Extreme Differences in the Interactions of 'Bare' Fe^+ and Fe^{2+} with Hydrogen Peroxide: *Fenton* Chemistry in the Gas Phase

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Short Communication

Dedicated to Professor *Hans-Jürgen Rosenkranz* on the occasion of his 60th birthday.

The interaction of bare iron mono- and dications with hydrogen peroxide in the gas phase is studied by *ab initio* calculations employing the B3LYP/6-311 + G* level of theory. For the monocation, the quartet and sextet coordination complexes $Fe(H_2O_2)_2^+$ are high-energy isomers that easily interconvert to the more stable iron dihydroxide monocation $Fe(OH)_2^+$ and hydrated iron oxide $(H_2O)FeO^+$ (quartet) or dissociate into $FeOH^+ + OH^•$ (sextet). On the dication surface, however, the order of stabilities is reversed in that $Fe(H_2O_2)^{2+}$ (quintet) corresponds to the most stable doubly charged species, while the formal Fe^{IV} compounds $Fe(OH)_2^{2+}$ and $(H_2O)FeO^{2+}$ are higher in energy.

Introduction. – As redox reactions are understood, the oxidation state plays an enormous role, despite the valency not corresponding to any physically observable property. In fact, what one considers a formal oxidation state is actually a subtle interplay of covalent, ionic, and dative interactions. A prominent example of where the simultaneous presence of reducing and oxidizing agents provides a rich redox chemistry is the well-known *Fenton* chemistry [1]. Here, the treatment of Fe^{II} salts with H_2O_2 gives rise to $HO^•$ radicals (*Eqn. 1*), which can initiate a broad variety of oxidation and degradation reactions *via* H-atom abstractions (*Eqn. 2*), addition to unsaturated systems [2], *etc*. In the presence of reducing agents[2]), $Fe^{II}(aq)$ can be regenerated (*Eqn. 3*), thus closing a catalytic cycle in which H_2O_2 serves to produce alkyl radicals (*Eqn. 4*).

$$Fe^{II}(aq) + H_2O_2 \rightarrow Fe^{III}(aq) + OH^- + HO^• \qquad (1)$$

$$R-H + HO^• \rightarrow R^• + H_2O \qquad (2)$$

$$Fe^{III}(aq) + e^- \rightarrow Fe^{II}(aq) \qquad (3)$$

$$R-H + H_2O_2 + e^- \rightarrow R^• + H_2O + OH^- \qquad (4)$$

Here, we report a computational study on the interaction of H_2O_2 with the Fe^+ and Fe^{2+} in the gas phase. Upon oxidation by H_2O_2, the Fe^I and Fe^{II} species Fe^+ and Fe^{2+} could give rise to the formation of $Fe^{II}-Fe^V$ compounds according to *Eqns. 5–8*. The

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[2]) Counterintuitively, the presence of oxidizers and reducing agents is required in several selective oxidations where O_2 is the terminal oxidant; for examples, see [3].

one-electron oxidation of the metal concomitant with homolytic cleavage of the O–O bond in *Eqns. 5* and *7* is analogous to *Fenton* chemistry, while *Eqns. 6* and *8* represent O-atom transfer from the peroxide to the metal concomitant with formal two-electron oxidation of the metal.

$$Fe^+ + H_2O_2 \rightarrow FeOH^+ + HO^\bullet \tag{5}$$

$$Fe^+ + H_2O_2 \rightarrow FeO^+ + H_2O \tag{6}$$

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + HO^\bullet \tag{7}$$

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \tag{8}$$

Previous gas-phase experiments have demonstrated that complexation of peroxides ROOR′ by transition-metal ions is followed by facile insertion of the metal into the peroxidic O–O bond with subsequent fragmentation [4][5]. In the case of Fe^+, formation of the insertion species $RO{-}Fe^+{-}OR'$ corresponds to a transition from formal Fe^I to Fe^{III}; here, RO and R′O are considered as one-electron acceptors, *i.e.*, $[R'O^- \cdots Fe^{3+} \cdots OR^-]$. When H_2O_2 ($R = R' = H$) is reacted with bare Fe^+, *Eqns. 5* and *6* are in competition to afford $FeOH^+$ and FeO^+ in a *ca.* 4:1 ratio [4b]. Similarly, collisional activation of $Fe(H_2O_2)^+$ gives rise to $FeOH^+$ and FeO^+ fragments with a preference for the former [4a]. However, the nature of the interaction between the metal and the peroxide, the structures of possible reaction intermediates involved, and the details of the competition between homolysis and O-atom transfer remained unknown for these fundamental processes[3]).

