

# Theoretical study of the gas-phase Fe<sup>+</sup>-mediated oxidation of ethane by N<sub>2</sub>O

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**Abstract** We report herein a comprehensive study of the gas-phase Fe<sup>+</sup>-mediated oxidation of ethane by N<sub>2</sub>O on both the sextet and quartet potential energy surfaces (PESs) using density functional theory. The geometries and energies of all the relevant stationary points are located. Initial oxygen-atom transfer from N<sub>2</sub>O to iron yields FeO<sup>+</sup>. Then, ethane oxidation by the nascent oxide involves C–H activation forming the key intermediate of (C<sub>2</sub>H<sub>5</sub>)Fe<sup>+</sup>(OH), which can either undergo C–O coupling to Fe<sup>+</sup> + ethanol or experience β-H shift giving the energetically favorable product of FeC<sub>2</sub>H<sub>4</sub><sup>+</sup> + H<sub>2</sub>O. Reaction of FeC<sub>2</sub>H<sub>4</sub><sup>+</sup> with another N<sub>2</sub>O constitutes the third step of the oxidation. N<sub>2</sub>O coordinates to FeC<sub>2</sub>H<sub>4</sub><sup>+</sup> and gets activated by the metal ion to yield (C<sub>2</sub>H<sub>4</sub>)Fe<sup>+</sup>O(N<sub>2</sub>). After releasing N<sub>2</sub> through the direct H abstraction and/or cyclization pathways, the system would be oxidized to ethenol, acetaldehyde, and oxirane, regenerating Fe<sup>+</sup>. Oxidation to acetaldehyde along the cyclization –C–to–C hydrogen shift pathway is the most energetically favored channel.

**Keywords** Gas phase · DFT · Oxidation · PES

## 1 Introduction

Selective oxidation of hydrocarbons catalyzed by transition metals is of fundamental importance in various branches of chemistry, biology, and chemical engineering [1–10]. In this respect, gas-phase experiments combined with theoretical works have provided a wealth of information of elementary steps and intermediates for various catalytic reactions [3, 11, 12]. As the simplest hydrocarbon model containing a single C–C bond, ethane oxidation mediated by transition metal ions and their oxides has been experimentally extensively investigated [4, 11–20]. It was found that none of the M<sup>+</sup> ions (M = Cr–Ni) activates ethane at thermal energies, but under the same reaction conditions, all the corresponding MO<sup>+</sup> ions can activate the C–H bond of ethane and give the subsequent losses of ethanol, ethylene, and/or water [13, 15–18].

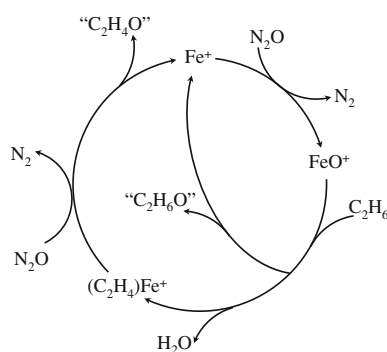
Owing to the low N<sub>2</sub>-oxygen affinity (OA(N<sub>2</sub>) = 40 kcal/mol [19]), N<sub>2</sub>O usually acts as a useful oxidant for the oxidation of organic compounds. In the gas-phase oxidation of ethane by N<sub>2</sub>O, however, only Fe<sup>+</sup> presents high reactivity among all 3d transition-metal ions [3, 4, 20]. For the Fe<sup>+</sup>-mediated C<sub>2</sub>H<sub>6</sub>/N<sub>2</sub>O reaction cycle (reactions 1–5, see Scheme 1), initial O-atom transfer from N<sub>2</sub>O to the metal ion affords the corresponding FeO<sup>+</sup> species (reaction 1) [20]. Then, the ethane oxidation by FeO<sup>+</sup> in part directly regenerates Fe<sup>+</sup> via liberating ethanol (reaction 2) but also mainly eliminates water producing FeC<sub>2</sub>H<sub>4</sub><sup>+</sup> (reaction 3). Finally, the reaction cycle is complete via the further reaction of FeC<sub>2</sub>H<sub>4</sub><sup>+</sup> with another N<sub>2</sub>O to regenerate Fe<sup>+</sup> (reaction 4) [20].

**Electronic supplementary material** The online version of this article (doi:10.1007/s00214-010-0873-9) contains supplementary material, which is available to authorized users.

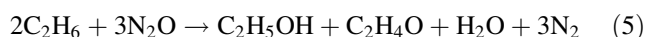
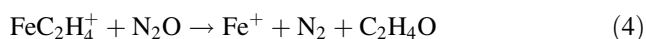
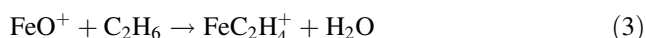
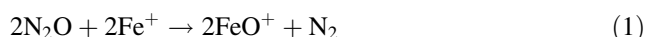
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**Scheme 1** Reaction cycle for the  $\text{Fe}^+$ -mediated oxidation of ethane by  $\text{N}_2\text{O}$  (Ref. [20])



For the sake of unveiling the reaction mechanisms, extensive theoretical studies on the reactions of ethane with  $\text{Fe}^+$ ,  $\text{Co}^+$ , and other transition metal ions have been reported [21–25]. However, to our knowledge, electronic structure calculations of hydrocarbon oxidation by corresponding metal oxide ions are still mainly limited to methane, propane, and several other organic substrates, but rather scarce for ethane [26–46]. The oxidation of methane to methanol by all 3d transition-metal oxide ions was reported to occur via a direct H abstraction followed by methyl migration [26–30]. We also found the reaction of  $\text{FeO}^+$  with propane involves initial C–H activation, and the products ( $\text{C}_3\text{H}_7\text{OH}$ ,  $\text{C}_3\text{H}_6$ ,  $\text{CH}_3$ , and  $\text{H}_2\text{O}$ ) are in relation to the encounter complexes and spin inversion [32].

In comparison with the facts that  $\text{FeO}^+$  brings about activation of methane with quite low efficiency and  $\text{FeO}^+$  reaction with propane involves both C–C and C–H activation,  $\text{FeO}^+$  was found to activate C–H bond in ethane efficiently at thermal energies [4, 15, 20, 47]. Hence, a theoretical study of the  $\text{FeO}^+/\text{C}_2\text{H}_6$  reaction is needed to systematically understand the reactivity of  $\text{FeO}^+$  toward hydrocarbons with different alkyl chains. In this article, we reported a comprehensive theoretical investigation of the  $\text{Fe}^+$ -mediated oxidation of ethane by  $\text{N}_2\text{O}$ . One interesting reason for this study is iron oxide ion was found to present a good activity toward the inert saturated hydrocarbons both experimentally and theoretically [3, 11, 20, 26–30]. Second, the title reaction represents one of the prototype systems for the transition metal ion-mediated oxidation of the saturated hydrocarbons by  $\text{N}_2\text{O}$ . Third, the reaction of  $\text{FeC}_2\text{H}_4^+/\text{N}_2\text{O}$  involved in the system associates with the

competitions of C–H and C–C activation vs. oxygen-atom transfer and carbonylation vs. epoxidation, which provides an efficient window to probe the selectivity for alkenes oxidation. Our main aim is to elucidate the reaction mechanisms and determine the activation barriers useful to give insight into kinetic aspects. This includes a complete description of all possible pathways on both the sextet and quartet PESs for the full oxidation process.

