A Density-Functional Theory Based Study on the $^{16}O/^{18}O$-Exchange Reactions of the Prototype Iron – Oxygen Compounds FeO^+ and $FeOH^+$ with $H_2{}^{18}O$ in the Gas Phase

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Abstract: The mechanism of the degenerate $^{16}O/^{18}O$ exchange in the reactions of FeO^+ and $FeOH^+$ with water is examined by density functional theory. Based on previous experimental work (*Chem. Eur. J.* **1999**, *5*, 1176), two possible reaction pathways are investigated for both systems. The first mechanism consists of one (for $FeOH^+ + H_2O$) or two (for $FeO^+ + H_2O$) 1,3-hydrogen migrations from one oxygen atom to the other; the iron atom is not directly involved in these OH bond activations. The second route comprises a series of two (for $FeOH^+ + H_2O$) or four (for $FeO^+ + H_2O$) 1,2-hydrogen migration steps which involve the intermediate formations of metal-hydrogen bonds. Both mechanisms are evaluated under consideration of the respective low- and high spin potential-energy surfaces. The computational results show a clear preference for the 1,3-routes occurring on the respective high-spin surfaces bypassing the intermediacy of high-valent iron compounds having FeH bonds.

Keywords: ab initio calculations · gas-phase chemistry · hydration · iron hydroxide · iron oxide · oxygen exchange

Introduction

Transition metal oxides are of fundamental importance in numerous oxidation processes and their properties have been studied in great detail.[1, 2] Their diversity and reactivity is responsible for their usefulness in several branches of chemistry, such as biochemistry, catalysis, and organic synthesis. Among others, iron oxides are of most outstanding importance, not only because of their high natural abundance, but also because of the biological relevance of FeO units as reactive sites in biomolecules.[3]

An option to obtain information about the electronic features of intermediates and the role of transients is provided by probing the gas-phase chemistry of iron oxides in the absence of obscuring effects, for example aggregates, counterions, and solvents.[4] The diatomic FeO^+ ion is the most simple model of a reactive iron – oxo species; it is even capable of activating methane.[5] Reactivity studies of "bare" FeO^+ provided detailed insight into the behavior of what is considered the "reactive species" in the industrial and biochemical oxidation of hydrocarbons. Among the many processes of FeO^+ studied in the gas phase,[4, 6] the degenerate $^{16}O/^{18}O$ exchange in the reaction with isotopically labeled water is of special interest because occurrence of $^{16}O/^{18}O$ exchange has been suggested as a mechanistic probe for the intermediacy of reactive metal – oxo units in catalytic oxidations.[7] Aside the occurrence of association reactions to afford $[Fe,O_2,H_2]^+$ and $[Fe,O_2,H_3]^+$, respectively, when trapping FeO^+ and $FeOH^+$ with water in the gas phase,[8, 9] previous experimental studies[10, 11] have also described $^{16}O/^{18}O$ exchange of FeO^+ and $FeOH^+$ with $H_2{}^{18}O$. To summarize the conclusions of these studies, $FeOH^+$ is found to undergo isotopic exchange three times faster than FeO^+. Two possible explanations for the different reaction rates have been suggested.[11] i) In the reaction of FeO^+ with water, $^{16}O/^{18}O$ exchange requires two hydrogen shifts from one O-atom to the other, whereas a single hydrogen migration is sufficient for $FeOH^+$. ii) Based on computational studies of related iron(III) compounds, a quartet ground state is postulated for the iron dihydroxide cation $Fe(OH)_2{}^+$ as the key intermediate in the FeO^+/H_2O system, while the FeO^+ reactant has a $^6\Sigma^+$ sextet ground state.[12] Hence, $^{16}O/^{18}O$ exchange in FeO^+ is assumed to require spin crossover between the sextet and quartet surfaces and vice versa, thus decreasing the reaction efficiency. Such kinetic restrictions due to spin constraints have been recently described in terms of two-state reactivity.[13] In contrast, no spin inversions need to be involved in the $FeOH^+/H_2O$ system.

In the present study, we aim at improving these tentative arguments towards a more elaborate understanding of the reactions of FeO^+ and $FeOH^+$ with water by means of a theoretical approach. To this end, we examine the different

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options of hydrogen migrations in the FeO^+/H_2O and $FeOH^+/H_2O$ systems. Particular attention is paid to the possible role of spin multiplicities of the relevant transition structures and intermediates.

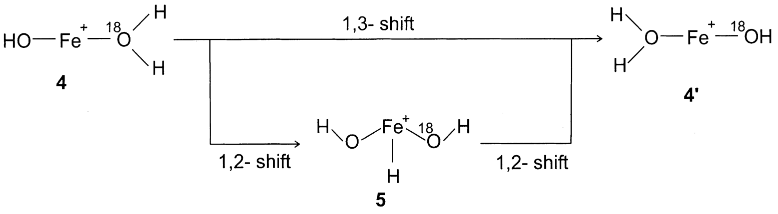
Theoretical Details

All calculations presented here are performed on either IBM/RS 6000 workstations or a Cray-YMP supercomputer with the program package Gaussian94,[14] and employ the density-functional theory (DFT)/Hartree–Fock hybrid-functional B3LYP with the $6-311+G^*$ basis set as implemented in Gaussian94.[15, 16] All stationary points are geometry optimized and further characterized by the evaluation of frequencies and normal modes. The connections between minima and transition structures are further ensured by internal reaction coordinate (IRC) calculations.[17] All energies given below include corrections for zero-point vibrational energy (ZPVE), and thus refer to relative energies at 0 K.