Computational chemistry offers a complementary way to examine the $[Fe,O_2,H_2]^{+/2+}$ potential-energy surfaces [7]. In the present computational study of singly and doubly charged $[Fe,O_2,H_2]^{+/2+}$, we employ the B3LYP functional implemented in GAUSSIAN94 together with 6-311+G* basis sets[4]) [8]. For the monocation, minima for the encounter complex $Fe(H_2O_2)^+$ are found on the quartet and sextet surfaces. The geometries of $^4\mathbf{1}^+$ and $^6\mathbf{1}^+$ are quite similar and featured by characteristic lengths of the O–O bonds of $r(O{-}O) \approx 1.45$ Å in $^4\mathbf{1}^+$ and $^6\mathbf{1}^+$; the major structural difference concerns r_{FeO}, which is somewhat larger in the high-spin species (*Fig. 1*). In these complexes, the geometry of H_2O_2 is hardly perturbed as compared to that of the free ligand, and both electromers can be described by predominating electrostatic interactions of the Fe^+ cation with the dipolar neutral. Because B3LYP tends to overestimate metal-ligand binding [9], the exchange reaction (*Eqn. 9*) is considered for estimation of the binding energy $D_0(Fe^+{-}H_2O_2)$, with the experimental value $D_0(Fe^+{-}H_2O) = 30.7 \pm 1.2$ kcal/mol [10a] as an anchor point[5]).

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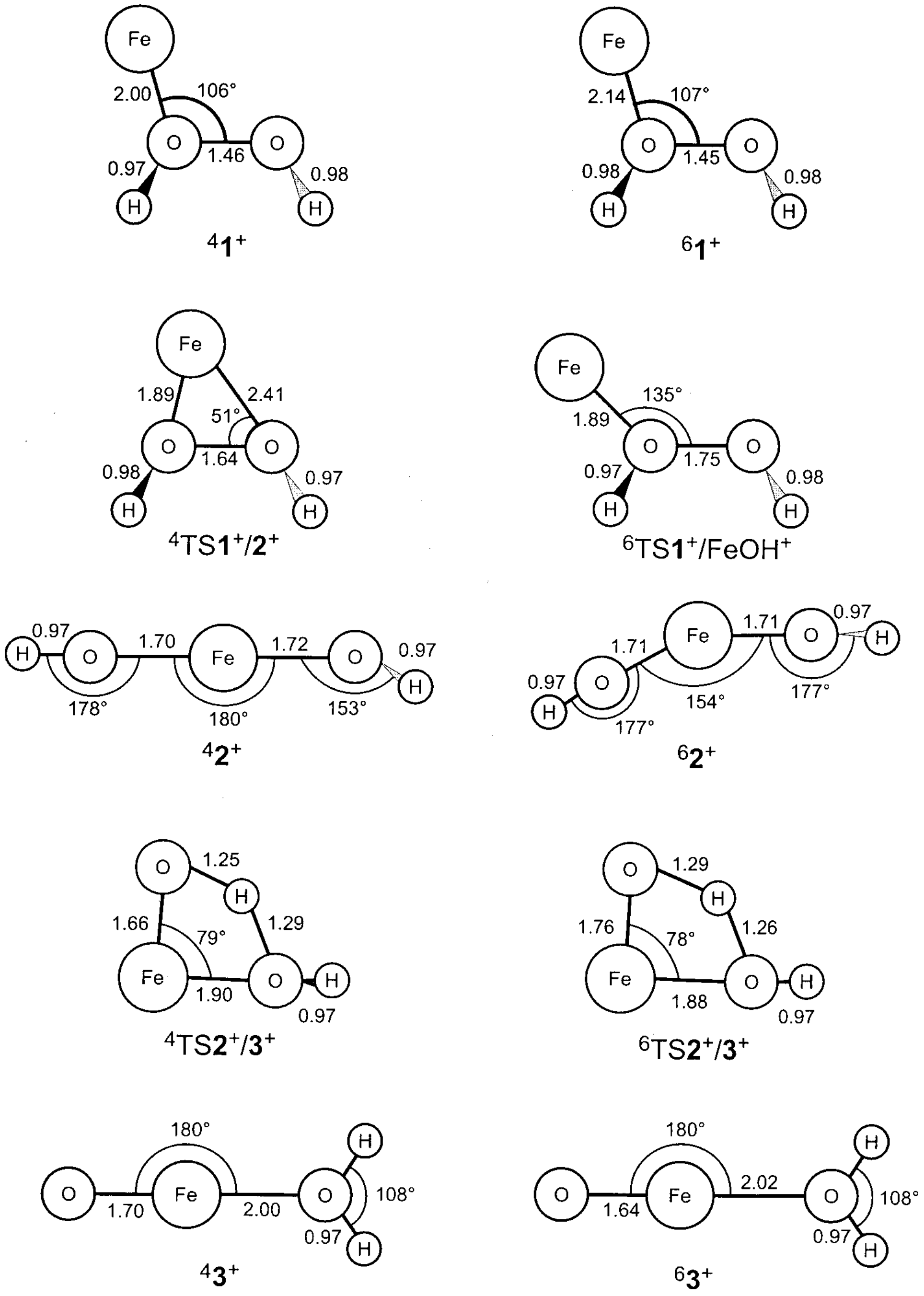
[3]) For experimental studies of $[Fe,O_2,H_2]^+$, see [6].