## 2 Computational details

All computations were carried out using the GAUSSIAN 03 program package [48]. Geometry optimizations and frequency calculations were carried out for all the relevant species using the hybrid density functional B3LYP [49–53] method together with the DZVP(opt + 3f) [31–34, 55] for  $\text{Fe}^+$  and 6-311++G(2d, 2p) basis set [54] for the non-metal atoms. Our recent work has shown the performance of this computational strategy for describing the features of the PESs of the  $\text{Fe}^+/\text{N}_2\text{O}/\text{hydrocarbon}$  systems [31, 32].

Intrinsic reaction coordinate (IRC) calculations were performed to identify the pathways between transition states and their connecting minima. The calculation method STABLE [56, 57] was used everywhere to ensure there were no instabilities in the wavefunction of stationary points. Natural bond orbital (NBO) [58–60] analyses were carried out to characterize the bonds and interactions inside some important complexes.

## 3 Results and discussion

In the following sections, we first establish the accuracy that is expected from the chosen level of theory for the  $\text{Fe}^+/\text{N}_2\text{O}/\text{C}_2\text{H}_6$  system. Then, we examine the title reaction in detail, including the geometries of various stationary points and PESs for all the oxidation processes. Finally, we briefly compare our theoretical results with the experimental findings [15, 17, 20]. For simplicity, calculated total energies, zero-point energies as well as  $\langle S^2 \rangle$  values for all the species involved are given as Supporting Information (see Table S1).

### 3.1 Calibration

To evaluate the reliability of the level of theory employed, we compare the experimentally thermochemical data with the results from our theoretical approach. Table 1 collects the theoretically predicted adiabatic bond dissociation energies (BDEs) and the most reliable experimental data for some relevant species [62–68]. As shown in Table 1, although the difference of the calculated excitation energy of  $\text{Fe}^+$  ( ${}^4\text{F}, 3\text{d}^7 \leftarrow {}^6\text{D}, 3\text{d}^6 4\text{s}^1$ ) with the experimental gap

**Table 1** Adiabatic bond dissociation energies and excitation energies (kcal/mol) at 0 K determined by calculations and experiments

Species	Calcd <sup>a,b</sup>	Expt
<sup>6</sup> [Fe <sup>+</sup> -O]	76.9 (-3.1 ± 1.4)	80.0 ± 1.4 <sup>c</sup>
<sup>4</sup> [Fe <sup>+</sup> -OH <sub>2</sub> ]	29.7 (-0.9 ± 1.2)	30.6 ± 1.2 <sup>d</sup>
<sup>5</sup> [Fe <sup>+</sup> -OH]	82.8 (0.2 ± 4)	82.6 ± 4 <sup>e</sup>
<sup>4</sup> [Fe <sup>+</sup> -CO]	33.4 (2.1 ± 1.8)	31.3 ± 1.8 <sup>f</sup>
<sup>4</sup> [Fe <sup>+</sup> -CH <sub>2</sub> ]	77.8 (-3.7 ± 1.0)	81.5 ± 1.0 <sup>g</sup>
<sup>4</sup> [Fe <sup>+</sup> -OCH <sub>2</sub> ]	33.9 (1.0 ± 1.6)	32.9 ± 1.6 <sup>h</sup>
<sup>4</sup> [Fe <sup>+</sup> -N <sub>2</sub> ]	13.4 (0.7 ± 0.9)	12.7 ± 0.9 <sup>i</sup>
<sup>4</sup> [Fe <sup>+</sup> -C <sub>2</sub> H <sub>4</sub> ]	45.5 (10.9 ± 2.5)	34.6 ± 2.5 <sup>j</sup>
Fe <sup>+</sup> ( <sup>4</sup> F ← <sup>6</sup> D)	12.5 (6.7)	5.8 <sup>k</sup>

<sup>a</sup> At the B3LYP/DZVP(opt + 3f):6-311 + G(2d,2p) level

<sup>b</sup> Values in the parentheses are error bars for the calculated BDEs, obtained by subtracting the experimental values from the calculated BDEs

<sup>c</sup> Ref. [61]

<sup>d</sup> Ref. [62]

<sup>e</sup> Ref. [63]

<sup>f</sup> Ref. [64]

<sup>g</sup> Ref. [65]

<sup>h</sup> Ref. [63]

<sup>i</sup> Ref. [66]

<sup>j</sup> Ref. [67]

<sup>k</sup> Ref. [68]

value is not small (12.5 vs. 5.8 kcal/mol [68]), the error of the calculated stability of both electronic states should be maintained during the overall reaction. Thus, the relative energies on the reaction energy profile should not be highly modified. It is also found from Table 1 that the calculations reproduce the experimental adiabatic BDEs well in most cases with the exception of <sup>4</sup>[Fe<sup>+</sup>-C<sub>2</sub>H<sub>4</sub>]. Our calculated binding of <sup>4</sup>[Fe<sup>+</sup>-C<sub>2</sub>H<sub>4</sub>] is overestimated by 10.9 kcal/mol, similar to the situation of the calculations by Holthausen et al. (52 kcal/mol at the B3LYP/Wachters: D95\*\* level [23]) and Zhang et al. (41.6 kcal/mol at the B3LYP/6-311 ++G(3df,3pd)//B3LYP/6-311 + G\*\* level [69]). The error may be as a systematic shortcoming of the B3LYP functional in the description of weakly bound complexes [23].

Due to the overbinding of <sup>4</sup>[Fe<sup>+</sup>-C<sub>2</sub>H<sub>4</sub>], the relative stability of the FeC<sub>2</sub>H<sub>4</sub><sup>+</sup> + N<sub>2</sub>O asymptote with respect to the remainder of the PES of the FeC<sub>2</sub>H<sub>4</sub><sup>+</sup>/N<sub>2</sub>O system is probably overestimated by 11 kcal/mol. However, the relative energies of the other parts of the PES are still described more satisfactorily. This is similar to the situation of the Fe<sup>+</sup>/C<sub>2</sub>H<sub>6</sub> system reported by Holthausen et al. [23]. The present shortcoming to some extent limits the predictive power in quantitative terms; nevertheless, we are confident that the approach employed describes correctly the qualitative features of the PES.