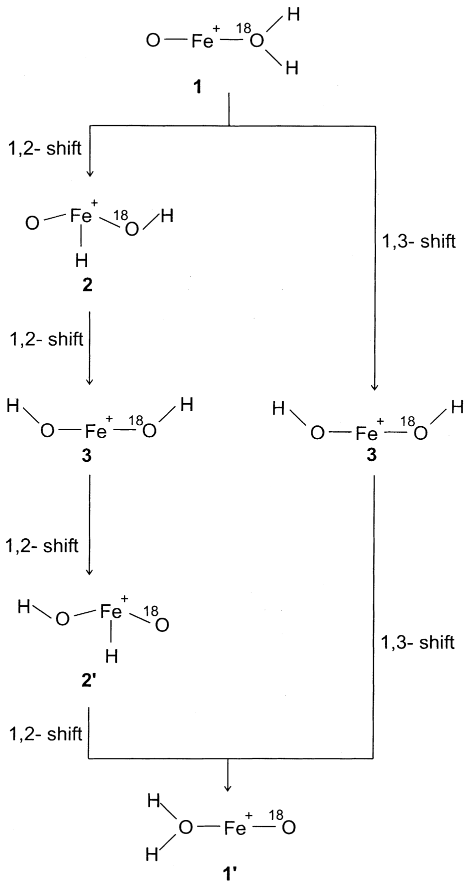
The B3LYP approach can efficiently describe transition metal compounds and often yields quite accurate geometries and frequencies. The averaged error of the relative energies calculated with B3LYP has been estimated as about $\pm 8\,kcal\,mol^{-1}$ for coordinatively unsaturated iron compounds.[18] Note, however, that calculations of atoms or atomic ions may be associated with even larger errors because of the known deficiency of the B3LYP approach to describe the low-spin/high-spin separation in transition metal atoms properly. This behavior is attributed to a bias of $3d^n$ over $3d^{n-1}4s^1$ configurations, which leads to an artificial preference for low spin $3d^n$ species.[18, 19] For example, the B3LYP/$6-311+G^*$ level of theory predicts Fe^+ (^4F) to be 4.1 $kcal\,mol^{-1}$ more stable than Fe^+ (^6D), while according to spectroscopy the Fe^+ ion has a ^6D ground state with a $3d^64s^1$ configuration which is 5.8 $kcal\,mol^{-1}$ lower in energy than Fe^+ (^4F).[20] Despite this erroneous ground-state assignment for the atom, the values given below refer to Fe^+ (^6D) when this asymptote is required. However, as bare iron cation plays a minor role in the system under investigation, we assume that the relative energetics of $[Fe,O_2,H_2]^+$ and $[Fe,O_2,H_3]^+$ can be described with the recommended accuracy of $\pm 8\,kcal\,mol^{-1}$ at this level of theory.

Results

For each of the reactants, FeO^+ and $FeOH^+$, two pathways are conceivable for oxygen-atom exchange with water. The reactions may proceed by direct 1,3-hydrogen migration steps or by sequential 1,2-hydrogen migrations. As a third variant, combinations of 1,2- and 1,3-shifts may be possible which are, however, not addressed explicitly. The 1,2-shift in the $FeO^+/H_2{}^{18}O$ system thus leads to formation of complex **2**, and a second 1,2-shift yields formation of the iron dihydroxide cation **3**, the latter is also the intermediate of the direct 1,3-migration (Scheme 1). The situation is slightly different in the $FeOH^+/H_2{}^{18}O$ system: here the 1,3-shift does not involve any reaction intermediates, while the consecutive 1,2-migrations proceed via intermediate **5** (Scheme 2). In both systems, the respective low- and high-spin surfaces are considered, that is quartet/sextet for FeO^+/H_2O and triplet/quintet for $FeOH^+/H_2O$. For the sake of simplicity, the notation used throughout this paper gives the spin multiplicities as superscripts preceding the formula while neglecting orbital symmetries, for example the sextet ground state FeO^+ ($^6\Sigma^+$) is referred to as $^6FeO^+$.



Scheme 2. Schematic description of the two calculated reaction pathways of the $FeOH^+/H_2{}^{18}O$ system. Note, that only the minima are displayed, transition structures that connect the minima are discussed in the text.



Scheme 1. Schematic description of the two calculated reaction pathways of the $FeO^+/H_2{}^{18}O$ system. Note, that only the minima are displayed, transition structures that connect the minima are discussed in the text.

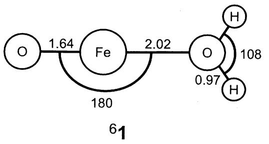
The system $FeO^+ + H_2O$

Reactants: In line with a number of previous theoretical studies using classical ab initio methods,[12, 13a, 21] pure DFT approaches,[22] as well as hybrid procedures,[21, 23] our computations predict a $^6\Sigma^+$ ground state for FeO^+ with an orbital occupation $1\sigma^2 2\sigma^2 1\pi^4 1\delta^2 2\pi^2 3\sigma^1$ in the valence space.[12, 13] The bond length is computed as $r_{FeO} = 1.64$ Å, and the calculated bond dissociation energy of $D_0(Fe^+{-}O) = 78.2\,kcal\,mol^{-1}$ agrees favorably with the experimental value of $80.0\,kcal\,mol^{-1}$;[24] however, this pleasing agreement is certainly due to a fortuitous error cancellation considering the erroneous ground-state assignment for bare Fe^+ (see above). Using B3LYP, we cannot unambiguously assign the electronic state of $^4FeO^+$, which may be either $^4\Pi$ or $^4\Phi$. The occupation for these quasi-degenerate states according to NBO analysis is $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3 2\pi^1 3\sigma^1$ in the valence space.[13] The calculated bond length of the quartet species ($r_{FeO} = 1.70$ Å) is large compared to previous ab-initio studies,[12, 13, 21] but matches the value of previous B3LYP calculations with different basis sets.[21, 22, 23] We note in passing that the potential-energy curve of $^4FeO^+$ is known to be quite flat in this region, that is a distortion by 0.01 Å translates to an energetic change of only about 0.2 kcal mol^{-1}.[12] Therefore, the long Fe–O bond in the quartet state should not be overrated. It is important to note, however, that the calculated state splitting of 8.2 kcal mol^{-1} between $^6FeO^+$ and $^4FeO^+$ is significantly lower than calculated in previous studies employing the CCSD(T) and CASPT2 levels of theory, resulting in $^4FeO^+/^6FeO^+$ splittings on the order of 12 – 19 kcal mol^{-1}.[13, 21] However, our result coincides with similar findings in recent B3LYP studies, where pure density functionals correlate much better with the CCSD(T) and CASPT2 splittings.[21, 22, 23] Nevertheless, we do not use pure density functionals as their performance is less adequate in the present case as is shown in an earlier study on the $[Fe,O,H_2]$ system.[22] In this context it needs to be noted that the hybrid functionals were in fact developed to overcome the shortcomings in the exchange term of the pure density functionals.

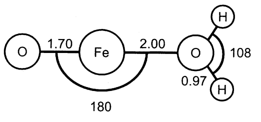
An $^1A_1$ ground state is computed for the water molecule with $r_{OH} = 0.96$ Å well reproducing experimental data, while the H-O-H angle $\alpha_{HOH} = 107.0°$ is slightly widened compared to the tabulated geometry.[25] In the following, all energetics of the FeO^+/H_2O system refer to the $^6FeO^+ + {}^1H_2O$ asymptote, which is arbitrarily set to $E_{rel}(FeO^+ + H_2O) = 0.0$ kcal mol^{-1}.

