—F bond activation mechanism of CF_3 radical by bare Co^+ has been studied by density functional theory. Three local minima and two first-order saddle points were located for the potential energy surface (PES) of $[Co, C, F_3]^+$. The activation barrier involving C—F bond activation was calculated to be only 14.73 kJ/mol, while the largest barrier of 149.29 kJ/mol on the PES involves Co—C bond rupture. The bonding mechanism between Co^+, C and F atoms were discussed based on Mulliken population. The relevant bond dissociation energy and thermochmistry data were calculated with the limited experimental values, and the results are in good agreement with the experimental findings.

Keyword density functional theory, C—F bond activation, bare Co^+

Introduction

Fluorinated organic compounds have many unique properties which are put to profit in a broad range of application.[1] The high C—F bond energies and electronegativity of fluorine have attracted a fundamental interest in various areas of chemical research.[2-6] Many studies have shown that bare transition metal ions are able to activate the C—F bond selectively.[7] Ridge and co-workers reported the first case of C—F activation by Fe^+ in its gas phase reaction with fluorobenzene.[8] Schwarz and coworkers described the gas-phase reaction of bare lanthanide monocation Ln^+ (Ln = La to Lu) with fluorobenzene, and the main reaction pathway proposed in all cases was fluorine atom abstraction to form LnF^+ and phenyl radical.[6] Furthermore, they also reported the reactions of several representative lanthanides, Ce^+, Pr^+, Sm^+, Ho^+, Tm^+ and Yb^+ with several fluorinated hydrocarbons, and proposed a general reaction mechanism with a $[Ln^{2+}\cdots F^-\cdots R]$ type intermediate, formed through a single electron transfer from Ln^+ to fluorine atom upon the coordination of R—F to Ln.[6] Recently, Schwarz and colleagues studied the reactions of bare calcium monocations with fluoromethane, and a similar C—F bond activation mechanism to the reactions of Ln^+ with fluorinated organic compounds was found. They proposed to refer to the mechanism as a bonded- or structured-harpoon route in order to contrast the classical harpoon-type reaction.[9]

In a more recent study, Freiser *et al*. reported the theoretical studies of the potential energy surfaces of $[M, C, F_3]^+$ (M = Fe or Ni).[10] Their calculations indicate a unique reaction mechanism in which C—F bond activation took place first followed by rotation of CF_2 group to the final (CF_2)-$(MF)^+$ ion-dipole structure.

We present here a complemented theoretical study for the $[Co, C, CF_3]^+$ potential energy surface by using density functional calculations, and expect to find the more details about the C—F bond activation mechanism and to explain the nature of the chemical bonds of the stationary points on the potential energy surface. The results from the theoretical calculations are also used to determine relevant bond dissociation energies and to discuss the thermochemistry of the reaction process.

Computation

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Density functional theory (DFT) was used in the work. DFT is known to be capable of providing accurate molecular geometries as well as system energies in many cases,[11,12] which has recently been widely applied to electronic structure calculations for systems that contain transition metals and has been proven to be particularly effective.[13,14] Our calculations were carried out by using DMol^3 package provided by Curius^2.[15] All calculations (geometry optimizations, transition state researches, and vibrational frequencies) were performed under non-local spin density (NLSD) approximations. And the generalized gradient approximation (GGA) calculations employ Beck's gradient-corrected exchange and Lee-Yang-Parr's correlation functionals. The Kohn-Sham equation is solved by employing a double numerical basis set augmented by polarization functions to ensure good accuracy. The spin-polarized computational scheme was utilized throughout the calculations to deal with the electronically open-shell systems. To insure accuracy, the "fine" convergence criteria on SCF (Seff-Consistent Field) and geometry are used, and corrections for zero-point vibrational energies (E_{zpv}) and relativistic effects that are important for heavy elements have been considered. All stationary points on the potential energy sarface (PES) were characterized as minima or the first-order transition structures by evaluating the frequencies and normal modes. All calculations were done on a Silicon Graphics O2 workstation in the Department of Chemistry of Nanjing University.

Results and discussion

Geometry optimizations were performed for the reactants, products, intermediates and transition states. The vibrational frequencies were obtained at the same level to determine the nature of different stationary points and the E_{zpv}. All the stationary points have been identified for minima (number of imagin ary frequencies $N_{img} = 0$) or transition state ($N_{img} = 1$). Three intermediates and two transition states were located on the [Co, C, F_3]$^+$ potential surface. The optimized geometries are shown in Fig. 1, and the potential energy surface of this system is shown in Fig. 2.