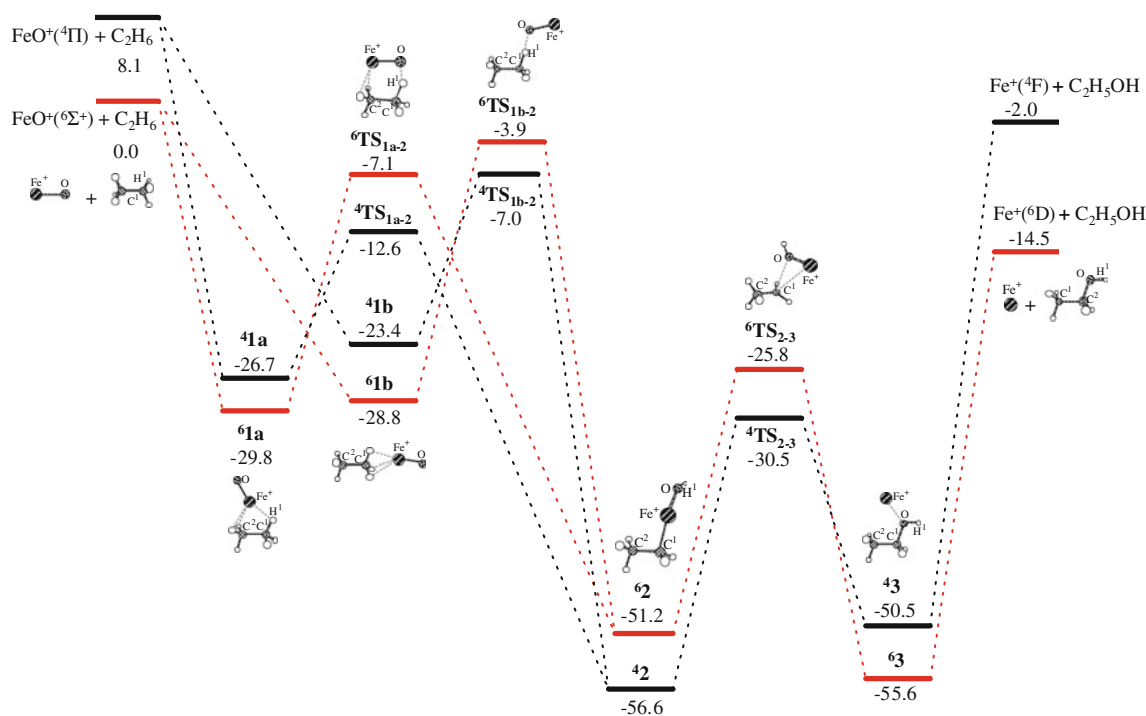
### 3.2 N<sub>2</sub>O reduction mediated by Fe<sup>+</sup>

The first step of the Fe<sup>+</sup>-mediated oxidation of ethane is the reaction between Fe<sup>+</sup> and N<sub>2</sub>O producing FeO<sup>+</sup>, which has been studied by us at the same level of theory [31]. Briefly, we found that FeO<sup>+</sup> is generated via a direct O-abstraction mechanism on the sextet PES, whereas on the quartet pathway, a N–O insertion mechanism is favored. Considering the two-state reactivity phenomenon, the rate-limiting barrier for the N<sub>2</sub>O reduction is located at 2.8 kcal/mol below the sextet entrance channel; and the overall reaction is exothermic by 35.9 kcal/mol.

### 3.3 C<sub>2</sub>H<sub>6</sub> oxidation by FeO<sup>+</sup>

PES together with schematic structures involved is shown in Figs. 1 and 2. Information about the relevant species is given in Fig. S1 (Supporting Information). Ethane oxidation by FeO<sup>+</sup> starts with the association of FeO<sup>+</sup> with C<sub>2</sub>H<sub>6</sub> forming two types of encounter complexes, i.e., **1a** and **1b**. Complexes **1a** and **1b** are characterized as η<sup>3</sup>-OFe<sup>+</sup>-C<sub>2</sub>H<sub>6</sub>, in which FeO<sup>+</sup> via Fe<sup>+</sup> is simultaneously coordinated with 2α,β-, and 3α-H atoms with the adiabatic binding energies of 29.8 (26.7) and 28.8 (23.4) kcal/mol in the sextet (quartet) state, respectively. As expected, the bindings are 6–7 kcal/mol stronger than OFe<sup>+</sup>-CH<sub>4</sub> (22.8 (16.4) kcal/mol at the B3LYP/Wachters:6-311G\*\* level [27, 28]) but 8–10 kcal/mol weaker than OFe<sup>+</sup>-C<sub>3</sub>H<sub>8</sub> (36.7 (33.6) kcal/mol at the same theoretical level [32]). The stability of OFe<sup>+</sup>-alkanes depends strongly on their structures, i.e., the η<sup>2</sup>-CH<sub>4</sub> complex [27, 28] accounts for the weakest binding, while the η<sup>4</sup>-C<sub>3</sub>H<sub>8</sub> complex [32] affords the strongest binding. The difference in stabilities of complexes can be explained by electron transfers between FeO<sup>+</sup> and the adjacent nucleophilic σ bonds in alkanes. NBO analysis shows that the association of OFe<sup>+</sup>-alkane favors strong electron donation from the adjacent σ(C–H) and σ(C–C) orbitals of alkanes to FeO<sup>+</sup>, suggesting that the number of adjacent σ bonds in alkanes is an important factor in determining the stability of OFe<sup>+</sup>-alkanes. This is perfectly consistent with the stability sequence as mentioned previously.

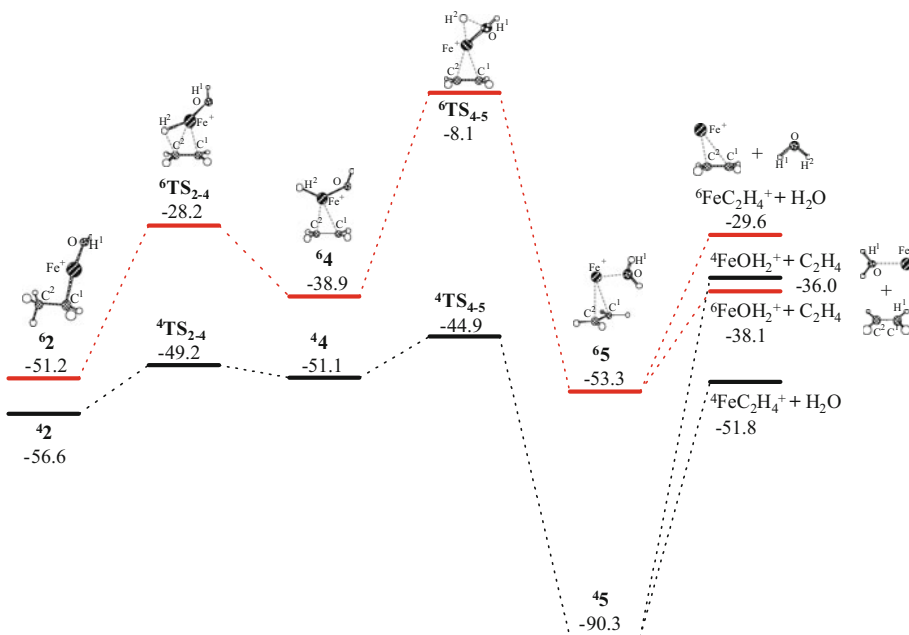
Through a direct C<sup>α</sup>-to-O H-shift, both **1a** and **1b** could give birth to hydroxyl complex (C<sub>2</sub>H<sub>5</sub>)Fe<sup>+</sup>(OH) (**2**), which lies at -51.2 (-56.6) kcal/mol in its sextet (quartet) state. The relevant transition states (TS<sub>1a-2</sub> and TS<sub>1b-2</sub>) lie at -7.1 (-12.6) and -3.9 (-7.0) kcal/mol, respectively, on the sextet (quartet) PES, suggesting a PESs crossing occurs before the transition state. Along the sextet coordinate, we also find a stepwise H-shift process from **1a** involving a (C<sub>2</sub>H<sub>5</sub>)Fe<sup>+</sup>H(O) minimum to **2** (See Fig. S2, Supporting Information). However, this path seems unlikely because it is located highly on the PES (*E*<sub>rel</sub> = ~16 kcal/mol).