Encounter complex: For the encounter complex $(H_2O)FeO^+$ (**1**) we find a sextet ground state with the first excited quartet state 4.9 kcal mol^{-1} higher in energy. For both, ^{6}**1** and ^{4}**1**, the geometrical features of the separated FeO^+ and H_2O building blocks are mainly preserved. The new Fe–O bonds to the water ligands have comparable lengths of $r_{FeO} = 2.02$ Å and $r_{FeO} = 2.00$ Å for ^{6}**1** and ^{4}**1**, respectively. Given the similar geometries of ^{6}**1** and ^{4}**1** in conjunction with the flatness of the Fe–O potential in the bonding region of FeO^+ (see above), crossing between the sextet and the quartet surfaces is expected to be facile. Both encounter complexes are energetically located well below the entrance channel ($E_{rel} = -53.1$ and -48.2 kcal mol^{-1} for ^{6}**1** and ^{4}**1**, respectively). These well depths correspond to the binding energy of the water molecule to the FeO^+ unit and are rather strong compared to $D_0(Fe^+{-}OH_2) = 30.7$ kcal mol^{-1} for naked iron;[24] we return to this effect in the Discussion section.

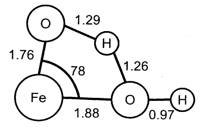
1,3-Mechanism: For reasons becoming obvious further below, the 1,3-route is discussed prior to the 1,2-variant. Along this mechanism, the reaction starting from **1** has to pass transition structure **TS1/3** to reach minimum **3**, $Fe(OH)_2{}^+$. The sextet state ^{6}**TS1/3** is located at $E_{rel} = -13.2$ kcal mol^{-1}, and the corresponding quartet state ^{4}**TS1/3** at $E_{rel} = -8.4$ kcal mol^{-1}. Three aspects are noteworthy in this context: i) the sextet and quartet TS lie well below the $^6FeO^+ + {}^1H_2O$ entrance channel, ii) in turn, the barriers for 1,3-hydrogen migration are sizable (ca. 40 kcal mol^{-1}) with respect to the encounter complexes, and iii) the sextet/quartet splitting is hardly changed going from **1** to **TS1/3**. As far as structural features are concerned, ^{6}**TS1/3** exhibits two different types of iron-oxygen bonds. The first one ($r_{FeO} = 1.88$ Å) shows a bond length between electrostatic bonding (as for instance $r_{FeO} = 2.12$ Å in $^6Fe(H_2O)^+)$[21b] and a formal Fe–O single bond (as for instance $r_{FeO} = 1.71$ Å in $^5FeOH^+$, see below). Compared to the iron – oxygen double bond in the iron – oxo unit of ^{6}**1** ($r_{FeO} = 1.64$ Å), the second Fe–O bond in ^{6}**TS1/3** is slightly elongated ($r_{FeO} = 1.76$ Å). While ^{4}**TS1/3** also shows one long Fe–O bond (1.90 Å), the second Fe–O bond (1.66 Å) is even shorter than that in the preceding minimum ^{4}**1**. However, except the differences in Fe–O bond lengths both transition structures are otherwise quite alike.



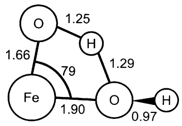
^{6}**1**



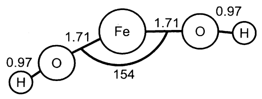
^{4}**1**



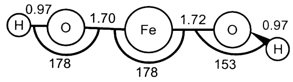
^{6}**TS1/3**



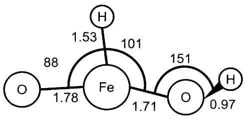
^{4}**TS1/3**



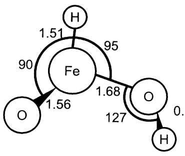
^{6}**3**



^{4}**3**



^{6}**2**



^{4}**2**

The imaginary frequencies of i1979 cm^{-1} (^{6}**TS1/3**) and i1939 cm^{-1} (^{4}**TS1/3**) correspond to migrations of a hydrogen atom from the water molecule to the oxo ligand without intermediate formation of an Fe–H bond. Note, that significant bending of the O-Fe-O units is required in the TS to allow migration of a hydrogen atom from one oxygen atom to the other without involving the metal center. Nevertheless, the minima connected to **TS1/3** show linear or at least almost linear arrangements. Therefore, prior to or simultaneously with the hydrogen migrations in the TSs, bendings of the O-Fe-O units are required. We have searched extensively for bent minimum structures of **1** and **3** in either spin states, but we have only been able to locate one such minimum, ^{6}**3**, at the applied level of theory. And even in ^{6}**3** the O-Fe-O angle is much less pronounced than in the corresponding transition state. Instead, the IRC calculations connecting **TS1/3** with their corresponding minima show two features. The first one, with steep slopes, corresponds to the hydrogen migration from the water ligand to the oxo unit, and the second, more smooth movements than comprise the widening of the O-Fe-O angle.

Following the reaction path, after passing **TS1/3** the dihydroxy-species **3** is reached. The sextet structure is predicted as global minimum on the $[Fe,O_2,H_2]^+$ surface ($E_{rel} = -66.4$ kcal mol^{-1} for ^{6}**3** and -52.7 kcal mol^{-1} for ^{4}**3**).

The geometrical features of the sextet structure are not very surprising, as both OH-moieties and their bonds to the iron cation are identical with $\alpha_{OFeO} = 154°$. In contrast, the OH groups are asymmetrically bound to iron in the quartet structure ^{4}**3**. While the Fe–O bond lengths are similar in ^{4}**3**, one Fe-O-H moiety is almost linear (178°) and the hydrogen atom of the second OH group is distinctly placed out of the plane of the rest of the molecule ($\theta_{OFeOH} = 154°$). Although dissimilar bonding in ^{4}**3** is conceivable, the computed geometry may also correspond to a spurious minimum due to symmetry breaking in the quasi-AB$_2$ type $Fe(OH)_2^+$ molecule. However, we have not further pursued this issue because the symmetrical sextet ^{6}**3** is assigned as the electronic ground state of $Fe(OH)_2^+$ ion.