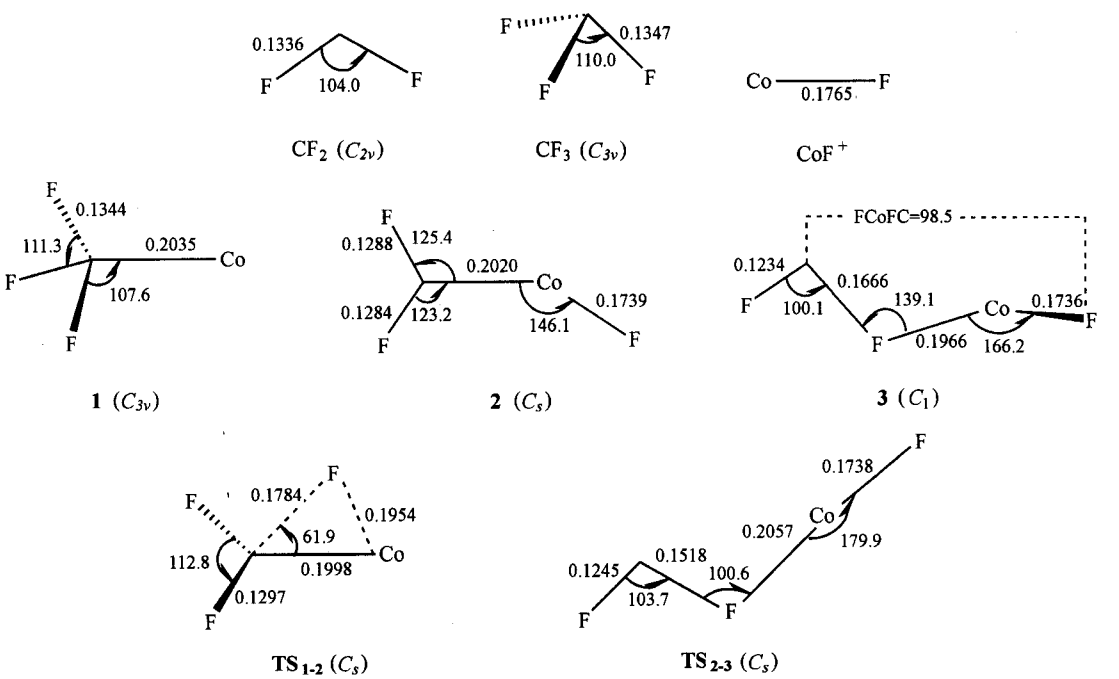

Fig. 1 Optimized structures of the reactants, products, intermediates and transition states. Bond distances are in nm and angles are in degree.

Initially, the interaction of Co^+ and CF_3 radical leads to a $Co(CF_3)^+$ complex, **1**, which has C_{3v} symmetry. The ground state of the complex, $^4A''$ state, is predicted to be more stable than the $Co^+ + CF_3$ entrance

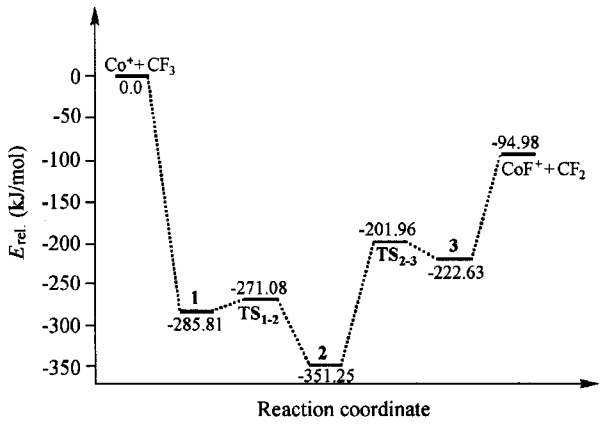

Fig. 2 Potential energy surface of $[Co, C, F_3]^+$ system.