**Fig. 1** Energy profile for the loss of ethanol involved in the  $C_2H_6$  oxidation by  $FeO^+$ . Numbers refer to the relative stabilities (kcal/mol) with respect to the reactants of  $C_2H_6 + FeO^+(^6\Sigma^+)$  evaluated at the

B3LYP/DZVP(opt + 3f):6-311 + G(2d,2p) level including ZPE corrections. Scaling factor for the ZPE is 0.961

**Fig. 2** Energy profile for the losses of ethylene and water from complex  $(C_2H_5)Fe^+(OH)$  involved in the  $C_2H_6$  oxidation by  $FeO^+$ . Parameters follow the same notation as in Fig. 1



As shown in Fig. 1, one exit of species **2** is the subsequent coupling of the two end ligands to yield the  $Fe^+$ (ethanol) adduct (**3**), in which the metal attaches to the O atom of  $C_2H_5OH$  with the  $Fe^+-O$  distance being 2.058 (1.980) Å for the sextet (quartet) state (see Fig. S1, Supporting Information). The new species is favored by the

high-spin state as its ground state (excitation energy of  $^6\mathbf{3} \rightarrow ^4\mathbf{3}$ : 5.1 kcal/mol) rather than the reverse order as for its direct precursor **2**. The relevant transition state  $^6TS_{2-3}$  ( $E_{rel} = -25.8$  kcal/mol) lies above the quartet one by 4.7 kcal/mol, indicating a PESs crossing occurs after the transition state. Direct dissociation of  $Fe^+$ -ethanol accounts

for the loss of ethanol and  $\text{Fe}^+(\text{}^6\text{D}$  or  $\text{}^4\text{F}$ ), with the overall exothermicity of 14.5 or 2.0 kcal/mol.

In the actual oxidation of ethane by  $\text{FeO}^+$ , ethanol elimination corresponds to only a branching ratio of 10–12% [15, 20]. Thus, the major part of species **2** undergoes  $\beta$ -H shift to form  $(\text{C}_2\text{H}_4)\text{Fe}^+(\text{OH}_2)$  (**5**), the direct precursor of water- and ethylene-loss products (see Fig. 2). Different from the situation of  $\text{}^6\mathbf{1a} \rightarrow \text{}^6\mathbf{2}$ , this process involves stepwise metal-mediated  $\beta$ -H shift ( $\mathbf{2} \rightarrow \mathbf{4} \rightarrow \mathbf{5}$ ). As shown in Fig. 2, the sextet  $\beta$ -H shift branch occurs via high-energy barriers  $\text{TS}_{2-4}$  and  $\text{TS}_{4-5}$  ( $E_{\text{rel}} = -28.2$  and  $-8.1$  kcal/mol), while the quartet process involves a low-energy pathway with the highest barrier located at  $-44.9$  kcal/mol ( $\text{TS}_{4-5}$ ). In both states, species **5** can be explained as the dicoordination of metal center with the difference that  $\text{Fe}^+\text{OH}_2$  and  $\text{FeC}_2$  unit are co-plane and the  $\text{Fe}^+\text{O}$  bond is along the  $\text{C}_2$  axis in the quartet ( $\text{C}_{2v}$ ), whereas the sextet association ( $\text{C}_s$ ) favors an out-of-plane location of the  $\text{Fe}^+\text{O}$  bond (the dihedral angle of  $\text{Fe}^+\text{O}$  to the  $\text{FeC}_2$ -unit plane is  $97.4^\circ$ ). NBO analysis suggests that the binding of  $\text{Fe}^+$  with both the  $\text{C}_2\text{H}_4$  and  $\text{H}_2\text{O}$  groups in **5** is dominated by electrostatic interaction as well as weak donor–acceptor stabilization due to the single occupation of the diffuse 4 s orbital of the metal. In the quartet, the relatively short distances between  $\text{Fe}^+$  and ligands (see Fig. S1, Supporting Information) and the relatively strong stability of the species (lying at  $-90.3$  kcal/mol or being 37.0 kcal/mol more stable than **5**) are caused by the much strong electron transfer ( $\Delta E^{(2)} = 192.6$  kcal/mol). Indeed, the quartet species constitutes the deepest energy well on the whole PES. Different bond cleavage of ethylene- $\text{Fe}^+$ -water (**5**) accounts for products  $\text{FeC}_2\text{H}_4^+ + \text{H}_2\text{O}$  and  $\text{FeOH}_2^+ + \text{C}_2\text{H}_4$ , with the overall exothermicities of 29.6 (51.8) and 38.1 (36.0) kcal/mol on the sextet (quartet) PES, respectively.

An overlook of the PESs of  $\text{FeO}^+$ /methane [27, 28], ethane, and propane [32] shows that all the neutral products' eliminations start with initial C–H activation (C–to–O H-shift) forming the key intermediate (alkyl) $\text{Fe}^+(\text{OH})$ , which is followed by three possible pathways, i.e., C–O coupling accounting for the common products, alcohols;  $\text{Fe}^+$ -mediated alkyl H-shift for yielding water and alkenes in the  $\text{FeO}^+/\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  systems; and  $\text{CH}_3$ -shift for producing methyl in the  $\text{FeO}^+ + \text{C}_3\text{H}_8$  reaction. The initial C–H activation with a sextet-to-quartet spin inversion constitutes the rate-determining step for all the three oxidation reactions. Considering the crossing of the PESs, ethane and propane experience almost same barriers to activate their C–H activation (17.2 v.s. 17.7 kcal/mol [32]), whereas the barrier for methane is slightly higher (22.1 kcal/mol [27, 28]). However, because the stability of  $\text{FeO}^+(\text{alkane})$  increases gradually with the alkyl chain length as discussed previously, the C–H activation barriers

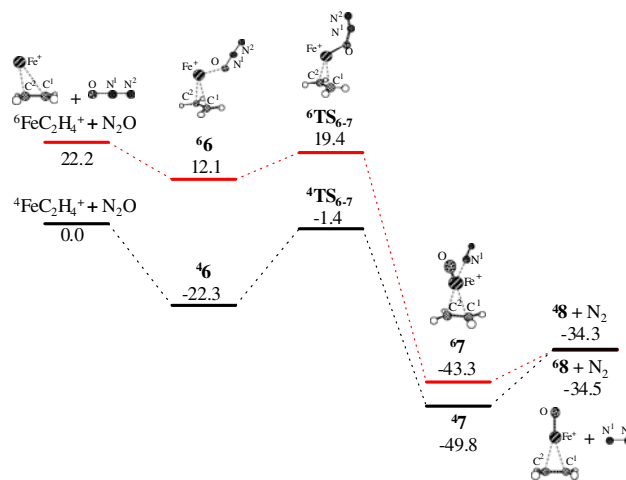
for  $\text{C}_n\text{H}_{2n+2}$  ( $n = 1-3$ ) are, respectively, 0.7 [27, 28], 12.6, and 19.0 [32] kcal/mol below the corresponding separated reactants ( $\text{FeO}^+(\text{}^6\Sigma^+) + \text{alkane}$ ), and the reaction inclination favors the order of  $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8$ . This is in line with the experimental results ( $k(\text{CH}_4) = (7.4 \pm 2.2) \times 10^{-10}$   $\text{cm}^3/\text{molecule}\cdot\text{s}$ ;  $k(\text{C}_2\text{H}_6) = 8.4 \times 10^{-10}$   $\text{cm}^3/\text{molecule}\cdot\text{s}$  at room temperature [20, 47, 70]).