From **3**, oxygen-atom exchange can proceed via **TS1/3** again in the reverse direction to reach the product side (Scheme 1: **1** → **3** → **1′**). Given the symmetry of ^{6}**3** and assuming a quasi-symmetric geometry of ^{4}**3**, both oxygen atoms are equilibrated in **3**. Overall, the computational prediction of **TS1/3**, lying 13.2 kcal mol^{-1} (^{6}**TS1/3**) and 8.4 kcal mol^{-1} (^{4}**TS1/3**) below the $^6FeO^+ + H_2O$ entrance channel can account for the $^{16}O/^{18}O$ exchange observed experimentally.[10, 11]

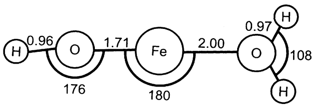
1,2-Mechanism: The separated reactants as well as the encounter complexes are common to both the 1,2- and 1,3-mechanisms (Scheme 1) and are therefore not presented again. From the encounter complex, the reaction continues by a 1,2-hydrogen transfer under formation of intermediate **2**, $(H)(OH)FeO^+$, where the metal center is surrounded by three ligands, that is H, O, and OH. The most prominent feature of **2** is the iron–hydrogen bond ($r_{FeH} = 1.53$ Å and 1.51 Å for ^{6}**2** and ^{4}**2**, respectively). The minima ^{6}**2** and ^{4}**2** are located at $E_{rel} = 30.8$ kcal mol^{-1} and $E_{rel} = 13.2$ kcal mol^{-1}. Because both structures are above the entrance channel as well as above any of the stationary points involved in the 1,3-pathways, we refrain from explicitly investigating the TSs for the 1,2-routes. Interestingly, however, the quartet ground state of the hydrido species ^{4}**2** is 17.6 kcal mol^{-1} below that of ^{6}**2**. Hence, if H–O bond insertion to yield **2** would occur at elevated energies, it would involve spin crossover in the lowest lying pathway. The computed high energy demand of **2** is in accord with the previous exclusion of the 1,2-mechanism based on the high oxidation states of the intermediates.[11] In fact, the bond lengths in either spin state of **2** indicate covalent bonding of iron to the ligands and thus its assignment as a formal Fe^V compound.

Finally, we note in passing that there exist other $[Fe,O_2,H_2]^+$ isomers, namely, the cationic iron(I) complexes of hydrogen peroxide $Fe(H_2O_2)^+$ on the quartet and sextet surfaces. However, these species are much higher in energy than **1** and **3** and even above the $FeO^+ + H_2O$ entrance channel.[26] Accordingly, the $Fe(H_2O_2)^+$ isomers cannot participate in the $^{16}O/^{18}O$ equilibration of the FeO^+/H_2O system under thermal conditions and are therefore not pursued any further.

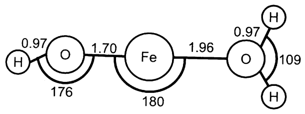
The system $FeOH^+ + H_2O$

Reactants: An $^5A''$ ground state is found for $FeOH^+$ when calculated in C$_s$ symmetry at the B3LYP/6–311 + G* level of theory. While quintet ground states of $FeOH^+$ are also found in previous studies,[18a, 21b] the exact assignment of the ground state is more difficult for the close lying $^5A'$ and $^5A''$ states.[22] Probably due to cancellation of errors, the computed $D_0(Fe^+{-}OH) = 88.7$ kcal mol^{-1} agrees quite well with the experimental value of 87.4 kcal mol^{-1}. The putative $HFeO^+$ isomers are situated much above $^5FeOH^+$ cation,[21b] and are therefore excluded from further consideration. Similarly, the lowest lying triplet state $FeOH^+$ ($^3A'$) is 38.8 kcal mol^{-1} higher in energy than $^5FeOH^+$. Therefore, it is reasonable to assume that the triplet surface will have only little influence on the minimum energy path of oxygen-atom exchange; consequently, the role of low-spin state species along the reaction coordinate will be kept short. The structures of quintet and triplet $FeOH^+$ are very much alike, being bent with similar bond lengths. As the water molecule was already mentioned above, it remains to note that the following energetic data are given with respect to the $^5FeOH^+ + {}^1H_2O$ asymptote, that is $E_{rel}(FeOH^+ + H_2O) = 0.0$ kcal mol^{-1}.

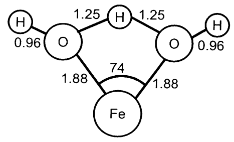
Encounter complex: The encounter complex **4** consists of a $FeOH^+$ ion complexed by an intact H_2O ligand on both spin surfaces. While the Fe-O-H units are almost linearized compared to free $FeOH^+$, the hydroxy and the water ligands reside on exactly opposite sides of the metal center ($\alpha_{OFeO} = 180°$). Although both spin states result in geometrically similar structures, the state splitting ($E_{rel} = -53.9$ kcal mol^{-1} and -11.6 kcal mol^{-1} for ^{5}**4** and ^{3}**4**, respectively) is even slightly larger than for the $FeOH^+$ reactant. Similar to the interaction between water and FeO^+ in **1**, the computed ligand binding energy $D_0(HOFe^+{-}OH_2) = 53.9$ kcal mol^{-1} is large compared to that of the bare metal, $D_0(Fe^+{-}OH_2) = 30.7$ kcal mol^{-1}.[24]



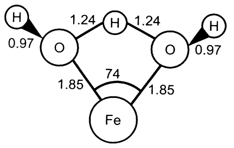
^{5}**4**



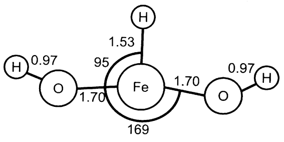
^{3}**4**



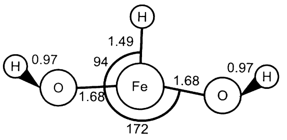
^{5}**TS4/4**



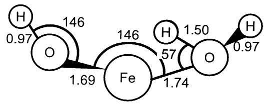
^{3}**TS4/4**



^{5}**5**



^{3}**5**



^{3}**TS4/5**

1,3-Mechanism: In contrast to the FeO^+/H_2O system, 1,3-hydrogen transfer is degenerate for **4** and results in immediate

