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Elimination of HF from CH_3F by As^+ and Bi^+: A comparative theoretical study

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ABSTRACT

The reactions of ground state As^+ and Bi^+ with CH_3F have been investigated at B3LYP and CCSD(T) levels of theory. Two pathways were found for the HF-elimination reactions for both the two atomic ions. The reaction $^3As^+ + CH_3F \rightarrow ^3AsCH_2^+ + HF$ is exothermic by 72.4 kJ/mol, whereas the reaction $^3Bi^+ + CH_3F \rightarrow ^3BiCH_2^+ + HF$ is endothermic by 45.7 kJ/mol. The lowest energy pathway for the reaction of As^+ with CH_3F has activation energy of 70.7 kJ/mol while the corresponding barrier for the reaction of Bi^+ with CH_3F is much higher (174.6 kJ/mol). The higher reactivity of As^+ toward CH_3F rationalizes the experimental results of the efficient formation of $AsCH_2^+$ and the absence of $BiCH_2^+$.

1. Introduction

Numerous experimental and theoretical studies in the field of the ion-chemistry in gas phase have shown that bare metal cations, especially transition metal cations, are able to activate different types of chemical bonds [1–5]. The most extensively studied processes are the activations of C–C and C–H bonds in hydrocarbons [2,4]. The activation of C–F bond in organic molecules has been a formidable task because the C–F bond is significantly stronger than the C–C and C–H bonds. Methyl fluoride is a simple model molecule well-suited for studies of C–F bond activation. Although some studies have been carried out to estimate the reactivity of different atomic cations in activating the C–F bond and to understand the reaction mechanism [6–10], the studies in this field have not been extensive. In the reactions of metal cations with CH_3F, the F-atom-transfer species MF^+ are found to be the dominant products. To understand the reaction mechanism, Harvey et al. theoretically studied the reaction of Ca^+ with CH_3F [8]. This study revealed a “harpoon mechanism ” for the F atom transferring from CH_3F to Ca^+. A later study of the reaction of lanthanide monocations (Ce^+, Pr^+, Yb^+) with CH_3F also shows a direct F-abstraction “harpoonlike” mechanism with a $[Ln\cdots FCH_3]^+$-type intermediate and a linear $[Ln^{2+}\cdots F^-\cdots CH_3]$-type charge-transfer transition state [11]. A recent study on the reaction of La^+ with CH_3F indicates that both F-abstraction and C–F bond insertion mechanisms are possible [12].

Recently, by using inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer, Bohme and co-workers surveyed reactions of CH_3F with 46 atomic cations, covering most of the fourth, fifth and sixth-period metal and non-metal atomic cations [13]. The results of this study show that the F-transfer products MF^+ are the dominant products for the early 3d, 4d and 5d transition metals. Among all the surveyed metal cations, Os^+, Ir^+, Pt^+, Au^+ and As^+ were found to be able to activate both C–F and C–H bond because the HF-elimination products were observed. The reactivity of As^+ to eliminate HF is remarkable because the species $AsCH_2^+$ is the dominant product, whereas only minor formation of MCH_2^+ for Os^+, Ir^+, Pt^+ and Au^+ was observed. Interestingly, the HF-elimination products were not observed for the same group ions Sb^+ and Bi^+, even though they have identical valence electronic configuration ($d^{10}s^2p^2$). In the area of gas phase ion-chemistry, in contrast with transition metals, the chemistry of the main-group bare atomic cations are relatively unexplored. To our knowledge, studies on the ion-chemistry of the As-group are very rare.

To reveal the reaction mechanism and compare the reactivity of the ions in this group, we present here a comparative theoretical study on the reactions of As^+ and Bi^+ with CH_3F. We firstly identified all the possible reaction pathways using DFT method and then recalculated all the energies of the stationary points on the potential energy surfaces at CCSD(T) levels of theory.

