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# Thermochemistry of neutral and cationic iron hydroxides $Fe(OH)_n^{0/+}$ ($n = 1, 2$) in the gas phase

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Dedicated to Robert C. Dunbar on the occasion of his 60th birthday.

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## Abstract

Mass spectrometry is used to investigate properties of the iron hydroxide cations $FeOH^+$ and $Fe(OH)_2{}^+$ in the gas phase. The results considerably improve the thermochemistry of neutral and cationic $Fe(OH)_n{}^{0/+}$ species ($n = 1, 2$). In terms of heats of formation at 0 K, the best estimates derived from an evaluation of literature data and the results of the present work are $\Delta_f H(FeOH) = 27.4 \pm 2.7$ kcal/mol, $\Delta_f H(FeOH^+) = 204.2 \pm 2.3$ kcal/mol, $\Delta_f H(Fe(OH)_2) = -75.7 \pm 2.7$ kcal/mol, and $\Delta_f H(Fe(OH)_2{}^+) = 135.3 \pm 3.5$ kcal/mol, respectively. Comparison of the corresponding neutral and cationic iron halides $FeX_n{}^{0/+}$ ($X = F, Cl$; $n = 1, 2$) highlights the necessity of an explicit consideration of the bonding situations in the application of additivity schemes or analogy-based principles.

*Keywords:* Ionization energies; Iron halides; Iron hydroxides; Mass spectrometry

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## 1. Introduction

Interactions of metal cations with arene ligands (L) have been examined since the very early days in the gas-phase chemistry of transition-metal cations $M^+$ [1]. In general, most bare or partially ligated transition-metal ions undergo consecutive associations with arenes according to Eqs. (1) and (2). In the diluted gas phase, these reactions involve the initial formation of "hot" encounter complexes $ML^{+*}$ and $ML_2{}^{+*}$ which are stabilized subsequently.

$$M^+ + L \rightarrow ML^{+*} \rightarrow ML^+ \quad (1)$$

$$ML^+ + L \rightarrow ML_2{}^{+*} \rightarrow ML_2{}^+ \quad (2)$$

Careful investigations of the reaction kinetics by Dunbar and co-workers [2–4] have demonstrated that in the diluted gas phase these formal association reactions not only proceed via collisional cooling of the intermediate encounter complexes $ML^{+*}$ and $ML_2{}^{+*}$, respectively, but also involve significant amounts of radiative stabilization [5]. In the corresponding kinetic description (Scheme 1), $k_f$ is the rate constant for the formation of the encounter complexes where $k_f$ is usually approximated by the gas-kinetic collision rate. Because $ML_n{}^{+*}$ still contains the entire complexation energy in the idealized gas phase, it will dissociate to the reactants ($k_d$), unless efficient

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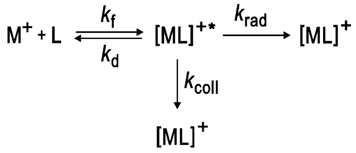

Scheme 1.

stabilization mechanisms remove part of the internal energy. These are either termolecular collisional cooling ($k_{coll}$) or unimolecular energy loss by emission of IR photons ($k_{rad}$).

Here, we report on examples where additional electron-transfer reactions between $M^+$ and L provide valuable thermochemical information about iron hydroxides in the gas phase. Aside from their obvious relevance in corrosion, iron oxides and hydroxides play important roles in various chemical processes. Bulk iron oxides, for example, are important heterogeneous catalysts in industrial processes, and mononuclear iron oxides are of considerable interest in diverse areas ranging from the time-honored iron-oxo species in the cytochrome P-450 enzymes [6] to the possible role of iron in ozone depletion in the upper atmosphere [7].

This contribution deals with the thermochemistry of the neutral and monopositive iron hydroxides $FeOH^{0/+}$ and $Fe(OH)_2{}^{0/+}$ in the gas phase where some energetics aspects are unclear for the time being. As shown below, the investigation of some simple reactions of iron-hydroxide cations with arenes can provide valuable insight in this respect.