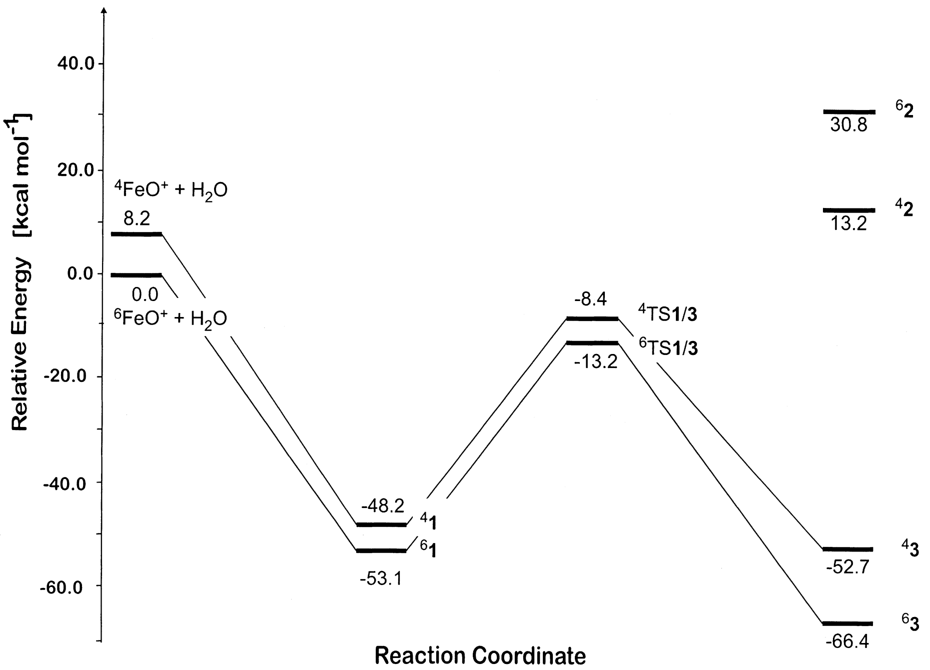


Figure 1. B3LYP/6–311 + G* surface of the FeO$^+$/H$_2$O system. All energies are given in kcal mol^{-1} relative to the entrance channel and include ZPVE contributions.

^{16}O/^{18}O exchange in the FeOH$^+$/H$_2$O system without involving a second step. On the quintet surface, the corresponding ^{5}**TS4/4** is located at $E_{rel} = -17.3$ kcal mol^{-1}; thus well below the energy demand of the isolated reactants FeOH$^+$ and H$_2$O ($E_{rel} = 0.0$ kcal mol^{-1}). While ^{3}**TS4/4** is clearly above the entrance channel ($E_{rel} =$ 6.1 kcal mol^{-1}), it is worth mentioning that the splitting between quintet and triplet surfaces is reduced from 38.8 kcal mol^{-1} in free FeOH$^+$ and 42.3 kcal mol^{-1} in **4** to only 23.4 kcal mol^{-1} in the TS. The TSs in the two spin states are structurally very much alike as are the imaginary frequencies (i1695 cm^{-1} and i1601 cm^{-1} for ^{5}**TS4/4** and ^{3}**TS4/4**, respectively). Not surprisingly, the Fe–O bonds, the O–H distances of the migrating hydrogen atom, and the two "stationary" O–H bonds are exactly equivalent in the transition structures. In analogy to **TS1/3** of the FeO$^+$/H$_2$O system, the OFeO units in **TS4/4** are bent, while these are almost linear in the corresponding minima. However, extensive computational search gives no indications for the existence of bent minima of **4** in either spin state.

1,2-Mechanism: In contrast to the 1,3-mechanism, the 1,2-route comprises two steps and a reaction intermediate which exhibits an iron–hydrogen bond, that is (H)Fe(OH)$_2^+$, **5**. This reaction intermediate is found at $E_{rel} = 11.2$ kcal mol^{-1} (^{5}**5**) and $E_{rel} = 23.3$ kcal mol^{-1} (^{3}**5**) on the respective spin surfaces. Although both structures of **5** almost have C_{2v} symmetry, the calculations proceeded only after reducing the symmetry to C_1. The hydrogen atoms are slightly bent out of plane in the optimized structures (1–2°), and seemingly equivalent bond lengths of the hydroxy bonds differ up to 0.04 Å. In analogy to the FeO$^+$/H$_2$O system, the location of these minima above the ^{5}FeOH$^+$ + ^{1}H$_2$O entrance channel as well as any of the stationary points associated with the 1,3-mechanism, leads us to exclude the participation of the 1,2-route in the oxygen-atom exchange of the FeOH$^+$/H$_2$O system under thermal conditions from further consideration. We note in passing, that ^{3}**TS4/5** ($E_{rel} = 35.3$ kcal mol^{-1}), which was located at an early stage of this investigation, is only slightly bent to form a O-Fe-O angle of 146° with an imaginary mode of i1140 cm^{-1} due to 1,2-hydrogen migration.

Discussion

The computed potential-energy surfaces of both reactions are depicted in Figures 1 and 2. Some general features are outlined first, followed by a comparison of the 1,2- versus 1,3-mechanisms and a discussion of the role of spin states in the isotopic exchange of the oxygen-atoms in FeO$^+$ and FeOH$^+$ with H$_2{}^{18}$O. Please keep in mind in this context, that the overall error of the calculations is estimated to be ±8 kcal mol^{-1}, as explained above.

In the description of the encounter complexes (H$_2$O)FeO$^+$ (**1**) and (H$_2$O)FeOH$^+$ (**4**), we noticed that the binding energies of water to FeO$^+$ and FeOH$^+$ are substantially increased compared to the bare metal, that is D_0(OFe$^+$–OH$_2$) = 53.1 kcal mol^{-1} and D_0(HOFe$^+$–OH$_2$) = 53.9 kcal mol^{-1} versus D_0(Fe$^+$–OH$_2$) = 30.6 kcal mol^{-1}.[24] While some enhancement of water binding upon ligation of iron cation has been reported in other cases, for example D_0(HFe$^+$–OH$_2$) = 32.7 kcal mol^{-1},[27] and D_0((H$_2$O)Fe$^+$–OH$_2$) = 39.2 kcal mol^{-1},[24] the present increases of the binding energies by about 80% indicate rather strong ligand effects. While no experimental thermochemistry is available for **1** and **4**, the observed difference of more than three orders of magnitude in the rates of termolecular association of bare Fe$^+$ and FeO$^+$ with water[8] supports the computational prediction of a substantially larger binding energy in the case of FeO$^+$. These effects can be explained in terms of increased ion–dipole interactions between the metal center and the water molecule in (H$_2$O)FeO$^+$ and (H$_2$O)FeOH$^+$ due to the presence of the electron-withdrawing oxygen or hydroxy ligands which increase the net positive charge on the metal. This conjecture is qualitatively consistent with the computed partial negative charges of the water ligands; according to Mulliken population analysis the charges increase from 0.12 in ^{6}Fe(OH$_2$)$^+$ to 0.22 in ^{6}(H$_2$O)FeO$^+$ and 0.19 in ^{5}(H$_2$O)FeOH$^+$.