### 3.4 $\text{FeC}_2\text{H}_4^+$ oxidation by $\text{N}_2\text{O}$

$\text{FeC}_2\text{H}_4^+$  oxidation by  $\text{N}_2\text{O}$  could result in five parallel neutral eliminations corresponding to  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CH}_2\text{O}$ ,  $\text{CH}_2\text{CH}$ , and  $\text{C}_2\text{H}_4\text{O}$  [20]. In the following, all possible mechanisms for these products are considered.

#### 3.4.1 $\text{N}_2\text{O}$ reduction by $\text{FeC}_2\text{H}_4^+$

PES together with the schematic structures involved is shown in Fig. 3. Information about the relevant species is given in Fig. S3 (Supporting Information). Initially,  $\text{N}_2\text{O}$  association with  $\text{FeC}_2\text{H}_4^+$  yields  $(\text{C}_2\text{H}_4)\text{Fe}^+(\text{N}_2\text{O})$  (**6**) stabilizing the system by 10.1 (22.3) kcal/mol in the sextet (quartet) state. Then, the system evolves into  $(\text{C}_2\text{H}_4)\text{Fe}^+(\text{N}_2)$  (**7**) through transition-state  $\text{TS}_{6-7}$  that lies at 19.4 (sextet) and  $-1.4$  (quartet) kcal/mol. Because of the relatively weak interaction between the metal and  $\text{N}_2$ , direct ejection of  $\text{N}_2$  from species **7** finally gives  $(\text{C}_2\text{H}_4)\text{Fe}^+(\text{O})$  (**8**), which is nearly energetically degenerated in the high- and low-spin states ( $-34.5$  and  $-34.3$  kcal/mol).



**Fig. 3** Energy profile for  $\text{N}_2\text{O}$  reduction by  $\text{FeC}_2\text{H}_4^+$  involved in the  $\text{FeC}_2\text{H}_4^+$  oxidation by  $\text{N}_2\text{O}$ . Numbers refer to the relative stabilities (kcal/mol) with respect to the reactants of  $\text{}^4\text{FeC}_2\text{H}_4^+ + \text{N}_2\text{O}$  evaluated at the B3LYP/DZVP(opt + 3f):6-311 + G(2d,2p) level including ZPE corrections. Scaling factor for the ZPE is 0.961

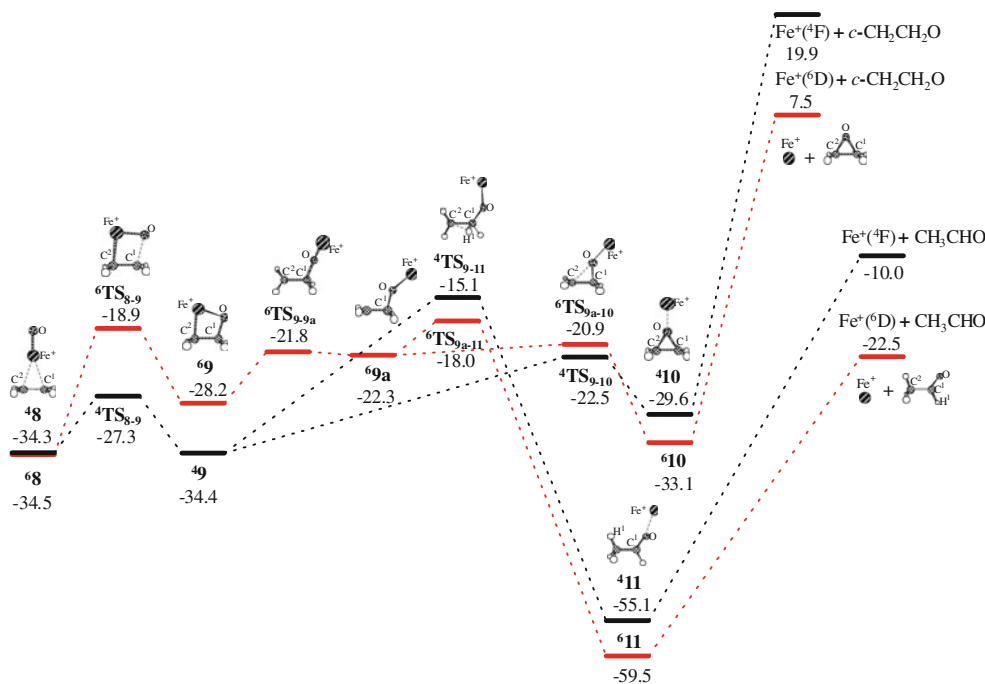
### 3.4.2 Regeneration of $\text{Fe}^+$

Using the internal energy acquired, species **8** could regenerate  $\text{Fe}^+$  affording oxirane, acetaldehyde, and/or ethenol via direct H-abstraction and/or cyclization mechanisms. PESs together with the schematic structures involved are shown in Figs. 4 and 5. The information about the relevant geometries is given as Supporting Information (see Figs. S4 and S6).

(a) *Loss of oxirane and acetaldehyde.* Loss of oxirane and acetaldehyde is found to occur through the cyclization

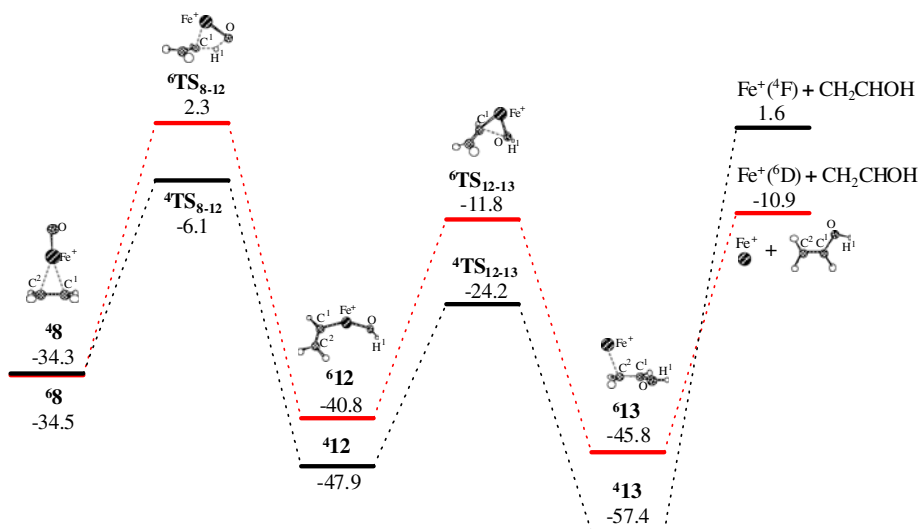
mechanism. From Fig. 4, we can find that the mechanism implies an intramolecular rearrangement of  $\text{FeO}^+$  in species **8** forming a “metallaoxacyclobutane” species (**9**), which lies at  $-28.2$  ( $-34.4$ ) kcal/mol in its sextet (quartet) state. This process is expected to take place readily, because the relevant activation energy is only  $15.6$  ( $7.0$ ) kcal/mol on the sextet (quartet) PES.