channel by 285.81 kJ/mol. The corresponding $^2A''$ state is less stable than the $^4A''$ state by 66.90 kJ/mol. The Co—C bond dissociation energy in the complex, $D°(Co^+\text{-}CF_3)$, is calculated to be 285.81 kJ/mol, which is similar to that of $Co^+\text{-}CH_3$, $D°(Co^+\text{-}CH_3) = 238.49 \pm 29.29$ kJ/mol.[16] The CF_3 group in the complex has C—F distance of 0.1344 nm and F-C-F bond angle of 111.3°, remaining almost unchanged compared to 0.1347 nm and 110.0° in free CF_3, respectively. The Co—C distance is calculated as 0.2035 nm. The Mulliken population analysis gives the charge distribution (q) and the spin density (s) as follows: $q = 0.822$, $s = 2.778$ for Co, and $q = 0.178$, $s = 0.223$ for CF_3 group. This implies that the interaction between Co^+ and CF_3 is covalent in nature and that the single electron on carbon atom is partly transferred to Co^+ during the formation of the complex. This situation is different from that of MCF_3^+ (M = Co or Ni) complex, where the interaction between the metal ion and CF_3 species mimics an electrostatic nature.[10]

The complex can rearrange to the second species **2**, the overall minimum of the potential energy surface. Note that the cobalt in **2** has inserted into C—F bond. The $^4A''$ ground state of this inserted species has C_s symmetry with a slightly distorted CF_2 group bonding to Co through carbon at distance of 0.2020 nm. Two C—F bond lengths and FCF bond angle in CF_2 group of the inserted species are calculated as 0.1288, 1.284 nm and 111.4°, respectively, compared to 0.1336 nm and 104.0° for its free CF_2 ground state. Both C—F bond lengths in CF_2 unit are slightly shortened, compared to that in **1**. The third Fatom is bonded to Co at a distance of 0.1739 nm. The Mulliken population analysis yields the following charge distribution: $q = 0.960$ for Co, $q = 0.396$ for the CF_2 group, and $q = -0.356$ for the third F atom. This complex is computed to be 351.25 kJ/mol more stable than the original entrance channel and to be 65.44 kJ/mol more stable than **1**. The corresponding doublet of **2** is less stable by 62.97 kJ/mol.

The isomerization **1**→**2** is connected with an activation barrier of 14.37 kJ/mol with respect to **1** proceeding via the saddle point $\mathbf{TS_{1\to2}}$, which has C_s symmetry. The C—F bond activation barrier is lower compared to the C—F bond activation barriers in $FeCF_3^+$ and $NiCF_3^+$, where the C—F bond activation barriers were calculated to be 26.78 and 56.90 kJ/mol, respectively.[10] The relative energy of this transition state is 271.08 kJ/mol below the energy of the separated reactants. The imaginary frequency is characterized as 224.6i cm^{-1} and its transition state vector corresponds to breaking of the C—F bond and forming of the Co—F bond.

Proceeding along the reaction coordinate, **2** is converted into **3**, which is found to be 222.63 kJ/mol more stable than the entrance channel and 128.62 kJ/mol less stable than **2**. The optimized structure **3** has C_1 symmetry. The CF_2 unit in **3** is bonded to Co through one F atom at a distance of 0.1966 nm and is distorted with one of C—F bond length increased to 0.1666 nm. The Mulliken charge distribution shows $q = -0.417$ for the F atom bound to Co in CF_2 group and $q = 0.802$ for CoF^+ group. This fact indicates that the CF_2 subunit binds to CoF^+ primarily by electrostatic interaction, which is similar to the situations of $FM^+\text{-}F_2C$ (M = Fe, Ni).[10] The complex **3** lies 127.65 kJ/mol below the exit channel of $CoF^+(^4\Sigma) + CF_2$, which is exothermic by 94.98 kJ/mol relative to the entrance channel. The corresponding doublet is less stable by 57.45 kJ/mol. The $D°(FCo^+\text{-}CF_2)$ is calculated to be 127.65 kJ/mol, which is in good agreement with the value of 129.29 ± 5.86 kJ/mol, the experimental estimation made by Freiser and co-workers.[10]

Structures **2** and **3** are connected through by a saddle point, $\mathbf{TS_{2\to3}}$, which has C_s symmetry and is located 201.96 kJ/mol below the entrance channel. The saddle point is formed after C—Co bond rupture. From a structural point of view, $\mathbf{TS_{2\to3}}$ bears already similarity to the structure **3**, and it is a later saddle point on the

PES. The activation barrier from **2** to $\mathbf{TS_{2\text{-}3}}$, is calculated to be 149.29 kJ/mol, which is much larger than C—F bond activation. This fact could result from the large Co—C bond energy. The situation is different from the potential surfaces of $Fe(CF_3)$ and $NiCF_3$,[10] where C—F bond activation has higher activation barrier than M—C (M = Fe or Ni) bond rupture. The imaginary frequency of the transition state is calculated to be 131.3i cm^{-1}. And its transition state vector corresponds to the bent vibration of the C-F-Co bond angle in the molecular plane.