[4]) The calculations were performed on either IBM/RS 6000 workstations or a *Cray-YMP* supercomputer employing the B3LYP hybrid-functional as implemented in GAUSSIAN94. All stationary points were fully geometry-optimized; the monocations were further characterized by evaluation of frequencies and normal modes. The monocations' energies given below include corrections for zero-point vibrational energy (ZPVE), and thus refer to relative energies at 0 K, while the dication data do not include this correction.

[5]) Auxiliary thermochemical data were taken from [11]. *Eqn. 9* is considered for both the quartet and the sextet species. The anchor point for the sextet is the experimental $D_0(Fe{-}H_2O)^+$ given above [10a]. The anchor point for the quartet reaction (*Eqn. 9*) is calculated from the experimental value on the basis of the calculated quartet/sextet CCSD(T) splitting by *Ugalde* and co-workers [9].



$^4\mathbf{1}^+$

$^6\mathbf{1}^+$

^{4}TS$\mathbf{1}^+/\mathbf{2}^+$

^{6}TS$\mathbf{1}^+$/FeOH$^+$

$^4\mathbf{2}^+$

$^6\mathbf{2}^+$

^{4}TS$\mathbf{2}^+/\mathbf{3}^+$

^{6}TS$\mathbf{2}^+/\mathbf{3}^+$

$^4\mathbf{3}^+$

$^6\mathbf{3}^+$

(*Fig. 1*)

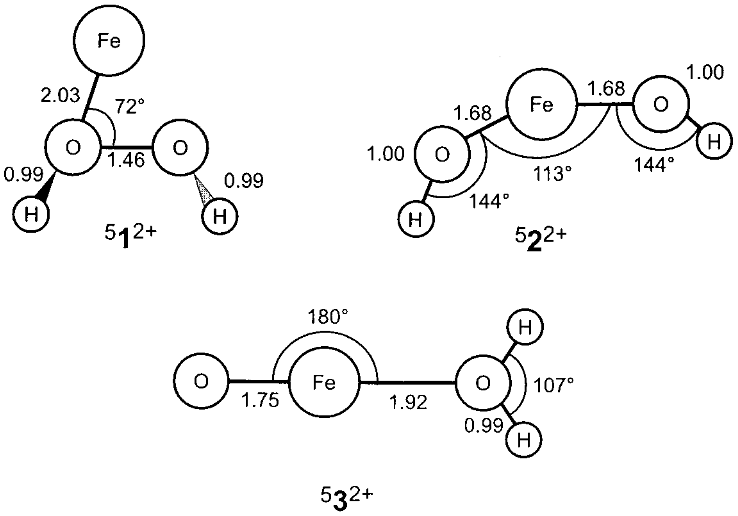


Fig. 1. *B3LYP/6-311 + G*-Optimized geometries of* $[Fe,O_2,H_2]^{+/2+}$ *mono- and dications* (bond lengths in Å and selected angles in degree)