Species **9** conversion to the  $\text{Fe}^+$ (oxirane) adduct (**10**) involves different pathways on the different PESs, that is, the direct coupling of the metal-coordinated O and C atoms mediated by an  $\text{O}-\text{C}^1-\text{C}^2$  scissor vibration along the



**Fig. 4** Energy profile for the losses of acetaldehyde and oxirane via the cyclization mechanism involved in the  $\text{FeC}_2\text{H}_4^+$  oxidation by  $\text{N}_2\text{O}$ . The ejected  $\text{N}_2$  is not shown. Parameters follow the same notation as in Fig. 3

**Fig. 5** Energy profile for the loss of ethenol via the direct hydrogen abstraction mechanism involved in the  $\text{FeC}_2\text{H}_4^+$  oxidation by  $\text{N}_2\text{O}$ . The ejected  $\text{N}_2$  is not shown. Parameters follow the same notation as in Fig. 3





quartet coordinate and the two-step reaction profile of homolytic ring-opening to  $\text{Fe}^+\text{OCH}_2\text{CH}_2$  (**9a**) and subsequent C<sup>2</sup>–O coupling on the sextet PES. The sextet stationary points ( ${}^6\text{TS}_{9-9a}$ ,  ${}^6\text{TS}_{9a-10}$ , and  ${}^6\mathbf{9a}$ ) are located in a flat region of  $-20.9$  to  $-22.3$  kcal/mol, slightly higher than the quartet barrier  ${}^4\text{TS}_{9-10}$  ( $E_{\text{rel}} = -22.5$  kcal/mol). Direct rupture of  $\text{Fe}^+$ -oxirane (**10**) accounts for  $\text{Fe}^+(\text{}^6\text{D}$  or  $\text{}^4\text{F}) + \text{oxirane}$ , which is endothermic by 7.5 kcal/mol or located at 19.9 kcal/mol with respect to the reactants of  ${}^4\text{FeC}_2\text{H}_4^+ + \text{N}_2\text{O}$ .

Alternatively, direct C-to-C H-shift from species  ${}^6\mathbf{9a}$  and  ${}^4\mathbf{9}$  yields the  $\text{Fe}^+$ (acetaldehyde) adduct (**11**). The new adduct is very stable, lying at  $-59.5$  and  $-55.1$  kcal/mol in its sextet and quartet states, and the relevant saddle points  ${}^6\text{TS}_{9a-11}$  and  ${}^4\text{TS}_{9-11}$  are located at  $-18.0$  and  $-15.1$  kcal/mol, respectively. Direct decomposition of  $\text{Fe}^+$ -acetaldehyde affords  $\text{Fe}^+(\text{}^6\text{D}$  or  $\text{}^4\text{F})$  and acetaldehyde, with the overall exothermicity of 22.5 or 10.0 kcal/mol. Furthermore, the  ${}^6\mathbf{9a}$  ( ${}^4\mathbf{9}$ )  $\rightarrow$  **11** conversion could also proceed via  $\text{Fe}^+$ -mediated H-transfer (see Fig. S5, Supporting Information), but it is less kinetically favorable due to the higher barrier as well as the more complex process involved.

(b) *Loss of ethenol.* Loss of ethenol is found to proceed via cyclization and/or direct H-abstraction mechanisms. The former involves metallacycle species **9** and then experiences a direct C<sup>z</sup>-to-O H shift yielding  $\text{Fe}^+$ (ethenol) adduct (**13**), which is assisted by the stretch of the  $\text{Fe}^+\text{O}$  bond (see Fig. S7, Supporting Information). However, the H-shift process needs to overcome a high-energy barrier ( $\sim 6$  kcal/mol above the energetic zero) and thus is kinetically unfavorable.

Alternatively, the direct H-abstraction mechanism offers a relative low-energy pathway. From Fig. 5, we can find that it occurs through direct C-to-O H shift from species **8** to form hydroxyl complex **12**, followed by a subsequent OH rebound yielding adduct **13**, with the H-shift barrier ( $\text{TS}_{8-12}$ ) as the rate-determining point ( $E_{\text{rel}} = 2.3$  ( $-6.1$ ) kcal/mol for the sextet (quartet)). An obvious feature of adduct  ${}^6\mathbf{13}$  is the attachment of the metal to the terminal C atom of  $\text{CH}_2\text{CHOH}$ , whereas the quartet counterpart favors a  $\text{Fe}^+-\text{C}^1-\text{C}^2$  triangle structure. Such a situation has also been found for the  $\text{Fe}^+$ (ethynol) association [31]. The stability of the quartet state (lying at  $-57.4$  kcal/mol or being 11.6 kcal/mol more stable than  ${}^6\mathbf{13}$ ) suggests that the triangle-type bonding stabilizes the species largely. Direct dissociation of  $\text{Fe}^+$ -ethenol accounts for  $\text{Fe}^+(\text{}^6\text{D}$  or  $\text{}^4\text{F}) + \text{ethenol}$ , with the overall exothermicity of 10.9 or  $-1.6$  kcal/mol.

Here, we make an inspection of the O-atom transfer PESs of  $\text{OFe}^+(\text{C}_2\text{H}_4)$  and  $\text{OFe}^+(\text{C}_2\text{H}_2)$  obtained at the same level of theory by us [31], which can be seen as the prototype of the oxidation of unsaturated hydrocarbons by late transition metal oxide ions. For both the ethylene and

acetylene oxidation by  $\text{FeO}^+$ , the O-atom transfer product ( $\text{C}_2\text{H}_4\text{O}/\text{C}_2\text{H}_2\text{O}$ ) could be carbonyl compound (acetaldehyde/ketene), hydroxy compound (ethenol/ethynol), and epoxy compound (oxirane/formylcarbene). From the point of view of applications, O-atom transfer to yield epoxides is one of the most important oxidation reactions of alkenes [4, 71]. However, although the oxirane formation experiences a simple cyclization and O–C coupling process, it is the least thermodynamically favorable due to the strong endothermicity, similar to the situation of formylcarbene. On the other hand, carbonylation (for acetaldehyde/ketene) is the most thermodynamically and kinetically favorable channel because of the strong exothermicity as well as low transition states along the production pathway (cyclization–C-to-C hydrogen shift). Hydroxylation (for ethenol/ethynol) as an energetically less-favorable oxidation channel proceeds according to direct H-abstraction and C–O coupling mechanism.