## 2. Methods

Ion/molecule reactions were examined with a Spectrospin CMS 47X Fourier-transform ion cyclotron resonance (FTICR) mass spectrometer equipped with an external ion source as described elsewhere [8,9]. In brief, $Fe^+$ was generated by laser ablation of an iron target using a Nd:YAG laser operating at 1064 nm. Using a series of potentials and ion lenses, the ions were transferred to the ICR cell which is positioned in the bore of a 7.05 T superconducting magnet. Mass-selected $^{56}Fe^+$ was then converted to $FeOH^+$ and $Fe(OH)_2{}^+$ by reactions with pulsed-in mixtures of $N_2O/CH_4$ and $N_2O/C_2H_6$, respectively. In both cases, oxidation of $Fe^+$ by $N_2O$ to yield $FeO^+$ [10] initiates the reaction sequences. This cation then reacts either with methane to afford $FeOH^+$ [11a,b] or with ethane to inter alia yield $Fe(OH_2)^+$ which is rapidly oxidized to $Fe(OH)_2{}^+$ in an excess of $N_2O$ [12a,b]. Because both cations are quasi-terminal products in gas-phase catalytic cycles, these methods allow the conversion of $Fe^+$ to the desired $Fe(OH)_n{}^+$ species in favorable yields [11a,b,12a,b]. Likewise, $Fe(OD)_2{}^+$ was prepared using a $N_2O/C_2D_6$ mixture. After subsequent mass selection of the desired iron-hydroxide cations, their reactivities were studied by introducing the neutral reactants specified below via leak valves. Further, the iron-dihalide ions $FeX_2{}^+$ (X = F, Cl) were prepared by reacting bare $Fe^+$ with pulsed-in $NF_3$ and 1,2-dichloroethane, respectively, then mass-selected and trapped in water in order to monitor the occurrence of exchange of X by hydroxy groups.

The experimental rate constants were evaluated assuming the pseudo first-order kinetic approximation after calibration of the measured pressure and acknowledgement of the ion gauge sensitivities [13]. The error of the absolute rate constants is ±30%, and the ion temperature is assumed as 298 K [14]. In consecutive reactions, kinetic modeling was applied to interpret the time dependencies of the product distributions observed. Within experimental error, all primary reactions described show strict pseudo first-order behavior, thus, supporting the assumed equilibration of the $Fe(OH)_n{}^+$ cations to 298 K.

Additional measurements of $LFeOH^+$ cations were performed using a VG BIO-Q mass spectrometer described elsewhere [15]. Briefly, the VG BIO-Q is a commercial instrument which consists of an electrospray ionization (ESI) source combined with a tandem mass spectrometer of QHQ configuration (Q stands for quadrupole and H for hexapole). In the present experiments, mmolar solutions of $FeSO_4$ and the desired arene ligand L (see below) in pure water were introduced through a stainless steel capillary to the ESI source via a syringe pump (ca. 5 μL/min). Nitrogen was used as nebulizing and drying gas at source temperatures of 80–120 °C. Maximal yields of the desired $LFeOH^+$ species were achieved by adjusting the cone voltage to about 50 V. For collision-induced dissociation (CID) at low collision energies, the $LFeOH^+$ ions were mass-selected using Q1, interacted with argon as a collision gas in the hexapole H under single-collision conditions (typically $4 \times 10^{-4}$ mbar) at variable collision energies ($E_{lab} = 0$–$40$ eV), while scanning Q2 to monitor the ionic products. At $E_{lab} = 0$ eV, no significant fragmentations of the mass-selected $LFeOH^+$ ions was observed under these conditions.

A few complementary ab initio computations reported here used precisely the same method as in our previous studies of iron hydroxide ions [16,17], i.e., the B3LYP hybrid functional in conjunction with 6-311+G* basis sets. While this level of theory is certainly far from being perfect, it provides a reasonable description of the thermochemistry of iron compounds [18].

Unless noted otherwise, the auxiliary data used in the thermochemical evaluations (Table 1) were taken from the compendium by Lias et al. [19], the NIST database [20], a detailed compilation of some small radicals by Berkowitz et al. [21], and a collection of thermochemical data of transition-metal compounds by Freiser [22]. Throughout the paper, all data refer to heats of formations ($\Delta_f H$) at 0 K, if not explicitly stated otherwise. The conversion of experimental data determined at other temperatures to 0 K is not deemed problematic in the present case, because Kellogg and Irikura have reported recently that thermal corrections are minor for iron-oxides and -hydroxides [23].