$$Fe(H_2O)^+ + H_2O_2 \rightarrow Fe(H_2O_2)^+ + H_2O \quad (9)$$

B3LYP/6-311 + G* predicts a reaction enthalpy of $\Delta_r H_0$ (*Eqn. 9*) = 4.6 kcal/mol for the quartet species⁶). Hence, H_2O is more strongly bound to Fe^+ than H_2O_2, and we assign $D_0(Fe^+-H_2O_2) = 26 \pm 3$ kcal/mol⁷). Weaker bonding of H_2O_2 than H_2O to Fe^+ correlates with the difference in proton affinities (*PA*s) of these two bases, *i.e.*, $PA(H_2O_2) = 161.1$ kcal/mol *vs.* $PA(H_2O) = 165.0$ kcal/mol⁸) [12]. Much more interesting than the binding energy is the stabilty of $\mathbf{1}^+$ with respect to insertion of the metal into the peroxidic O–O bond of the ligand. Before addressing this issue, let us briefly discuss some relevant exit channels towards evaluating the performance of the theoretical approach as far as energetics are concerned. Inspection of the data compiled in *Table 1* reveals that the B3LYP approach reproduces the experimental values reasonably well. Although calculations of bare transition-metal atoms are associated with considerable errors [9][14], the data set reported in *Table 1* justifies adoption of the ±6 kcal/mol error margins previously suggested for B3LYP studies of Fe-containing compounds [15]. Nevertheless, a note of caution is indicated in this respect. Recent calculations by *Ugalde* and co-workers [9] on the reaction of transition-metal cations with H_2O show, for some species, strong discrepancies between DFT and high-level *ab initio* results. Therefore, single-point calculations at a higher level of

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⁶) The B3LYP function fails in predicting the correct sextet ground state for $Fe(H_2O)^+$ (see [9]), therefore we include the CCSD(T)-state splitting of $Fe(H_2O_2)^+$ ($^6A_1$) and $Fe(H_2O_2)^+$ ($^4B_2$) (2.6 kcal/mol) in estimating the error range.

⁷) Calculated binding energies relative to bare $^4Fe^+$, $^6Fe^+$, and $^5Fe^{2+}$, respectively: $D_0(Fe^+-H_2O_2) = 37.1$ kcal/mol for $^4\mathbf{1}^+$ and 29.1 kcal/mol for $^6\mathbf{1}^+$, $D_0(Fe^+-H_2O) = 41.8$ kcal/mol for the quartet and 37.2 kcal/mol for the sextet, $D_e(Fe^{2+}-H_2O_2) = 100.8$ kcal/mol for $^5\mathbf{1}^{2+}$, and $D_e(Fe^{2+}-H_2O) = 100.5$ kcal/mol for the quintet.

⁸) Correlations between metal-ligand binding energies and the ligands' *PA*s are quite frequently reported in gas-phase chemistry of metal-ions; for examples, see [13].

Table 1. *Experimental*[a])[b]) *and Calculated*[c]) *Reaction Enthalpies* (Δ_rH at 0 K in kcal/mol) *and the Resulting Deviations* ΔE *Related to the Monocationic* $[Fe,O_2,H_2]^+$ *System*

Reaction[d])	Δ_rH_{exp}	Δ_rH_{calc}	ΔE[e])
${}^6Fe^+ \rightarrow {}^4Fe^+$	5.8[f])	– 4.2	10.0
${}^6Fe^+ + H_2O_2 \rightarrow {}^6FeO^+ + H_2O$	– 47.0	– 46.7	– 0.3
${}^6Fe^+ + H_2O_2 \rightarrow {}^5FeOH^+ + {}^2OH$	– 37.7	– 45.1	7.4
${}^6FeO^+ \rightarrow {}^6Fe^+ + {}^3O$	80.0	78.2	1.8
${}^6FeO^+ \rightarrow {}^4FeO^+$	12.5[g])	8.0	4.5
${}^5FeOH^+ \rightarrow {}^6Fe^+ + {}^2OH$	87.4	88.7	– 1.3
${}^6Fe(H_2O)^+ \rightarrow {}^6Fe^+ + H_2O$	30.7	37.2	– 6.5
${}^4Fe(H_2O)^+ \rightarrow {}^4Fe^+ + H_2O$	33.7[h])	41.8	– 8.1
${}^6FeO^+ + {}^4Fe(H_2O)^+ \rightarrow 2\ {}^5FeOH^+$	– 50.1	– 41.1	– 9.0
${}^6FeO^+ + {}^6Fe(H_2O)^+ \rightarrow 2\ {}^5FeOH^+$	– 47.4	– 49.9	2.5
${}^5FeOH^+ + {}^2OH \rightarrow {}^6FeO^+ + H_2O$	– 9.3	– 1.6	– 7.7
${}^6Fe(H_2O)^+ + {}^2OH \rightarrow {}^5FeOH^+ + H_2O$	– 56.7	– 51.5	– 5.2
		average[i])	± 5.3