### 3.4.3 Formation of $\text{FeX}^+$ ( $X = \text{CO}$ , $\text{OH}$ , $\text{C}_2\text{H}_2$ , and $\text{CH}_2$ )

We have extensively surveyed all possible pathways for the formation of by-products  $\text{FeX}^+$  ( $X = \text{CO}$ ,  $\text{OH}$ ,  $\text{C}_2\text{H}_2$ , and  $\text{CH}_2$ ). It is found that yielding  $\text{FeCO}^+$  from  $\text{Fe}^+$ (acetaldehyde) (**11**) is too complex to compete with the direct  $\text{CH}_3\text{CHO}$ -loss channel (see Fig. S5, Supporting Information), explaining the minor  $\text{FeX}^+$  ( $<12\%$ ) observed by the fourier transform ion cyclotron resonance (FTICR) experiment [20]. Interestingly, we found the water-loss channel yielding  $\text{FeC}_2\text{H}_2^+$  is exothermic by 30.7 kcal/mol, which proceeds according to direct H abstraction from  $(\text{C}_2\text{H}_4)\text{Fe}^+\text{O}$  (**8**) followed by stepwise  $\beta$ -H shift with the highest barrier at  $-6.1$  kcal/mol (see Fig S10, Supporting Information). Thus, loss of water is indeed a thermodynamically and kinetically favorable channel, which is different with the FTICR result ( $\text{FeX}^+ < 12\%$  [20]). The difference can be rationalized by the fact that  $\text{FeC}_2\text{H}_2^+$  could be quickly further oxidized to  $\text{Fe}^+ + \text{C}_2\text{H}_2\text{O}$  by another  $\text{N}_2\text{O}$  due to the high reactivity of  $\text{Fe}^+$ . This fact is supported by the efficient  $\text{Fe}^+$ -catalyzed oxidation of  $\text{C}_2\text{H}_2$  by  $\text{N}_2\text{O}$ , which has been studied in detail both experimentally and theoretically [31, 72]. Therefore, although C–C bond activation ( $\text{FeCO}^+$ ) in the  $\text{FeC}_2\text{H}_4^+ + \text{N}_2\text{O}$  reaction is kinetically unfavorable, the competing activation of C–H bond for producing  $\text{FeC}_2\text{H}_2^+$  would decrease the selectivity of the O-atom transfer.

Formation of  $\text{FeOH}^+$  and  $\text{FeCH}_2^+$  is calculated to be endothermic by 8.2 and 2.1 kcal/mol, respectively (see Figs. S8 and S9, Supporting Information). However, as mentioned previously, owing to the over stability ( $\sim 11$  kcal/mol) of the  $\text{FeC}_2\text{H}_4^+ + \text{N}_2\text{O}$  asymptote that should be taken into account, both two product channels would be really exothermic. Indeed, the exothermicities of

1.0 (−0.7) and 14.5 (12.8) kcal/mol for yielding  $\text{FeOH}^+$  and  $\text{FeCH}_2^+$  at 0 (298) K have been estimated through thermochemical calculations [73]. Note that except the  $\text{FeC}_2\text{H}_4^+ + \text{N}_2\text{O}$  asymptote, the relative energies of the other dissociation channels are still described well at the present level of theory. Therefore, it is the high locations of the exit channels that explain the minor production of  $\text{FeOH}^+$  and  $\text{FeCH}_2^+$ , as observed in the experiment [20].

### 3.5 $\text{FeOH}_2^+$ oxidation by $\text{N}_2\text{O}$

The PES with the schematic structures involved is shown in Fig. 6. Information about the relevant species is given in Fig. S11 (Supporting Information).  $\text{N}_2\text{O}$  initially attaches to the metal of  $\text{FeOH}_2^+$  forming  $(\text{H}_2\text{O})\text{Fe}^+(\text{ON}_2)$  (**14**) and then is activated to yield  $(\text{H}_2\text{O})\text{Fe}^+\text{O}(\text{N}_2)$  (**15**). The relevant ground barrier ( ${}^4\text{TS}_{14-15}$ ) lies at 7.0 kcal/mol above species **14** and 19.9 kcal/mol below  ${}^6\text{FeOH}_2 + \text{N}_2\text{O}$ , suggesting it should occur more readily, in comparison with the  $\text{N}_2\text{O}$  activation by  $\text{FeC}_2\text{H}_4^+$  as described earlier. As shown in Fig. S11,  ${}^4\text{TS}_{14-15}$  is featured by a cyc- $\text{Fe}^+\text{O}-\text{N}^1$  structure, which favors formation of two singly occupied  $\sigma(\text{Fe}^+\text{O})$  and  $\sigma(\text{Fe}^+\text{N})$  orbitals, whereas for the analogous reaction with  $\text{FeC}_2\text{H}_4^+$ , the metal center in  ${}^4\text{TS}_{6-7}$  attaches at O from the end side of  $\text{N}_2\text{O}$ , forming only one singly occupied  $\sigma(\text{Fe}^+\text{O})$  orbital. Thus, the O- $\text{N}_2$  activation by  $\text{FeOH}_2^+$  favors an energetically lower-lying barrier in comparison with that by  $\text{FeC}_2\text{H}_4^+$ .

Direct ejection of  $\text{N}_2$  from **15** would account for the  $(\text{H}_2\text{O})\text{FeO}^+$  oxide (**16**) ( $E_{\text{rel}} = -52.5$  (46.2) kcal/mol for the sextet (quartet)), which could either release  $\text{H}_2\text{O}$  to form  $\text{FeO}^+$ , or undergo direct O-to-O H shift yielding the energetically more stable complex  $\text{Fe}(\text{OH})_2^+$  (**17**) ( $E_{\text{rel}} = -66.9$  (−55.3) kcal/mol). The sextet (quartet) transition

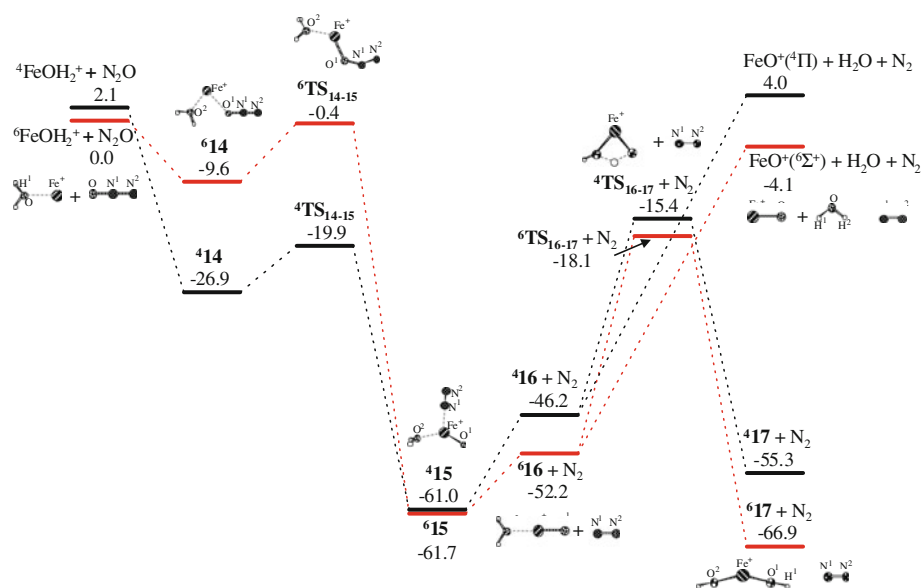
state ( ${}^6\text{TS}_{16-17}$ ) for the H-shift is located at 18.1 (15.4) kcal/mol below the entrance channel and 14.0 (19.4) kcal/mol more stable than the exit channel of  $\text{FeO}^+ + \text{H}_2\text{O}$  ( $E_{\text{rel}} = -4.1$ (4.0) kcal/mol). Thus, the reactive  $\text{FeO}^+$  regeneration is energetically unfavorable.

### 3.6 Gas-phase $\text{Fe}^+$ -mediated oxidation of $\text{C}_2\text{H}_6$ by $\text{N}_2\text{O}$

Gas-phase FTICR and collision-induced dissociation (CID) experiments have inferred that this reaction mainly produces  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_4\text{O}$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  (reactions 1–4) [15, 20]. Owing to the formation of the  $[\text{Fe}, \text{O}_2, \text{H}_2]^+$  as a side product, the turnover number for the reaction cycle is limited to about 2.5 [15, 20].