## 3. Thermochemical data of $Fe(OH)_n{}^{0/+}$ ($n$=1, 2)

Because of their obvious importance in oxidation reactions and corrosion processes, the iron hydroxides $Fe(OH)_n{}^{0/+}$ ($n = 1, 2$) have already been studied quite extensively by various experimental and theoretical methods. In order to outline the remaining problems, it is therefore indicated to summarize the present knowledge before describing the results obtained here. Further, the accuracy as well as the reliability of theoretical predictions of thermochemical data has meanwhile increased considerably [24], such that we deliberately include selected theoretical data in the thermochemical evaluation of the gaseous $Fe(OH)_n{}^{0/+}$ species under study.

Table 1
Auxiliary heats of formation at 0 K ($\Delta_f H$ in kcal/mol) and ionization energies (IE in eV) of neutral and ionic species used in the data analysis[a]

| | $\Delta_f H_{neutral}$ | IE | $\Delta_f H_{ion}$ |
|---|---|---|---|
| Fe | 98.7 ± 0.3[b] | 7.9024[c] | 280.9 ± 0.3[d] |
| FeO | 56.2 ± 3.3[e] | 8.8 ± 0.15[b] | 259.8 ± 1.2[e] |
| FeCl | 47 ± 3[f] | 7.9 ± 0.1[f] | 229 ± 2[f] |
| $FeCl_2$ | −33.8 ± 0.5[f] | 10.28 ± 0.15[f] | 203.3 ± 3.5[f] |
| FeF | 4.0 ± 1.0[g] | 8.6 ± 0.3[g] | 199 ± 5[e] |
| $FeF_2$ | −109.5 ± 2.0[g] | 11.3 ± 0.3[g] | 151 ± 7[d] |
| H | 51.63[h] | | |
| O | 59.0[h] | | |
| OH | 9.3[i] | | |
| F | 18.5[h] | | |
| Cl | 29.0[h] | | |
| HCl | −22.0[i] | | |
| HF | −65.3[i] | | |
| $H_2O$ | −57.1[i] | | |

[a] Only those values given which are required in the present context.
[b] From [36].
[c] Taken from: http://physics.nist.gov/cgi-bin/AtData/main_asd.
[d] Derived from the other properties listed.
[e] Derived from [31].
[f] Taken from [51].
[g] Taken from [65].
[h] Taken from [19].
[i] Taken from [21].

### 3.1. *Iron hydroxide $FeOH^{0/+}$*

As pointed out by Smoes and Drowart [25] as well as Kellogg and Irikura [23], there exist two conflicting sets of data for the neutral compound, i.e., $\Delta_f H(FeOH) = 31.9 \pm 4$ kcal/mol determined by Murad [26] vs. $\Delta_f H(FeOH) = 16.5 \pm 5$ kcal/mol derived by Jensen and Jones [27]. Based on a previous [28] and their own theoretical prediction of $D$(Fe–OH), Kellogg and Irikura [23] preferred Murad's measurements, while their best estimate of $\Delta_f H(FeOH) = 21.7 \pm 5$ kcal/mol is somewhat between both figures.

Table 2
Survey of experimentally determined bond dissociation energies $D(\mathrm{Fe}^+\text{–OH})$ of the $\mathrm{FeOH}^+$ cation (in kcal/mol)

| Year | $D(\mathrm{Fe}^+\text{–OH})$ | Method[a] |
|---|---|---|
| 1979 | >91[b] | IMR |
| 1980 | 76 ± 6[c] | KC |
| 1984 | 73 ± 3[d] | PD |
| | 77 ± 6[d] | PT |
| 1989 | 85.3 ± 3.0[e] | TCID |
| 1990 | 90 ± 7[f] | KC |
| 1992 | 87.5 ± 2.8[g] | eIMR |
| 1997 | 83.8 ± 4.6[h,i] | Theory (B3LYP) |
| 1999 | 85.1 ± 2[j,k,l] | Theory (CCSD(T)) |
| 2000 | 88.7 ± 5.3[i,m] | Theory (B3LYP) |
| This work | 86.0 ± 2.3 | Evaluation |

[a] IMR: bracketing using ion/molecule reactions; KC: Knudsen cell; PD: photodissociation, PT: proton-transfer reactions; TCID: threshold collision-induced dissociation, eIMR: threshold of an endothermic ion/molecule reaction. In the theoretical approaches, the method is listed; see original sources for further details.

[b] J. Allison, D.P. Ridge, J. Am. Chem. Soc. 101 (1979) 4998.