[a]) Derived from [10a][5] unless mentioned otherwise. [b]) Errors $< \pm 3$ kcal/mol. [c]) B3LYP/6-311 + G* + ZPVE; this work. [d]) For the sake of clarity, spin states of open-shell compounds are denoted as superscripts preceding the formula, *e.g.*, ${}^6Fe^+$ corresponds to the $Fe^+({}^6D)$ ground state. [e]) Defined as $\Delta E = \Delta_rH_{exp} - \Delta_rH_{calc}$. [f]) Atomic splitting of Fe^+ taken from [10b]. [g]) Calculated ${}^6FeO^+/{}^4FeO^+$ splitting on the basis of CCSD(T)/TZVP + G(3df2p) taken from [9]. [h]) Calculated ${}^6Fe(H_2O)^+/{}^4Fe(H_2O)^+$ splitting on the basis of CCSD(T)/TZVP + G(3df2p) taken from [9]. [i]) Mean of absolute deviations.

theory may be indicated in the present study as well. However, two observations lead us to refrain from this task, and instead we view the present results in a more qualitative sense: *i*) comparison between known literature thermochemistry and our calculations lead to good agreement with an error of ± 6 kcal/mol, and *ii*) high-level *ab initio* calculations are useful only if a very large basis set with many diffuse functions is used to correctly describe the O–O bond in H_2O_2. This type of calculation would require computational efforts which far exceed our current possibilities. Nevertheless, to obtain quantitative rather than qualitative results, calculations at a higher level of theory are indicated.

Total and relative energies of the species under investigation, as well as the $\langle S^2 \rangle$ eigenvalues are summarized in *Table 2*. Evaluation of the $\langle S^2 \rangle$ values shows no relevant spin contamination for the high-spin species and only a small degree of spin-contamination (max. 15% for ${}^4FeO^+$) in the low-spin species. The encounter complexes ${}^4\mathbf{1}^+$ and ${}^6\mathbf{1}^+$ are located far above the global minimum of the monocation surface, which corresponds to $Fe(OH)_2^+$ in its sextet ground state, ${}^6\mathbf{2}^+$; the quartet ${}^4\mathbf{2}^+$ is by 13 kcal/mol higher in energy[9]) [7]. Further, even the dissociation channels to afford $FeO^+ + H_2O$ and $FeOH^+ + HO^{\bullet}$ are lower in energy than $\mathbf{1}^+$. Given the weakness of the peroxidic O–O bond, insertion of the metal is expected to proceed easily. Indeed, the associated quartet transition structure ${}^4TS\mathbf{1}^+/\mathbf{2}^+$ (*i633* cm^{-1}) to afford formation of ${}^4\mathbf{2}^+$ lies only by 3.9 kcal/mol above ${}^4\mathbf{1}^+$. Similarly, the sextet TS associated with O–O bond cleavage is only by 7.7 kcal/mol above minimum ${}^6\mathbf{1}^+$. However, the high-spin TS is not associated with insertion of Fe into the peroxidic bond, but leads to homolysis to afford $FeOH^+$ concomitant with liberation of $HO^{\bullet}$ radical according to *Eqn. 5*. Hence, this structure is

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[9]) Similarly, high-spin ground states were predicted for $Co(OH)_2^+$ and $Ni(OH)_2^+$; see [16].