The calculated energies can be compared to experimentally determined literature values. For Eq. (1) involved in this work, the $\Delta H_{rxn\,(1)}$ can be determined from Eq. (2).

$$Co^+ + CF_3 \longrightarrow CoF^+ + CF_2 \qquad (1)$$

$$\Delta H_{rxn\,(1)} = \Delta H_f(F) + \Delta H_f(CF_2) - D°(Co^+\text{-}F) - \Delta H_f(CF_3) \qquad (2)$$

Unfortunately, no precise thermochemical information is available for the dissociation energy in the diatomic species Co^+-F, instead a theoretically calculated value obtained in this work, $D°(Co^+\text{-}F)$ = 469.03 kJ/mol, can be used. If the experimental values $\Delta H_f(F)$ = 79.54 ± 0.42 kJ/mol, $\Delta H_f(CF_2)$ = − 205.02 ± 12.55 kJ/mol and $\Delta H_f(CF_3)$ = − 460.24 kJ/mol are used, then the $\Delta H_{rxn\,(1)}$ is calculated to be − 125.94 ± 25.10 kJ/mol. This value is in fair agreement with our calculated value of − 94.98 kJ/mol, indicating an exothermic reaction.

Similarly, on the basis of the experimentally available data and the calculated bond energies, the thermochemistry information of the reaction expressed by Eq. (3) can be estimated from Eq. (4)

$$Co^+ + CF_3I \longrightarrow CoCF_3^+ + I \qquad (3)$$

$$\Delta H_{rxn\,(3)} = \Delta H_f(F) + \Delta H_f(CF_2) + \Delta H_f(I) - D°(Co^+\text{-}F) - D°(CoF^+\text{-}CF_2) - \Delta H_f(CF_3I) \qquad (4)$$

If the calculated $D°(CoF^+\text{-}CF_2)$ = 127.65 kJ/mol for the complex **3**, and $D°(Co^+\text{-}F)$ = 469.03 kJ/mol are used, together with $\Delta H_f(CF_3I)$ = − 589.94 ± 20.92 kJ/mol, $\Delta H_f(I)$ = 106.69 kJ/mol, $\Delta H_f(F)$ = 79.50 ± 0.42 kJ/mol and $\Delta H_f(CF_2)$ = − 205.02 ± 12.55 kJ/mol,[17] $\Delta H_{rxn\,(3)}$ is calculated to be 25.52 ± 12.55 kJ/mol. This fact indicates that the reaction (3) is near thermoneutral or slightly exothermic and the complex CoF_3^+ can be readily formed from the reaction (3), which matches the experimental finding.[10]

Comparing the PES of $[Co, C, F_3]^+$ with that of $[Fe, C, F_3]^+$ or $[Ni, C, F_3]^+$ reported earlier, it is found that Fe^+, Co^+ and Ni^+ react very similarly with CF_3 radical, even though the ground electronic configuration of Fe^+ is a $4s^13d^6$, whereas the ground electronic configurations for Co^+ and Ni^+ are $3d^8$ and $3d^9$, respectively. The similarity in reactivity of transition metal ions was found in the C—H and C—C bond activations of hydrocarbons.[18,19] It could be expected that this C—F bond activation mechanism presented in this paper also apply to the reactions of other transition metal ion with CF_3 radical, and that the transition state structures computed in the present investigation could be as building blocks for obtaining the corresponding saddle point geometries in the more complex systems.

Conclusion

Density functional calculations provide the information of the PES of $[Co, C, F_3]^+$, on which three local minima and two transition structures are found. Initially, an intact Co^+-CF_3 complex is formed, which goes on to the global minimum structure of the inserted F_2C-Co^+-F isomer. A transition structure connecting the two local minima indicates an activation barrier of only 14.73 kJ/mol for C—F bond activation process. From the inserted species to the other minimum structure of CoF^+-CF_2, there is a large activation barrier of 149.29 kJ/mol, involving C—Co bond rupture. $D°(CoF^+\text{-}CF_2)$ is calculated to be 127.65 kJ/mol, which is in good agreement with the experimental finding. And the relevant thermochemical information obtained in this work is also in fair agreement with the experimental estimations. Once again, density functional theory provides a powerful means for studying a reaction system in details.

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