Despite the stabilizing effect of the water ligand, **1** is not the global minimum of the [Fe,O$_2$,H$_2$]$^+$ system. Instead, hydrogen

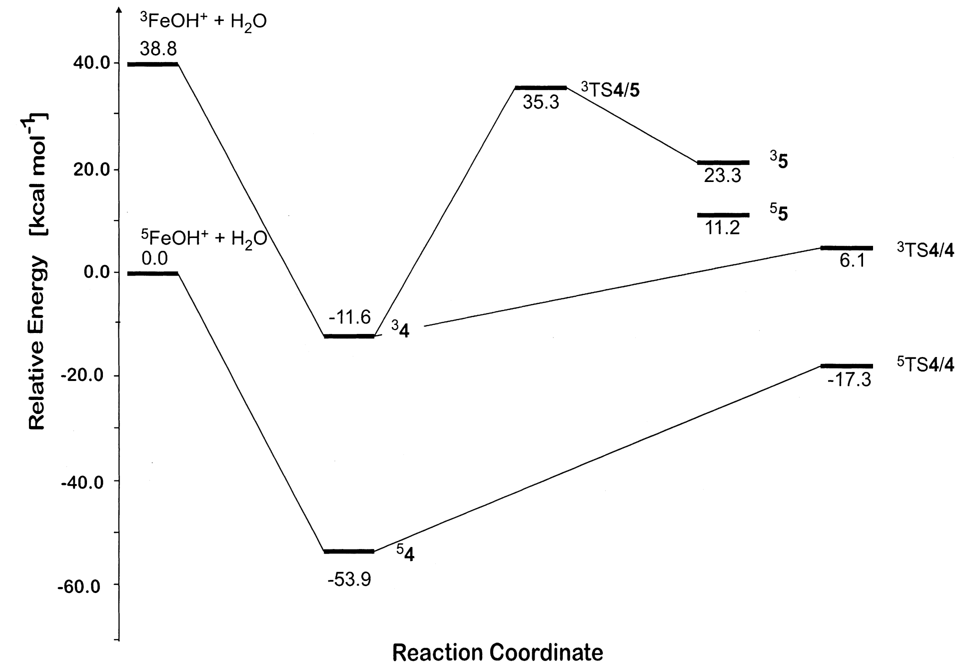


Figure 2. B3LYP/6-311+G* surface of the FeOH$^+$/H$_2$O system. All energies are given in kcal mol^{-1} relative to the entrance channel and include ZPVE contributions.

migration leads to the iron dihydroxide cation **3** which is 13.3 kcal mol^{-1} more stable than **1** on the lowest lying sextet surface. In passing, we note that this result has considerable implications for the conceptual understanding of oxidation catalysis. Metal–oxo units are often considered as essential reactive units in various bond-activation processes,[28] not only in gas-phase oxidations,[4] but also in other reactions induced by ionic metal fragments, for example the oligomerization of butadiene induced by ligated lanthanide cations.[29] In contrast, the corresponding dihydroxides, although bearing the same formal oxidation state, are often much less reactive.[29, 30] In particular, formation of Fe(OH)$_2^+$ has been identified as the limiting sink to the turnover number in the catalytic gas-phase oxidation of ethane.[31] Asides the role of kinetic aspects, also the consideration of thermochemical patterns derived from this work and additional literature data[24] underlines the non-negligible influence of water on the oxidizing strengths of the formal iron(III) compounds FeO$^+$ and (H$_2$O)FeO$^+$. For example, one-electron reduction to formal iron(II) [Reaction (1)] is much more exothermic for the metal–oxo species FeO$^+$ and (H$_2$O)FeO$^+$ compared to the dihydroxide Fe(OH)$_2^+$.

$$FeO^+ + H^\bullet \rightarrow FeOH^+ \qquad \Delta_rH = -109.3\ \text{kcal mol}^{-1} \qquad (1a)$$

$$(H_2O)FeO^+ + H^\bullet \rightarrow (H_2O)FeOH^+ \qquad \Delta_rH = -110.1\ \text{kcal mol}^{-1} \qquad (1b)$$

$$Fe(OH)_2^+ + H^\bullet \rightarrow (H_2O)FeOH^+ \qquad \Delta_rH = -96.8\ \text{kcal mol}^{-1} \qquad (1c)$$

$$FeO^+ \rightarrow Fe^+ + O \qquad \Delta_rH = -80.0\ \text{kcal mol}^{-1} \qquad (2a)$$

$$(H_2O)FeO^+ \rightarrow (H_2O)Fe^+ + O \qquad \Delta_rH = -102.4\ \text{kcal mol}^{-1} \qquad (2b)$$

$$Fe(OH)_2^+ \rightarrow (H_2O)Fe^+ + O \qquad \Delta_rH = -115.7\ \text{kcal mol}^{-1} \qquad (2c)$$

Further, the Fe–O bond in FeO$^+$ [Reaction (2a)] is significantly weaker than in (H$_2$O)FeO$^+$ [Reaction (2b)]; liberation of an oxygen atom from the dihydroxide is even more energy demanding [Reaction (2c)]. Given $\Delta_rH = -88.6$ kcal mol^{-1} for the oxygenation of methane according to $CH_4 + O \rightarrow CH_3OH$, the bare FeO$^+$ ion is thus capable of transferring an O atom to methane, while (H$_2$O)FeO$^+$ and Fe(OH)$_2^+$ are not. Likewise, hydroxylation of the weaker tertiary C–H bond in isobutane ($\Delta_rH = -102$ kcal mol^{-1}) is exothermic for FeO$^+$, thermoneutral for (H$_2$O)FeO$^+$, and considerably endothermic for Fe(OH)$_2^+$. Consequently, hydration of metal–oxo species can result in the formation of less, or even unreactive metal dihydroxides. In other words, the catalytic activity of metal–oxo units is likely to be reduced in the presence of water. Generalization of this microscopic behavior to a macroscopic scale is, however, not straightforward, because the addition of water to the reactant stream can also have positive effects on the performance of catalysts, for example the removal of catalyst poisons as well as surface soot.[32]