Table 2. *Total Energies* (including ZPVE, in Hartree), *Relative Energies* (including ZPVE, in kcal/mol), *and* $\langle S^2 \rangle$ *Eigenvalues of the Monocationic* $[Fe,O_2,H_2]^+$ *System*

Species	Total energy (+ ZPVE)	Relative energy (+ ZPVE)	$\langle S^2 \rangle$
$^4FeO^+ + H_2O$	– 1414.9807	8.0	4.48
$^6FeO^+ + H_2O$	– 1414.9935	0.0	8.77
^{4}**1**$^+$	– 1414.9849	5.4	3.80
^{6}**1**$^+$	– 1414.9655	17.6	8.75
^{4}**2**$^+$	– 1415.0775	– 52.7	4.02
^{6}**2**$^+$	– 1415.0982	– 65.7	8.76
^{4}**3**$^+$	– 1415.0664	– 45.8	4.47
^{6}**3**$^+$	– 1415.0742	– 50.6	8.77
^{4}TS**2**$^+$/**3**$^+$	– 1415.0076	– 8.9	3.94
^{6}TS**2**$^+$/**3**$^+$	– 1415.0164	– 14.4	8.76
^{4}TS**1**$^+$/**2**$^+$	– 1414.9786	9.3	3.98
^{6}TS**1**$^+$/FeOH$^+$	– 1414.9532	25.3	8.80

denoted ^{6}TS**1**$^+$/FeOH$^+$ (*i653* cm^{-1}); despite an extensive search, a saddle point corresponding to ^{6}TS**1**$^+$/**2**$^+$ could not be found. Given the shape of both spin surfaces, interaction of bare Fe^+ with H_2O_2 is likely to produce $Fe(H_2O_2)^+$ only as a transient that then rapidly rearranges to $Fe(OH)_2^+$ along the quartet PES or decomposes to $FeOH^+ + HO^{\bullet}$ on the sextet PES (*Fig. 2*). Interestingly, the branching between these options is a matter of spin multiplicity in that only the low-spin species can access the insertion intermediate **2**$^+$, while the high-spin surface solely leads to homolysis and thus dissociation into $FeOH^+$ and $HO^{\bullet}$ (*Eqn. 5*)[10]. In contrast to related systems [17b][18], in the present investigation no indications for a crossing between the quartet and sextet PES is observed. However, it should be kept in mind that if such crossings occur they may affect the topology of the overall PES dramatically. In this respect, higher-level calculations may be helpful to resolve any doubts remaining from the present calculations.

Irrespective of the spin state in which the dihydroxide **2**$^+$ is formed from $Fe^+ + H_2O_2$, it is generated with a large amount of excess energy (> 95 kcal/mol) sufficient for fragmentation into $FeOH^+ + OH^{\bullet}$ (*Eqn. 5*), as well as rearrangement of **2**$^+$ *via* TS**2**$^+$/**3**$^+$ to the hydrated iron oxide cation **3**$^+$ and subsequent fragmentation into $FeO^+ + H_2O$ (*Eqn. 6*). Given the excess energy and the considerable height of the barrier associated with TS**2**$^+$/**3**$^+$, direct dissociation of **2**$^+$ is expected to be preferred, thereby accounting for the experimentally observed preference for the $FeOH^+$ product [4], even though the generation of FeO^+ according to *Eqn. 6* is more exothermic (*Table 1*). When *Fig. 2* is viewed in terms of redox behavior, one sees that H_2O_2 can easily oxidize Fe^I to the Fe^{II} compound $FeOH^+$, as well as to the Fe^{III} species FeO^+.

Interestingly, the sequence of relative stabilities of the possible isomers is completely reversed on the dication surface; only quintet species are considered here [7a]. H_2O_2 coordinated to bare Fe^{2+}, *i.e.*, **1**$^{2+}$, is the most stable dicationic species of the $[Fe,O_2,H_2]^{2+}$ surface, while the isomers **2**$^{2+}$ and **3**$^{2+}$ are by *ca.* 10 kcal/mol higher in energy (*Fig. 3*). Preference for **1**$^{2+}$ clearly demonstrates the avoidance of high oxidation states of the formal Fe^{IV} compounds **2**$^{2+}$ and **3**$^{2+}$. While differences or even

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[10] For other examples of spin effects in the gas-phase chemistry of Fe, see [17].

