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Density Functional Studies of the Reaction of Ytterbium Monocation with Fluoromethane: C-F Bond Activation and Electron-Transfer Reactivity

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Abstract: The potential energy surface and reaction mechanism corresponding to the reaction of ytterbium monocation with fluoromethane, which represents a prototype of the activation of C-F bond in fluorohydrocarbons by bare lanthanide cations, have been investigated for the first time by using density functional theory. A direct fluorine abstraction mechanism was revealed, and the related thermochemistry data were determined. The electron-transfer reactivity of the reaction was analyzed using the two-state model, and a strongly avoided crossing behavior on the transition state region was shown. The present results support the reaction mechanism inferred from early experimental data and the related thermochemistry data can provide a guide for further experimental researches.

Keywords: C-F bond activation, electron transfer, ytterbium monocation, fluoromethane, DFT

It is well known that C-F bond activation is a formidable task in organometallic chemistry[1]. In recent years, C-F bond activation by metal centers has attracted a great deal of interest[2-6] and many theoretical and experimental studies have shown that bare metal monocations are able to activate the C-F bond selectively[5-9]. Recently, Schwarz and co-workers demonstrated the gas-phase reactions of several bare lanthanide monocations Ln^+ with various fluorinated hydrocarbons[6]. As a supplement of the experimental studies reported by Schward and co-workers, we present here further theoretical study of the reaction of Yb^+, a representation of lanthanide monocations, with fluoromethane. The theoretical predictions presented here for the reaction of Yb^+ with CH_3F can provide a template for further comprehension of the reactions of lanthanide cations with fluorohydrocarbons.

Computational Method

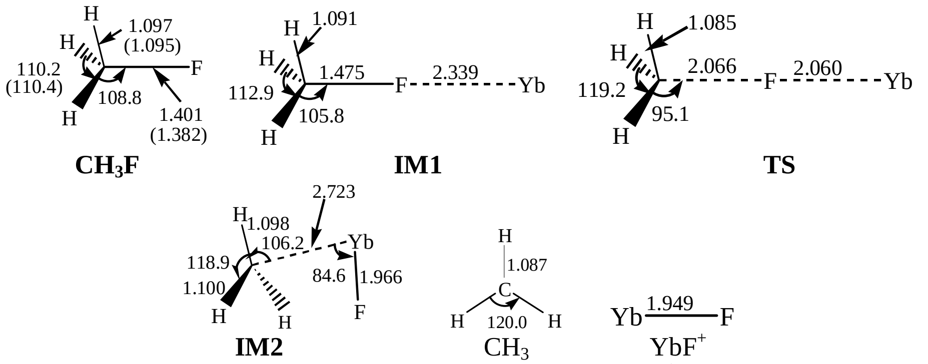
The present calculations employ the DFT method provided by the Dmol^3 programs[10]. We first optimized the structures of all the stationary points on the PES $[Yb, C, H_3, F]^+$ at the Generalized Gradient Approximation (GGA) level. And then the vibrational frequencies are obtained at the same theoretical level to determine the nature of the stationary points and the zero-point vibrational energy (ZPE). The Kohn-Sham equation is solved using a double numerical basis set augmented with polarization functions. The relativistic effects have been taken into account for all electrons. The PW91[11] exchange and correlation functionals are used in the GGA calculations.

Results and Discussion

Geometries

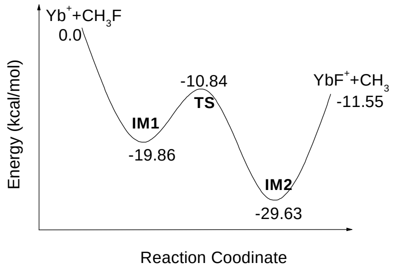
The optimized geometrical parameters of various stationary points on the PES are shown in **Figure 1**. The PES profile of the reaction of Yb^+ with CH_3F is shown in **Figure 2**.

Figure 1 Optimized geometrical parameters for the stationary points on the potential energy surface of $[Yb, C, H_3, F]^+$.



The values in parenthesis are experimental results. Distances are in Å and angles are in degree.

Figure 2 Potential energy surface profile of the reaction of Yb^+ with CH_3F



Reaction Mechanism

Two alternative reaction mechanisms could be proposed for the reaction of Yb^+ with CH_3F. One could be a direct abstraction reaction, in which CH_3F could first coordinate to Yb^+ through the electronegative fluorine atom to form a initial ion/molecule complex (**IM1**) and then this complex crosses a barrier (**TS**) to form the YbF^+ and CH_3. The other could be an insertion-elimination process, if so, a three-number-cycle initial complex and a three-center transition state should be occur along the reaction coordinate to insert Yb^+ into C-F bond. In our calculations, however, these cyclic structures could not be delocated on the potential energy surface of $[Yb, C, H_3, F]^+$ in spite of careful searching. Thus we conclude that the reaction of Yb^+ with CH_3F involve a direct abstraction mechanism, and that the insertion-elimination mechanism is not applicable in the reaction. If the mechanism is constant along the 4f row elements, we conclude that the ability of Ln^+ to abstract a F atom from CH_3-F should be related to the second ionization energy of the lanthanide. Schwarz and co-workers observed the different reactivities of six lanthanide with CH_3F and found that the lower the second ionization energy of the lanthanide is, the higher its abstraction reactivity on the fluorine atom in CH_3F is. The fact also supports the direct abstraction mechanism. Thus our calculated results are fully in line with the early experimental findings.

