Competitive Hydrogen Transfer Reactions between Fe^+ and $C_2H_5OC_2H_5$

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It is well known that gas phase atomic metal ions interact with organic molecules aggressively to cleave rather high energy bonds, essentially catalyzing the organometallic reactions.[1] A fundamental understanding of the energetic requirements, dynamics, and mechanism associated with metal-induced organic bond cleavage may be of practical significance to a diverse range of biological, chemical, and physical processes.[2] The gas-phase reactions of bare Fe^+ ions with dimethyl ether (DME) have been studied by many experimental groups.[3] These experiments revealed that Fe^+ can activate DME to afford the Fe^+/formaldehyde complex as ionic and methane as neutral product.

$$Fe^+ + CH_3OCH_3 \rightarrow Fe^+OCH_2 + CH_4 \qquad (1)$$

Recently, Ding and co-workers have reported the density functional theory results of Fe^+ (^4F and ^6D) mediated demethanation of DME.[4] The calculation indicated that, for quartet Fe^+ (^4F), the demethanation reactions were exclusively induced by metal ion mediated C–O bond activation followed by β-H migration: while for sextet Fe^+ (^6D), both the C–O and methyl C–H activation could result in the demethanation reaction through a planar skeleton tricoordinated intermediate $(CH_3)Fe^+H(OCH_2)$. Despite the various experimental and theoretical results, the role of metal ions, especially the two-state reactivity,[5] in the demethanation and dehydrogenation reaction of ethers is still not well-understood. In the present study, we investigated gas phase reactions between $Fe^+ + C_2H_5OC_2H_5$ system to unravel the competitive ion-molecule reactions. The experimental apparatus used in this work has been described elsewhere.[6]

Figure 1 shows a mass spectrum obtained when Fe^+ reacts with DEE. The spectrum contains triad peaks corresponding to the Fe isotopes (^{54}Fe, 5.8%; ^{56}Fe, 91.7%; ^{57}Fe, 2.2%), with the relative intensities of these isotopomers reflecting their natural abundance. The prominent peaks in the mass spectrum consist of heterocluster ions with formulas $Fe^+(C_2H_4)$, $Fe^+(OC_2H_4)$, and $Fe^+(C_2H_5OH)$, formed by the ion-molecule reactions within the intact association complex $Fe^+(DEE)$. The formation of these product ions implies that Fe^+ readily reacts with DEE molecule. These three observed ionic products, along with their corresponding neutrals, can be represented by the following equations:
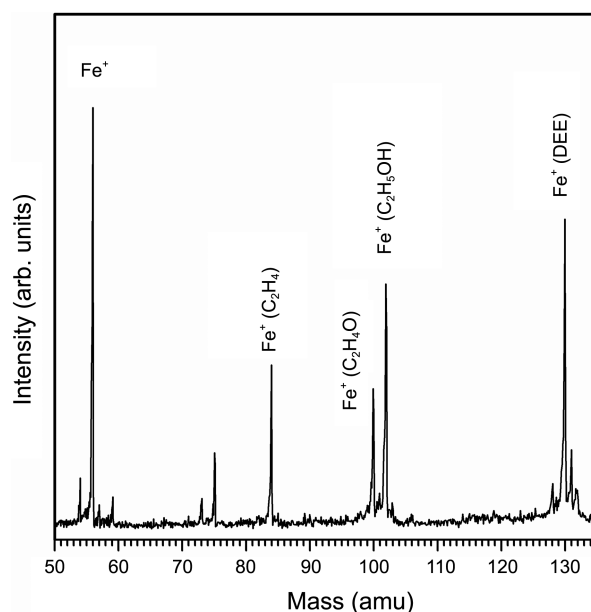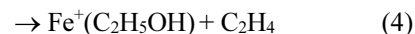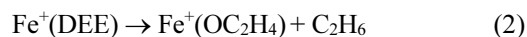

Figure 1. Mass spectrum of product ions formed from the reactions of Fe^+ and diethyl ether (DEE).

$$Fe^+(DEE) \rightarrow Fe^+(OC_2H_4) + C_2H_6 \qquad (2)$$
$$\rightarrow Fe^+(C_2H_4) + C_2H_5OH \qquad (3)$$
$$\rightarrow Fe^+(C_2H_5OH) + C_2H_4 \qquad (4)$$

To interpret the experimental findings and gain further insight into the reaction mechanism, we calculated the molecular geometries (reactants, products, intermediates, and transition states) and absolute energies, which were fully optimized at the B3LYP/6-311++G(*d,p*) level using the Gaussian03W package.[7] This includes Becke's three parameter nonlocal hybrid exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr.[8] Because the chemical reactivity of transition metal ions with organic molecules is greatly influenced by the spin state of the metal ion, we considered both quartet (^4F) and sextet (^6D) states of the Fe^+ ion in our model.