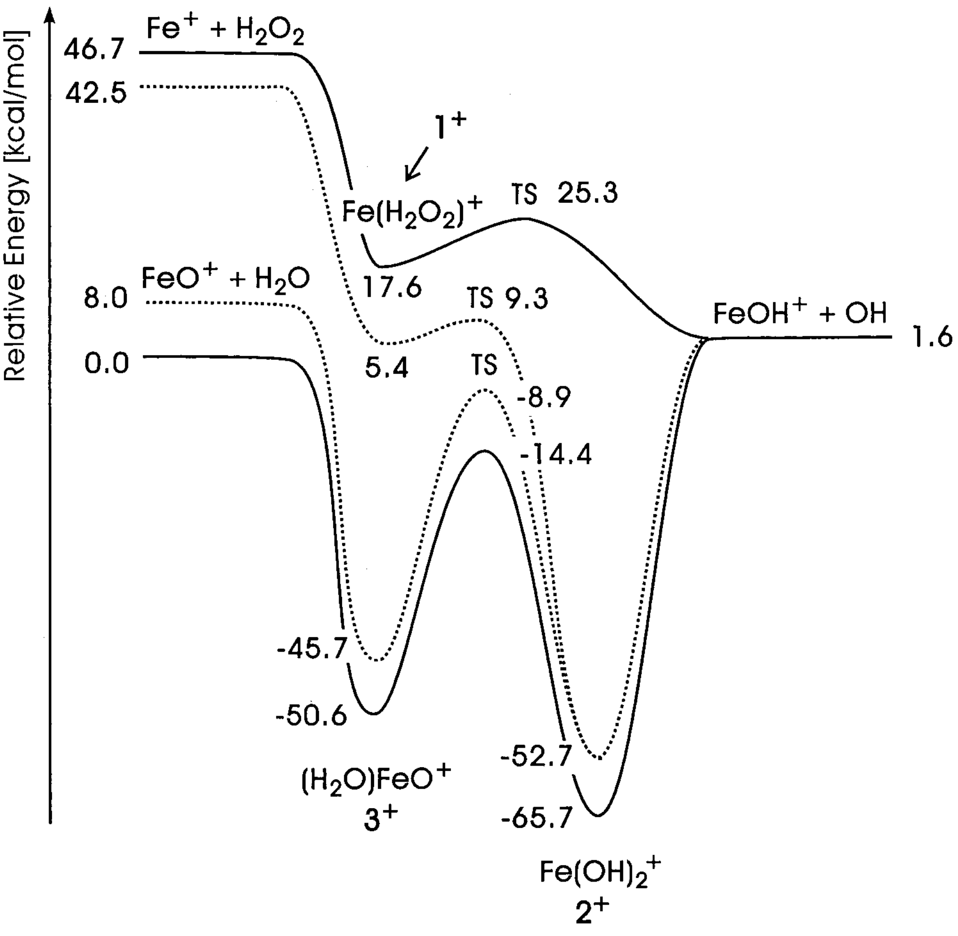

Fig. 2. *Schematic potential-energy surface of [Fe,O_2,H_2]$^+$ calculated at the B3LYP/6-311 + G* level of theory* (solid line: sextet; dotted line: quartet; energies, including zero-point vibrational energies, in kcal/mol). Note that due to a bias in DFT in the calculation of atomic ions, the quartet $Fe^+ + H_2O_2$ state appears to be too stable. The experimental state splitting of $Fe^+(^6D)$ *vs.* $Fe^+(^4F)$ is by 5.8 kcal/mol in favor of $Fe^+(^6D)$.

reversals in isomer stabilities of mono- and dications are not at all uncommon [19] [20], comparison of *Figs. 2* and *3* reveals enormous stability differences between the mono- and dication surfaces for $[Fe,O_2,H_2]^{+/2+}$. With respect to the lowest-lying electronic states, the $Fe(OH)_2^+$ monocation is by 71.1 kcal/mol more stable than $Fe(H_2O_2)^+$, whereas $Fe(H_2O_2)^{2+}$ is preferred by 12.7 kcal/mol compared to $Fe(OH)_2^{2+}$ for the dications. A rationale for this change in relative stabilities by more than 80 kcal/mol is provided by consideration of the formal valence of Fe. Thus, $\mathbf{1}^{2+}$ and $\mathbf{2}^{+}$ share the common Fe^{II}/Fe^{III} oxidation states, whereas structures $\mathbf{1}^{+}$ and $\mathbf{2}^{2+}$ correspond to less favorable Fe^{I} and Fe^{IV} compounds, respectively[11]). Notwithstanding the favorable energetics of $Fe(H_2O_2)^{2+}$, all molecular $[Fe,O_2,H_2]^{2+}$ dications are metastable with respect to the charge-

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[11]) A similar reversal of stabilities occurs for the $FeCl_2^+/Fe(Cl_2)^+$ and $FeCl_2^{2+}/Fe(Cl_2)^{2+}$ couples, see [21].