In the present theoretical investigation, after formation of  $\text{FeO}^+$  via  $\text{N}_2\text{O}$  reduction by  $\text{Fe}^+$ , ethane could be oxidized by the nascent oxide and partly converts via the C–O coupling mechanism to ethanol with 14.5 kcal/mol exothermicity. Also, it experiences an energetically more favorable  $\beta$ -H shift channel yielding water and ethylene, exothermic by 51.8 and 38.1 kcal/mol, respectively. This situation agrees with the CID and FTICR experimental findings, in which the  $\text{H}_2\text{O}/\text{C}_2\text{H}_4/\text{C}_2\text{H}_5\text{OH}$  branching ratio was approximately determined to be 70: 20: 10 [15] (67: 21: 12 [20]). Note that the calculated exothermicities for losses of ethanol and ethylene match well with the experimental estimations by Schröder and Schwarz (14.5 vs. 13 and 38.1 vs. 31 kcal/mol) [20]. Furthermore, the calculated  $\text{H}_2\text{O}$ -loss exothermicity (51.8 kcal/mol) is much larger than that estimated by Schröder and Schwarz (36 kcal/mol [20]) but agrees well with that estimated by Jackson et al. (51 kcal/mol [15]).

**Fig. 6** Energy profile for  $\text{FeOH}_2^+$  oxidation by  $\text{N}_2\text{O}$ . Numbers refer to the relative stabilities (kcal/mol) with respect to the reactants of  ${}^6\text{FeOH}_2^+ + \text{N}_2\text{O}$  evaluated at the B3LYP/DZVP(opt + 3f):6-311 + G(2d,2p) level including ZPE corrections. Scaling factor for the ZPE is 0.961





Another  $\text{N}_2\text{O}$  could react with the  $\text{H}_2\text{O}$ -loss partner  $\text{FeC}_2\text{H}_4^+$  to yield  $(\text{C}_2\text{H}_4)\text{Fe}^+\text{O}(\text{N}_2)$  (7). Due to the high barrier at  $-1.4$  kcal/mol (see Fig. 3), the N–O activation forms the rate-determining step of the whole oxidation. The thermal  $(\text{C}_2\text{H}_4)\text{Fe}^+\text{O}(\text{N}_2)$  would release a  $\text{N}_2$  molecule and then is further oxidized to acetaldehyde, ethenol, and oxirane, regenerating  $\text{Fe}^+$  (exothermic by 22.5, 10.9, and  $-7.5$  kcal/mol, respectively). Carbonylation to acetaldehyde appears to be the most thermodynamically and kinetically favored channel as discussed previously.

The  $\text{C}_2\text{H}_4$ -loss partner  $\text{FeOH}_2^+$  could also reduce  $\text{N}_2\text{O}$  yielding  $(\text{H}_2\text{O})\text{FeO}^+$ . In comparison with  $\text{C}_2\text{H}_4$ , the  $\text{H}_2\text{O}$  ligand is found to observably “enhance” the reactivity of  $\text{Fe}^+$  toward  $\text{N}_2\text{O}$ , as mirrored by the O– $\text{N}_2$  activation barriers of 12.7, 20.9, and 7.0 kcal/mol with respect to the corresponding encounter complexes of  $\text{Fe}^+\text{ON}_2$ ,  $(\text{C}_2\text{H}_4)\text{Fe}^+\text{ON}_2$ , and  $(\text{H}_2\text{O})\text{Fe}^+\text{ON}_2$ , respectively. This fact is also supported by the FTICR experimental study, in which the corresponding rate constant  $k$  of the three reactions was determined to be  $0.7 \times 10^{-10}$ ,  $0.5 \times 10^{-10}$ , and  $6 \times 10^{-10}$   $\text{cm}^3/\text{molecules}$ , respectively, at room temperature [20]. However,  $(\text{H}_2\text{O})\text{FeO}^+$  favors conversion into  $\text{Fe}(\text{OH})_2^+$ , rather than the reactive  $\text{FeO}^+$ , explaining a low turnover number (about 2.5) of reaction cycles as observed in experiment [20].

#### 4 Conclusions

The present theoretical work adds new insight into the gas-phase  $\text{Fe}^+$ -mediated oxidation of ethane by  $\text{N}_2\text{O}$ . After initial  $\text{N}_2\text{O}$  reduction by  $\text{Fe}^+$  yielding  $\text{FeO}^+$ , ethane oxidation by  $\text{FeO}^+$  as the second step of the reaction cycle involves initial C–H activation followed by two possible pathways, i.e., C–O coupling (for  $\text{Fe}^+$  and ethanol),  $\text{Fe}^+$ -mediated  $\beta$ -H shift (for the most energetically favorable products  $\text{FeC}_2\text{H}_4^+ + \text{H}_2\text{O}$ , with minor  $\text{FeOH}_2^+ + \text{C}_2\text{H}_4$ ).

$\text{FeC}_2\text{H}_4^+$  reaction with another  $\text{N}_2\text{O}$  constitutes the third step of the oxidation. The initial O– $\text{N}_2$  activation by  $\text{FeC}_2\text{H}_4^+$  to yield  $(\text{C}_2\text{H}_4)\text{Fe}^+\text{O}(\text{N}_2)$  constitutes the rate-determining step of the whole oxidation. The thermal  $(\text{C}_2\text{H}_4)\text{Fe}^+\text{O}(\text{N}_2)$  would release  $\text{N}_2$  and then is further oxidized via a cyclization mechanism for yielding oxirane, acetaldehyde, and/or direct H-abstraction mechanism accounting for ethenol. The most favorable channel is the oxidation to acetaldehyde along the cyclization-C-to-C H-shift pathway. The  $\text{C}_2\text{H}_4$ -loss partner  $\text{FeOH}_2^+$  could rapidly react with  $\text{N}_2\text{O}$  to form  $\text{Fe}(\text{OH})_2^+$ , rather than the reactive  $\text{FeO}^+$ .

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73. On the basis of the following thermochemical data:  $\Delta H_f^0(\text{C}_2\text{H}_4) = 12.5$  kcal/mol,  $\Delta H_f^0(\text{N}_2\text{O}) = 19.61$  kcal/mol,  $\Delta H_f^0(\text{CH}_2) = 92.45$  kcal/mol,  $\Delta H_f^0(\text{OH}) = 9.32$  kcal/mol,  $\Delta H_f^0(\text{CH}_2\text{O}) = -25.96$  kcal/mol ((1970) *Trans. Faraday Soc*, 66:794),  $\Delta H_f^0(\text{H}_2\text{CCH}) = 71.5$  kcal/mol ((1996) *Heats of Formation of Organic Free Radicals by Kinetic Methods in Energetics of Organic Free Radicals*, Blackie Academic and Professional, London),  $\text{BDE}(\text{Fe}^+-\text{C}_2\text{H}_4) = 35.0$  kcal/mol (ref 41),  $\text{BDE}(\text{Fe}^+-\text{CH}_2) = 82.2$  kcal/mol (ref 39), and  $\text{BDE}(\text{Fe}^+-\text{OH}) = 83$  kcal/mol (ref 37) at 298 K. Other data are from (1998) *NIST-JANAF Thermochemical Tables, Fourth Edition*, *J Phys Chem Ref Data*, Monograph 9, American Institute of Physics, New York