Figure 2 shows the potential energy surfaces (PES) associated with the reaction pathways, where IM and TS represent the intermediate and the transition state, respectively. The
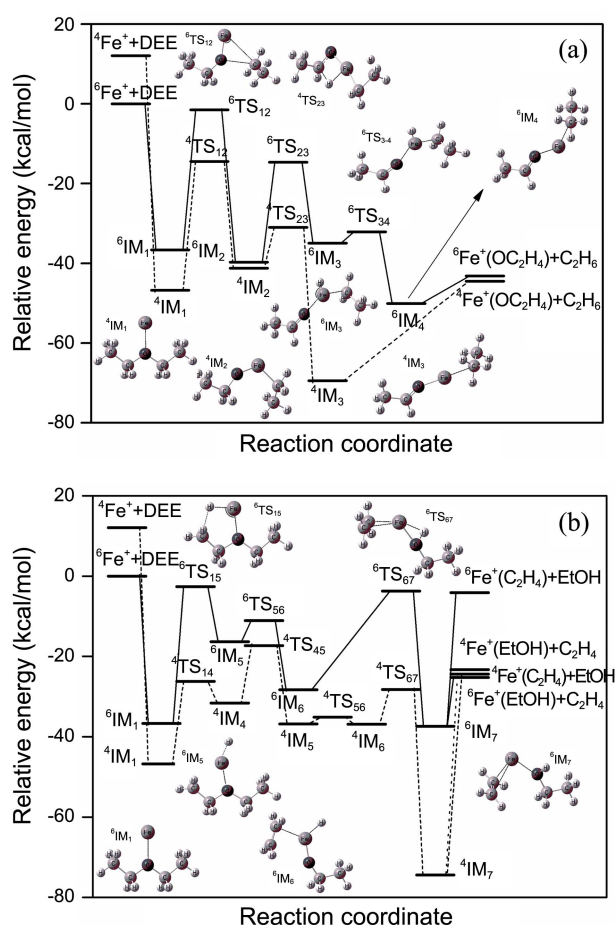
Figure 2. Potential energy surface diagrams along the reaction pathways of (a) $Fe^+OC_2H_4 + C_2H_6$ formation and (b) $Fe^+(C_2H_4) + C_2H_5OH$ and $Fe^+(C_2H_5OH) + C_2H_4$ formation.

superscript denotes the spin multiplicity. The detailed geometries of the stationary points are depicted in the Supporting Information. Initially, the encounter of Fe^+ ion with DEE leads to the formation of $Fe^+(DEE)$ association complexes $^6IM_1$ and $^4IM_1$. Energetically, these complexes are predicted to be more stable, by 36.65 kcal/mol ($^6IM_1$) and 46.77 kcal/mol ($^4IM_1$), respectively, than the separated reactants.

Once the association complex IM_1 is formed, oxidative insertion of Fe^+ ion across the C–O bond produces the intermediate IM_2, C_2H_5–Fe^+–OC_2H_5, *via* transition state TS_{12} (Figure 2(a)). The energy of $^6IM_2$ is, for example, 3.03 kcal/mol lower than that of the association complex $^6IM_1$, and 39.68 kcal/mol less than that of the entrance channel. The β-H transfer from the OCH_2 group to the Fe^+ ion within $^6IM_2$ generates the analogous tricoordinated species $^6IM_3$, H–$Fe^+(C_2H_5)OC_2H_4$, which was similarly found in the reaction of $^6Fe^+$ with DME.[4] This β-H transfer reaction is one of the most common elimination reactions in transition metal chemistry.[9] Here, both $^6IM_3$ and $^4IM_2$ rearrange to the precursor ions $C_2H_6\cdots Fe^+$–OC_2H_4 ($^6IM_4$ and $^4IM_3$), of C_2H_6 elimination reaction. $^4IM_3$ constitutes the most stable species on the whole PES, and its energy is calculated to be 69.45 kcal/mol more stable than the separated reactants.

As an alternative reaction pathway, Burnier *et al.* have also suggested that a β-H transfer from the ethyl ligand in the intermediate IM_2, C_2H_5–Fe^+–OC_2H_5, produces C_2H_4–Fe^+–$(H)OC_2H_5$.[3a] It is quite surprising, however, that our current calculations produce only the $^6IM_5$ or $^4IM_4$ from the association complexes IM_1 for either the quartet or sextet states, not from C–O insertion intermediate IM_2 (see Figure 2(b)). This step involves γ-H transferring from CH_3 group to Fe^+ through five-membered complex $^6TS_{15}$ (or $^4TS_{14}$) with a barrier of 34.02 kcal/mol (or 20.58 kcal/mol). Along the PES, hydrogen transfer from the Fe^+ ion to the O atom *via* transition state TS_{67} yields the product complex IM_7, thus $Fe^+(C_2H_4)$ and $Fe^+(C_2H_5OH)$ ions are expected to form after simple Fe^+–O or Fe^+–C bond breakage, respectively. Considering the reaction energies, both the $Fe^+(C_2H_4)$ and $Fe^+(C_2H_5OH)$ formation channels are exothermic in both electronic states and hence thermodynamically favorable.

In conclusion, the reaction pathways of IM_1 can be divided into two categories: (*i*) the insertion of an Fe^+ ion into the C–O bond of DEE followed by β-H transfer and neutral ethane loss; (*ii*) the γ-H transfer to an O atom followed by C_2H_4/C_2H_5OH elimination. The high exothermicity of these two reaction pathways (both for quartet and sextet states) is consistent with our current observation of intense peaks corresponding to the $Fe^+(OC_2H_4)$, $Fe^+(C_2H_4)$, and $Fe^+(C_2H_5OH)$ ions in the mass spectrum.

Supporting Information. The Supporting Information is available on request from the correspondence author (E-mail: kwjung@wku.ac.kr).

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