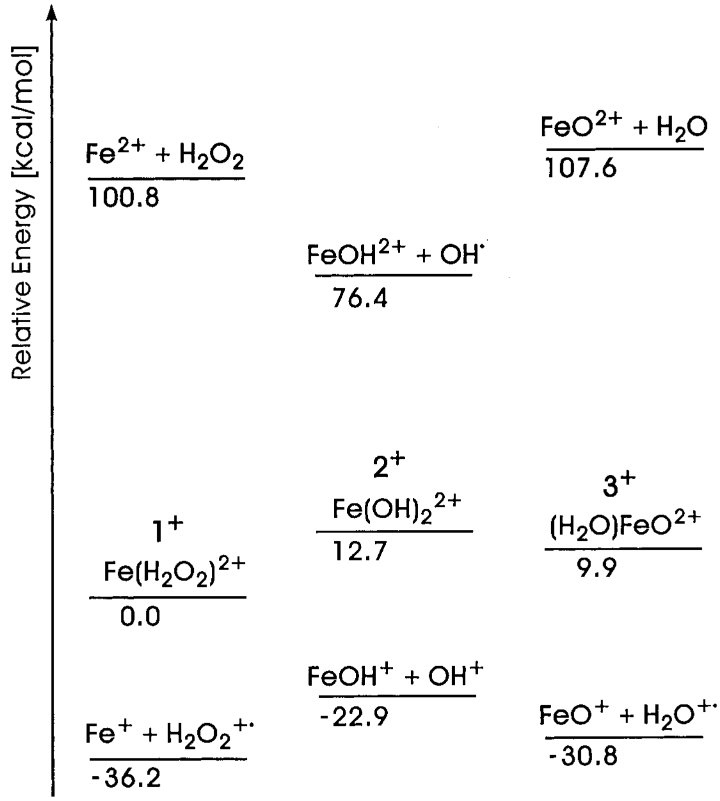

Fig. 3. *Thermochemistry of* $[Fe,O_2,H_2]^{2+}$ *calculated at the B3LYP/6-311 + G* level of theory* (energies in kcal/mol)

separation asymptotes of the corresponding monocationic fragments, *i.e.*, $Fe^+ + H_2O_2^{+\bullet}$, $FeO^+ + H_2O^{+\bullet}$, and $FeOH^+ + OH^+$ (*Fig. 3*). Nevertheless, long-lived $[Fe,O_2,H_2]^{2+}$ dications can exist in the gas phase [7a], because charge separation of dications is hindered by a barrier due to coulombic repulsion of the monocation fragments [20].

Returning to the redox reactions in *Eqns. 5–8*, the B3LYP results clearly predict both oxidations of Fe^+ to formal Fe^{II} in *Eqn. 5* and to Fe^{III} in *Eqn. 6* as considerably exothermic; *i.e.*, Δ_rH(*Eqn. 5*) = −45.1 kcal/mol and $\Delta_rH(6) = -46.7$ kcal/mol. Similarly, oxidation to Fe^{III} is exothermic for the Fe^{2+} dication, Δ_rH(*Eqn. 7*) = −24.4 kcal/mol, whereas the generation of a formal Fe^{IV} compound in *Eqn. 8* is endothermic, *i.e.*, Δ_rH(*Eqn. 8*) = 6.8 kcal/mol. Although these results refer to isolated species in the gas phase, the trends correspond quite well with the *Fenton* chemistry of Fe salts with H_2O_2 in solution, *i.e.*, Fe^{II}(aq) reacts with H_2O_2 under liberation of $HO^\bullet$ radicals concomitant with formation of Fe^{III}(aq), rather than yielding high-valent metal-oxo species. The remarkable features of *Fenton* chemistry can be traced back to the particular role of formal oxidation states that are accessible in the Fe^{II}/H_2O_2 couple and thus represent intrinsic properties of the system irrespective of the possible role of oxidants, solvents, substrates, *etc.* in *Fenton*-like reactions [1c].

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