As far as the mechanistic course of oxygen-atom exchange is concerned, in both systems the clear energetic preference for the 1,3-route is beyond any doubt. Specifically, the associated transition structures **TS1/3** and **TS4/4**, respectively, are well below the entrance channels thereby accounting for the experimental observation of $^{16}O/^{18}O$ exchange under thermal conditions.[10, 11] In contrast, the occurrence of the 1,2-mechanism is excluded from further considerations for both systems because already the reaction intermediates **2** and **5** lie above the respective entrance channels. This result validates the previous speculation that the 1,2-mechanisms are unlikely in terms of unfavorable high oxidation states of the putative intermediates.[11]

In both systems, the reactions can be envisioned to proceed on the respective high-spin surfaces exclusively. While this result was expected for the FeOH$^+$/H$_2$O couple, precisely the opposite was suggested in the FeO$^+$/H$_2$O system in which a quartet ground state for the iron–dihydroxy intermediate was assumed. In fact, the statement "if the lessons learned from the FeO$^+$/H$_2$ and FeO$^+$/CH$_4$ systems... are taken into account, Fe(OH)$_2^+$ can be deduced to have a quartet ground state"[11] is not confirmed as the ground state of Fe(OH)$_2^+$ corresponds to a sextet state. The previous argument was based on the quartet ground states predicted for the various insertion intermediates of iron, for example HFeOH$^+$,[13, 21b, 22] CH$_3$FeOH$^+$,[23] C$_6$H$_5$FeOH$^+$,[33] and CH$_3$FeCH$_3^+$;[34] note, that a recent study of Ugalde and coworkers suggests that

$^6HFeOH^+$ is slightly lower in energy than $^4HFeOH^+$.[21b] In marked contrast to these perfect pairing situations, the $FeCl_2^+$ cation is predicted to have a sextet ground state.[35] Quite obviously, the electronegativity of the substituents plays a role in the determination of the electronic ground states, in that more electronegative ligands can better accommodate high-spin situations by localization of electrons on the ligands. Further, the O-Fe-O angle of 154° in sextet $Fe(OH)_2^+$ disfavors efficient overlap of the π-type molecular orbitals, thus also facilitating a high-spin situation. The $Fe(OH)_2^+$ ion is somewhat in between these examples, but more similar to the $FeCl_2^+$ case. Thus, the B3LYP assignment of a sextet ground state to **3** appears quite plausible. In contrast to the previous suggestion,[11] oxygen-atom exchange in the FeO^+/H_2O can therefore proceed on a single spin surface and there is no need to involve two-state reactivity.[13]

After having mapped out the relevant parts of the potential-energy surfaces, there remains to be answered the key question why the $^{16}O/^{18}O$ exchange is faster for $FeOH^+/H_2{}^{18}O$ than for $FeO^+/H_2{}^{18}O$. At first it is essential to note that the computed barriers for the rate-determining 1,3-hydrogen migrations are both well below, but yet relatively close to the respective entrance channel. This computational result is in accord with the experimental finding that $^{16}O/^{18}O$ exchange does not occur with collision frequency in either system. Secondly, the computed barrier is about 4 kcal mol^{-1} lower for $FeOH^+/H_2O$ than for FeO^+/H_2O. Such an energy difference of the transition structures may well be responsible for the 3:1 ratio of the rate constants observed experimentally, as in an Arrhenius-type formalism already small differences in barrier heights lead to large differences in the apparent rate constants. Thirdly, even if the barriers were of the same height relative to the entrance channel in both systems, isotopic exchange in FeO^+/H_2O is statistically disfavored over that in $FeOH^+/H_2O$, as both reactions do not have unit efficiency.

Let us briefly refer to a "Gedankenexperiment" in order to further illustrate this argument. To this end, we consider the same schematic potential-energy profiles for the oxygen exchange in FeO^+/H_2O and $FeOH^+/H_2O$, that is the barriers have similar locations with respect to the entrance channels and the same kinetic restrictions apply. The only difference is that O-atom exchange in $FeOH^+$ is completed after a single hydrogen migration, whereas FeO^+ requires two steps. In the diluted gas phase, formation of the encounter complexes occurs at the gas kinetic collision rate k_c. If the intermediate barriers are low, the forward reaction k_f is fast relative to redissociation into the reactants k_d (Figure 3a). For degenerate isotopic exchange, the backward reaction rate k_b is of course equal to k_f. Accordingly, for $k_f \gg k_d$ complete isotope equilibration occurs at the collision rate. If, however, the intermediate barriers are closer to the entrance channels—which is the case in both systems studied here—dissociation of the encounter complexes competes with the exchange, thereby reducing the reaction efficiency. In the extreme case of $k_f \ll k_d$ (Figure 3b) isotopic exchange in FeO^+ is only half as efficient as for $FeOH^+$, because the kinetic restriction imposed by the barrier applies twice in the FeO^+/H_2O system.

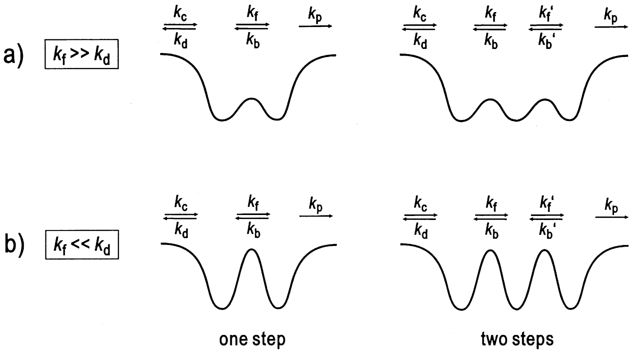


Figure 3. Hypothetical energy profiles for degenerate ion–molecule reactions involving two and three intermediates: a) negligible barrier and thus $k_f \gg k_d$, b) high barrier and thus $k_f \ll k_d$.