Heat of Reaction and Bond Dissociation Energy

As far as we know, no precise thermochemical information is available for the reaction, $Yb^+ + CH_3F \rightarrow YbF^+ + CH_3$. In the present work, the calculated heat of reaction for the reaction is exothermic by 11.63 kcal/mol. If the theoretical value is used, together with a value of 112±0.3 kcal/mol for the bond dissociation energy (BDE) of the C-F bond in fluoromethane, the BDE for diatomic species Yb^+-F is determined to be 123.63±0.3 kcal/mol. This result is in good agreement with a lower bound of 123 kcal/mol proposed by Schwarz *et al* 6 from the experimental data.

Potential Energy Surface Crossing Behavior on the Transition State Area

Since both the wavefunctions of **IM1** and **IM2**, which correspond to respectively a reactant-like species and a product-like species and clearly differ by a single electron transfer from the 6s orbital of Yb^+ to the σ^* orbital of CH_3F, belong to the A_1 irreducible representation of C_{3v} point group, they should in principle mix and avoid the crossing. **IM1** is an electrostatic complex between Yb^+ and CH_3F and a 6s electron is basically located on the metal ion. Proceeding along the reaction coordinate the electron transfer occurs from Yb to F, which favors the homolytic cleavage of the C-F bond to form **IM2**. Consequently, **IM1** correlates with an excited state of **IM2**. Similarly, **IM2** correlates with the excited state of **IM1.** In present calculations, vertical excited energies of the reactant-like and products-like species are respectively 375.35 kcal/mol and 87.66 kcal/mol.

We denote the electronic state energies of the reactant-like and product-like species by E_r and E_p, respectively, when $H_{rp}=0$. The two-state electronic secular equation at any geometry can be expressed as,

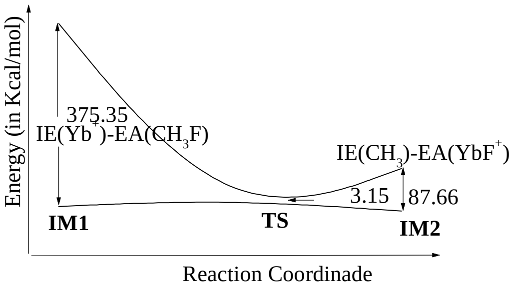
$$\begin{vmatrix} E_r - E & H_{rp} - ES_{rp} \\ H_{rp} - ES_{rp} & E_p - E \end{vmatrix} = 0 \qquad (1)$$

where S_{rp} is the overlaps of the two states. The difference between the two eigenvalues at the avoided crossing point, if $S_{rp} = 0$, is

$$\Delta = E_1 - E_2 = 2H_{rp} \qquad (2)$$

where H_{rp} is the matrix element coupling these two electronic states. The magnitude of H_{rp} determines whether the reaction proceeds adiabatically ($H_{rp} \geq RT$) or nonadiabatically ($H_{rp} \leq RT$)[17]. Our calculated state split energy is 3.15 kcal/mol (1101.61cm^{-1}) for the $Yb^+ + CH_3F$ system by using Koopmans' Theorem. This magnitude of H_{rp} is larger than RT (0.59 kcal/mol). The result indicates that the mixing of the two states is significant in the transition state region, which leads to strongly avoided crossing behavior. So the reaction of Yb^+ with CH_3F occurs on an adiabatic potential energy surface and does not involve nonadiabatic surface-hopping behavior. The state correlation diagram is given in **Figure 3**.

Figure 3 State correlation diagram for the reaction of Yb^+ with CH_3F



Conclusion

The following conclusions can be drawn from this work.

1. The reaction of the prototype system is a direct abstraction reaction of fluorine atom by Yb^+. After coordination of CH_3F to Yb^+, the electron transfer from Yb^+ to the fluorine takes place, and then the C-F bond homolytically rupture to form the formally inserted species, which exits by forming YbF^+ and methyl radical.
2. The reaction is substantially adiabatic, and the state split energy between the ground and excited states was calculated to be 3.15 kcal/mol (1101.62 cm^{-1}).
3. The calculated heat of reaction for $Yb^+ + CH_3F \rightarrow YbF^+ + CH_3$ is exothermic by 11.63 kcal/mol, and the BDE is 123.63 kcal/mol for Yb^+-F diatomic species.

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