[c] Taken from [26].

[d] Taken from [35].

[e] Taken from [32].

[f] Taken from [29].

[g] P.B. Armentrout, D.E. Clemmer, in: J.A. Martinho Simoes (Ed.), Energetics of Organometallic Species, Kluwer Academic Publishers, Dordrecht, 1992, p. 321; also see [31].

[h] Derived from [28].

[i] Mean deviation of theory and experiment as stated by the authors.

[j] Derived from [33].

[k] $D(\mathrm{HO–H}) = 118.1$ kcal/mol [21] used as auxiliary quantity.

[l] Deviation based on a comparison of the CCSD(T) results with the experimental data given in [33].

[m] Taken from [18].

Another, more recent study of Russian authors predicts $\Delta_f H(\mathrm{FeOH}) = 25.4 \pm 4.1$ kcal/mol [29]. Further, a value of $\Delta_f H(\mathrm{FeOH}) = 26.8 \pm 6$ kcal/mol has been predicted in a recent ab initio study by Rollason and Plane [30].

Also for the cationic species $\mathrm{FeOH}^+$, some conflicting values have been obtained (Table 2). However, the most salient experimental data $D_0(\mathrm{Fe}^+\text{–OH}) = 87.5 \pm 2.8$ kcal/mol [31] and $85.3 \pm 3$ kcal/mol [32] agree with each other quite well and also nicely compare with the most reliable ab initio prediction of this quantity, $D_0(\mathrm{Fe}^+\text{–OH}) = 85.1 \pm 2$ kcal/mol [33]. As a benchmark in the further evaluation, let us use the average $D_0(\mathrm{Fe}^+\text{–OH}) = 86.0 \pm 2.3$ kcal/mol of these three values from which $\Delta_f H(\mathrm{FeOH}^+) = 204 \pm 3$ kcal/mol is derived. Combining $D_0(\mathrm{Fe}^+\text{–OH})$ with the experimental $\mathrm{IE}(\mathrm{FeOH}) = 7.9 \pm 0.2$ eV [26] and $\mathrm{IE}(\mathrm{Fe}) = 7.9024$ eV (Table 1) leads to $D_0(\mathrm{Fe–OH}) = 86 \pm 5$ kcal/mol for the neutral species and hence $\Delta_f H(\mathrm{FeOH}) = 22 \pm 5$ kcal/mol. This figure is closer to the value of Jensen and Jones [27], but crucially depends on the reliability of the appearance-energy measurements used to determine IE(FeOH) [26]. In fact, a recent theoretical study by Glukhovtsev et al. [28] casts some doubt upon the latter in predicting a slightly lower value of $\mathrm{IE}(\mathrm{FeOH}) = 7.66$ eV which would result in $\Delta_f H(\mathrm{FeOH}) = 28$ kcal/mol. Likewise, MP2 and CCSD(T) studies predict $\mathrm{IE}(\mathrm{FeOH}) = 7.64$ and 7.50 eV, respectively [34]. Our own, yet unpublished calculations of neutral and cationic FeOH using density functional theory (DFT) as well as wavefunction-based methods also indicate a somewhat lower IE(FeOH) between 7.4 and 7.7 eV. Further, $\mathrm{IE}(\mathrm{FeOH}) = 7.6 \pm 0.3$ eV was determined by Knudsen cell mass spectrometry [29]. Finally, a low value of $D(\mathrm{Fe}^+\text{–OH}) = 77 \pm 6$ kcal/mol has been derived from the proton affinity $\mathrm{PA}(\mathrm{FeO}) = 219 \pm 5$ kcal/mol determined in bracketing experiments [35]. Adjustment of $\Delta_f H(\mathrm{FeO})$ used as a reference in that study with more recent data [31] brings about excellent agreement, i.e., $\Delta_f H(\mathrm{FeOH}^+) = \Delta_f H(\mathrm{FeO}) + \Delta_f H(\mathrm{H}^+) - \mathrm{PA}(\mathrm{FeO}) = 56.2 \pm 3.5$ kcal/mol/mol $+ 365.2$ kcal/mol $- 219 \pm 5$ kcal/mol $= 202 \pm 6$ kcal/mol which leads to $D_0(\mathrm{Fe}^+\text{–OH}) = 88 \pm 6$ kcal/mol.