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2. Computational method

All stationary points were fully optimized by using density functional theory (DFT) method B3LYP [14,15]. The all-electron basis set TZVP [16] was used for C, H and F atoms. The recently introduced correlated consistent basis set aug-cc-pvdz-pp of Peterson [17] was used for As^+ and Bi^+. The aug-cc-pvnz-pp (n = D, T, Q, 5) basis sets are not all electron basis set. They employ a small-core relativistic pseudopotential where the $d^{10}s^2p^2$ electrons of As^+ and Bi^+ are treated explicitly in the valence space. These basis sets have been shown to be of high quality when they are used on heavy atoms [18]. For convenience, this theoretical level is denoted as B3LYP/TZVP. Harmonic vibrational frequencies were calculated at the same level, both to characterize the stationary points and to estimate the contributions of zero-point vibration to relative energies. The intrinsic reaction coordinate (IRC) calculations were performed to track the reaction pathways. In order to improve accuracy of the energetic results, single point calculations were performed using CCSD(T) [19] method with larger basis set 6-311+G(d,p) [20,21] on C, H and F atoms and aug-cc-pvdz-pp basis set on As and Bi. This theoretical level is denoted as CCSD(T)/6-311+G(d,p). To estimate the effect of diffuse function on the geometry optimizations, since TZVP basis set does not include diffuse function, we re-optimized all the stationary points at B3LYP/6-311++G(d,p) level which uses 6-311++G(d,p) on C, H and F elements and aug-cc-pvdz-pp basis set on As and Bi. Using the same basis set, single point calculations were performed at CCSD(T) level with the re-optimized geometries. All calculations were carried out with Gaussian98 program package [22].

3. Results and discussion

The optimized geometries of the stationary points are shown in Fig. 1. The relative energies including zero-point energy corrections are collected in Table 1. In Fig. 1, the selected geometry parameters without underline refer to those obtained at B3LYP/TZVP level and the underlined values correspond to the results obtained at B3LYP/6-311++G(d,p) level. It can be seen in Fig. 1 that the geometries obtained at the two levels are very close, which indicates that the effect of diffuse functions on the geometry optimization are very slight in the $[As(Bi), CH_3F]^+$ systems. As a result, the relative energies calculated at CCSD(T)/6-311+G** level using the geometries optimized at B3LYP/TZVP are very close to those calculated at CCSD(T)/6-311++G(d,p) level using the geometries obtained at B3LYP/6-311++G(d,p) level. Further, the relative energies calculated at the two CCSD(T) levels are consistently higher than those obtained at B3LYP levels, especially for the transition states. But, it is not surprising since the DFT calculations frequently underestimate the energy barrier [23–26]. Considering that the experimental thermochemistries for the title reactions are unavailable, unless otherwise specified, the energies discussed below refer to the results obtained at CCSD(T)/6-311++G(d,p) level. The potential energy diagrams are shown in Figs. 2 and 3.

As shown in Fig. 1, the reactions of As^+ and Bi^+ with CH_3F undergo with similar mechanisms. Two possible HF-elimination pathways are identified and they are denoted as a and b. Although Bohme et al. have confirmed that the excited As^+ and Bi^+ contribute little to the reactions [13], we have also carefully searched the possible reaction pathway on the singlet surface, but no pathway was found. Thus we speculate that the singlet As^+ and Bi^+ may be inert toward CH_3F and the unpaired *p* electrons in the triplet ground state may be necessary to activate the C–F bond. It should be claimed that the products $As(Bi)CHF^+$ corresponding to the H_2-elimination reaction were not observed in the experiment [13] and we also did not find such pathway despite of numerous careful searches.

3.1. Reaction pathway a

As shown in Fig. 1, at the initial step of this reaction pathway, the F-end collision complexes ^{3}As-IM1 and ^{3}Bi-IM1 with C_s symmetry are formed. NBO calculation indicates that there is no covalent bond formed between the atomic cations and F atom and shows that such complexes basically arises from the electrostatic interaction and strong donor–accepter interaction ($lp(F) \rightarrow p_x(As/Bi)$). The binding energies of ^{3}As-IM1 and ^{3}Bi-IM1 are calculated to 152.1 and 110.6 kJ/mol, respectively, and they are the most stable species on the surfaces. We believe such complex is the experimentally observed CH_3F addition complex which is minor channel for As^+ (3%) but the unique channel for Bi^+.