Finally, let us briefly consider the previous use of bond additivity schemes in the discussion of the different mechanistic scenarios.[11] For the isomers **1** and **3**, bond additivity predicts a difference of 47 kcal mol^{-1} in favor of the dihydroxide **3**,[36, 37] while theory predicts a difference of only 13 kcal mol^{-1}. Consideration of the extra stabilization of the oxo cation by the water ligand as predicted by theory, that is $D_0(OFe^+{-}OH_2) - D_0(Fe^+{-}OH_2) = 22.5$ kcal mol^{-1}, diminishes the difference between **1** and **3** to about 25 kcal mol^{-1}, but the deviation from the computed value remains significant. It is obvious that the discrepancy is due to the neglection of the effect of the formal valence state on the Fe−OH bonds, that is the assumption $D_0(HOFe^+{-}OH) \approx D_0(Fe^+{-}OH)$[24] $= 87.4$ kcal mol^{-1} is not justified. Instead, increasing valency of the iron obviously reduces the ability to form further covalent bonds. Thus, our B3LYP calculations predict $D_0(Fe^+{-}OH) = 88.7$ kcal mol^{-1} in good agreement with experiment, but only $D_0(HOFe^+{-}OH) = 67.4$ kcal mol^{-1} for the second bond of iron cation to a hydroxy ligand. Similarly, the exclusion of the 1,2-mechanism based upon assuming simple bond additivity suggests that hydrogen migration from the water ligand in **1** to the metal to form **2** is endothermic by only about 12 kcal mol^{-1},[38] while the B3LYP calculations predict a stability difference of as much as 66 kcal mol^{-1} in favor of **1**. Quite evidently, the assumption of bond additivity fails completely for high-valent iron compounds. Thus, while the qualitative implications of the additivity scheme may be applicable as far as the relative ordering of the isomers is concerned, the quantitative considerations are almost meaningless. This result questions—but by no means refutes–the use of additivity schemes when no other information is available, as changes in the formal oxidation states must be taken into account.

Conclusion

Theoretical analysis of the degenerate $^{16}O/^{18}O$ exchange reactions of FeO^+ and $FeOH^+$ with $H_2{}^{18}O$ confirms previous speculations about the mechanism of these fundamental reactions. Specifically, both reactions proceed by 1,3-hydrogen shifts from one oxygen atom to the other, thereby circumventing high-valent intermediates having Fe−H bonds. The explanation why $FeOH^+$ reacts more rapidly than FeO^+ is attributed to the joint action of two facts: i) the requirement of a two-step reaction in FeO^+/H_2O versus a one-step reaction in $FeOH^+/H_2O$ and ii) the energetically slightly more demanding transition structure involved in the FeO^+/H_2O system. However, the previous suggestion[11] that spin constraints may cause the different rate constants is disproved by the theoretical study, as the isotopic exchange can occur on the high-spin surface for both systems without any need to involve spin crossovers.

From a conceptual point of view, it is interesting to note that the role of the water in the passivation of the iron–oxo unit in FeO^+ has two facettes. At first, the mere coordination complex exhibits a pronounced binding to the water ligand, thereby enhancing the Fe–O bond strength and in turn reducing the ability of the oxo unit to act as an oxidizing agent. Second, O–H bond activation of water by the metal–oxo unit leads to a metal dihydroxide having a significantly reduced oxidizing strength as compared to the metal oxide.

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[36] This estimation works as follows (thermochemical data are taken from refs. [24] and [36]): $\Delta_fH_0(\mathbf{1}) \approx \Delta_fH_0(\mathrm{Fe^+}) + \Delta_fH_0(\mathrm{O}) + \Delta_fH_0(\mathrm{H_2O}) - D_0(\mathrm{Fe^+{-}O}) - D_0(\mathrm{Fe^+{-}OH_2})$ and $\Delta_fH_0(\mathbf{3}) \approx \Delta_fH_0(\mathrm{Fe^+}) + 2\,\Delta_fH_0(\mathrm{OH}) - 2\,D_0(\mathrm{Fe^+{-}OH})$, thus $\Delta_fH_0(\mathbf{1}) - \Delta_fH_0(\mathbf{3}) = \Delta_fH_0(\mathrm{O}) + \Delta_fH_0(\mathrm{H_2O}) - 2\,\Delta_fH_0(\mathrm{OH}) - D_0(\mathrm{Fe^+{-}O}) - D_0(\mathrm{Fe^+{-}OH_2}) + 2\,D_0(\mathrm{Fe^+{-}OH})$. With $\Delta_fH_0(\mathrm{O}) + \Delta_fH_0(\mathrm{H_2O}) - 2\,\Delta_fH_0(\mathrm{OH}) = -16.78 \pm 0.07\ \mathrm{kcal\,mol^{-1}}$, $D_0(\mathrm{Fe^+{-}H}) = 80.0 \pm 1.4\ \mathrm{kcal\,mol^{-1}}$, $D_0(\mathrm{Fe^+{-}OH_2^+}) = 30.6 \pm 1.2\ \mathrm{kcal\,mol^{-1}}$, and $D_0(\mathrm{Fe^+{-}OH}) = 87.4 \pm 3.4\ \mathrm{kcal\,mol^{-1}}$, **1** is estimated to be $47.4 \pm 3.9\ \mathrm{kcal\,mol^{-1}}$ less stable than **3**.

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[38] This estimation works as follows (thermochemistry taken from refs. [24] and [36]): $\Delta_fH_0(\mathbf{1}) \approx \Delta_fH_0(\mathrm{FeO^+}) + \Delta_fH_0(\mathrm{H_2O}) - D_0(\mathrm{Fe^+{-}OH_2})$ and $\Delta_fH_0(\mathbf{2}) \approx \Delta_fH_0(\mathrm{FeO^+}) + \Delta_fH_0(\mathrm{OH}) + \Delta_fH_0(\mathrm{H}) - D_0(\mathrm{Fe^+{-}OH}) - D_0(\mathrm{Fe^+{-}H})$, thus $\Delta_fH_0(\mathbf{1}) - \Delta_fH_0(\mathbf{2}) = -D_0(\mathrm{H{-}OH}) - D_0(\mathrm{Fe^+{-}OH_2}) + D_0(\mathrm{Fe^+{-}OH}) + D_0(\mathrm{Fe^+{-}H})$. With $D_0(\mathrm{H{-}OH}) = 118.08 \pm 0.05\ \mathrm{kcal\,mol^{-1}}$, $D_0(\mathrm{Fe^+{-}OH_2^+}) = 30.6 \pm 1.2\ \mathrm{kcal\,mol^{-1}}$, $D_0(\mathrm{Fe^+{-}OH}) = 87.4 \pm 3.4\ \mathrm{kcal\,mol^{-1}}$, and $D_0(\mathrm{Fe^+{-}H}) = 48.9 \pm 1.4\ \mathrm{kcal\,mol^{-1}}$, **1** is estimated to be $12.4 \pm 3.9\ \mathrm{kcal\,mol^{-1}}$ more stable than **2**.

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