In summary, a reasonably consistent set of data has been achieved for the $\mathrm{FeOH}^+$ cation, whereas considerable uncertainty remains with respect to the conflicting thermochemical data of neutral iron hydroxide.

### 3.2. Iron dihydroxide $\mathrm{Fe(OH)}_2{}^{0/+}$

For the neutral species, a surprisingly precise experimental value $\Delta_f H(\mathrm{Fe(OH)}_2) = -77.2 \pm 0.5$ kcal/mol [36] is in good agreement with theoretical predictions of $\Delta_f H(\mathrm{Fe(OH)}_2) = -77.2 \pm 5$ kcal/mol [23] and $\Delta_f H(\mathrm{Fe(OH)}_2) = -72.6 \pm 3$ kcal/mol [30]. For the sake of consistency, let us adopt the strategy pursued above by using the average $\Delta_f H(\mathrm{Fe(OH)_2}) = -75.7 \pm 2.7$ kcal/mol for the neutral compound.

In ion/molecule reactions, the formation of the gaseous iron-dihydroxide cation has been observed in several occasions. Thus, $\mathrm{Fe(OH)_2}^+$ is formed in the reaction of bare $\mathrm{Fe}^+$ with peroxides [37], 1,2-diols [38], and nitroalkanes [39,40], upon association of $\mathrm{FeO}^+$ with water [41,42], oxidation of $\mathrm{Fe(OH_2)}^+$ with $\mathrm{N_2O}$ [12a,b], and in the reactions of $\mathrm{FeO}^+$ with alkanols [43]. Despite the fact that $\mathrm{FeO}^+$ and $\mathrm{Fe(OH)_2}^+$ are both formal iron(III) compounds, the latter cation is much less reactive than the oxo species. In fact, the formation of $\mathrm{Fe(OH)_2}^+$ has been identified as the major sink in the $\mathrm{Fe}^+$-catalyzed oxidations of hydrogen and ethane in the gas phase [12a,b,44]. Despite the frequent observation of this ion, the experimental thermochemistry of $\mathrm{Fe(OH)_2}^+$ has not been considered in detail so far.

$$\mathrm{Fe(OH)_2}^+ + \mathrm{C_2H_5OH} \rightarrow \mathrm{Fe(CH_3CHO)}^+ + 2\mathrm{H_2O} \tag{3}$$

In conjunction with experimental data available, additional information about $\mathrm{Fe(OH)_2}^+$ can be derived from the occurrence of reaction (3) under thermal conditions [37]. While we have neglected the effect of temperature so far, reaction (3) has a non-negligible entropic component because three molecules are formed out of two. B3LYP calculations suggest a thermal correction of 7.5 kcal/mol at 298 K in favor of the products of reaction (3).[1] Using this correction and the 298 K thermochemistry of reactants and products [19] in conjunction with $D(\mathrm{Fe^+{-}CH_3CHO}) = 35.6 \pm 2.5$ kcal/mol [45], a lower bound of $\Delta_f H(\mathrm{Fe(OH)_2}^+) > 138 \pm 3$ kcal/mol is obtained.[2]

$$\mathrm{FeO}^+ + \mathrm{C_2H_5OH} \rightarrow \mathrm{Fe(OH)_2}^+ + \mathrm{C_2H_4} \tag{4}$$

$$\mathrm{FeO}^+ + \mathrm{C_3H_7OH} \rightarrow \mathrm{Fe(OH)_2}^+ + \mathrm{C_3H_6} \tag{5}$$

$$\mathrm{Fe}^+ + \mathrm{C_2H_5NO_2} \rightarrow \mathrm{Fe(OH)_2}^+ + \mathrm{CH_3CN} \tag{6}$$

$$\mathrm{Fe(OH_2)}^+ + \mathrm{N_2O} \rightarrow \mathrm{Fe(OH)_2}^+ + \mathrm{N_2} \tag{7}$$

All other reactions in which $\mathrm{Fe(OH)_2}^+$ is formed, e.g., reactions (4)–(6), provide upper limits of $\Delta_f H(\mathrm{Fe(OH)_2}^+) < 192$ kcal/mol, respectively [12a,b, 39,43], which are almost trivial because they just require that $D(\mathrm{HOFe^+{-}OH})$ exceeds a marginal value of about 20 kcal/mol; in the case of reaction (7), the second hydroxyl ligand could in fact be more or less unbound from a thermochemical point of view. The heights of these upper bounds can obviously be attributed to the exothermicities of the associated redox processes occurring. With respect to the heat of formation of $\mathrm{Fe(OH)_2}^+$, we arrive at an unacceptably large range of $138 \pm 3$ kcal/mol $< \Delta_f H(\mathrm{Fe(OH)_2}^+) < 192 \pm 3$ kcal/mol for the cationic species.