With As^+ and Bi^+ swinging toward the C atom, via ^{3}As-TS1 and ^{3}Bi-TS1, the atomic cations insert into the C–F bond to form the insertion intermediates ^{3}As-IM2 and ^{3}Bi-IM2, respectively. The energy barrier of this step for As^+ is 137.1 kJ/mol which is lower than that of Bi^+ (191.1 kJ/mol). NBO analysis indicates that in the two insertion–transition states the C–F bond has been partially broken meanwhile the covalent As–F and Bi–F bond have almost been formed. With the complete rupture of C–F bond and the formation of As–C and Bi–C bond, the insertion intermediates ^{3}As-IM2 and ^{3}Bi-IM2 are formed. ^{3}As-IM2 has C_s symmetry while ^{3}Bi-IM2 has C_1 symmetry. Moreover, ^{3}As-IM2 is much more stable than ^{3}Bi-IM2 since ^{3}As-IM2 lies below than the reactants by 110.4 kJ/mol while ^{3}Bi-IM2 is 8.9 kJ/mol above the reactants, which is consistent with the short As–C bond (2.239 Å) and much longer Bi–C bond (2.669 Å).

At the second step of this pathway, from the insertion intermediates, one of the hydrogen atom migrates from C atom to F atom via a four-member-ring transition states ^{3}As-TS2 and ^{3}Bi-TS2. ^{3}As-TS2 has an activation energy of 70.7 kJ/mol, whereas this barrier for ^{3}Bi-TS2 is much higher (174.6 kJ/mol). For both As^+ and Bi^+, this step is rate-determining step. NBO calculations show that in ^{3}As-TS2 covalent interactions exist between C and As, As and F, F and C atoms. In ^{3}Bi-TS2, only the C–Bi bond has obvious feature of covalent bond, the covalent F–Bi bond has been nearly broken and the F–C interaction is not found in this transition state. Obviously, ^{3}As-TS2 and ^{3}Bi-TS2 are similar in geometry but they are different in bonding patterns. The different stability of the two transition states indicates that the bonding pattern in ^{3}As-TS2 is in favor of stabilizing the transition state. Another easy way to understand this result is that As^+ has higher F and C affinity than Bi^+ and this can be seen from the relative stability of the initial F-bounded complexes and the insertion intermediates.

IRC calculations demonstrate that with the breakage of the activated C–H bond, the hydrogen atom migrates to F atom to produce the intermediates ^{3}As-IM3 and ^{3}Bi-IM3, respectively, in which the HF unit is attached to As and Bi atom by a weak F–As or F–Bi bond. The dissociations of ^{3}As-IM3 and ^{3}Bi-IM3 into products cost 46.3 and 49.4 kJ/mol, respectively. As shown in Figs. 2 and 3, the formation of $^3AsCH_2^+$ is exothermic by 72.4 kJ/mol while the formation of $^3BiCH_2^+$ is endothermic by 45.7 kJ/mol. It should be pointed out that the ground state of $AsCH_2^+$ and $BiCH_2^+$ is not triplet state but singlet state. According to our calculations at CCSD(T)/6-311+G(d,p) level, the singlet–triplet splitting energies for them are 101.2 and 64.5 kJ/mol (not list in Table 1), respectively. As we mentioned at the beginning, the reaction pathway on the singlet surface was not found, therefore the possibility of singlet ground state $AsCH_2^+$ and $BiCH_2^+$ formed through surface crossing can be ruled out. Thus in the experiment the triplet $AsCH_2^+$ and $BiCH_2^+$ can decay into singlet ground state. The bond energy $D(As^+–CH_2)$ of ground state $AsCH_2^+$ is calculated to be 135.5 kcal/mol which is higher than those of $D(M^+–$