In addition, there exists some ambiguity as far as ion structure is concerned in that besides the dihydroxide cation $\mathrm{Fe(OH)_2}^+$ also the hydrated oxide $\mathrm{OFe(OH_2)}^+$ appears as a conceivable isomer; for the neutral counterpart this tautomerism is considered less relevant due to the lack of ion/dipole interaction in neutral $\mathrm{OFe(OH_2)}$. This structural dichotomy was already outlined in one of the first [39] as well as a recent [46] experimental study of $\mathrm{FeO_2H_2}^+$ in that collision-induced dissociation affords $\mathrm{FeO}^+$ at low collision energies and $\mathrm{FeOH}^+$ at higher energies; the former product ion might be indicative for $\mathrm{OFe(OH_2)}^+$ and the latter for $\mathrm{Fe(OH)_2}^+$. Further, interconversion of both isomers has been inferred from labeling experiments [42]. In such a situation the interpretation of most mass spectrometric experiments is ambiguous because it always needs to be ascertained whether or not isomerization precedes the actual measurements used to probe the ion structure [21,39,42,47].

### 3.3. Additivity approaches

Before describing the more accurate information obtained in this work, let us address the structural

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[1] Total B3LYP/6-311+G* energies (in Hartree) at 0 K: $^6\mathrm{Fe(OH)_2}^+$ −1415.098198, $^1\mathrm{C_2H_5OH}$ −155.001485, $^4\mathrm{Fe(CH_3-CHO)}^+$ −1417.260735, $^1\mathrm{H_2O}$ −76.422601; total energies at 298 K: $^6\mathrm{Fe(OH)_2}^+$ −1415.127391, $^1\mathrm{C_2H_5OH}$ −155.026855, $^4\mathrm{Fe(CH_3CHO)}^+$ −1417.291996, $^1\mathrm{H_2O}$ −76.44024. Thus, $\Delta_r H_0 = \Delta_r G_0 = -3.9$ kcal/mol vs. $\Delta_r G_{298} = -11.4$ kcal/mol leads to a thermal correction of 7.5 kcal/mol in favor of the products.

[2] Erroneously, reactions (4) and (5) were referred to yield an upper, instead of a lower bound in [43].

dichotomy of $FeO_2H_2^+$ by means of plausibility considerations. As both $Fe(OH)_2^+$ and $OFe(OH_2)^+$ correspond to formal iron(III) compounds, their relative stabilities may be derived from additivity approaches [48] which are used quite frequently when other information is not available. For example, the heats of formation of the isomers $Fe(OH)_2^+$ and $OFe(OH_2)^+$ may be determined via Eqs. (8) and (9) using literature data (Table 1).

$$\begin{aligned}\Delta_f H(\mathrm{Fe(OH)_2}^+) &\\ &= \Delta_f H(\mathrm{Fe}^+) + 2\Delta_f H(\mathrm{OH}) - 2D(\mathrm{Fe}^+\text{–OH}) + \delta_1\\ &= 128 \pm 4\,\mathrm{kcal/mol} + \delta_1 \qquad (8)\end{aligned}$$

$$\begin{aligned}\Delta_f H(\mathrm{OFe(OH_2)}^+) &\\ &= \Delta_f H(\mathrm{FeO}^+)+\Delta_f H(\mathrm{H_2O})-D(\mathrm{Fe}^+\text{–OH}_2) + \delta_2\\ &= 172 \pm 3\,\mathrm{kcal/mol} + \delta_2 \qquad (9)\end{aligned}$$

In simple additivity schemes, cooperative effects are neglected; e.g., in the recent analysis of the fragmentation behavior of $FeO_2H_2^+$ ions generated by electrospray ionization [46]. Instead, we employ the correction terms $\delta_1$ and $\delta_2$ in order to account for cooperative effects as defined in Eqs. (10) and (11).

$$\delta_1 = D(\mathrm{Fe}^+\text{–OH}) - D(\mathrm{HOFe}^+\text{–OH}) \qquad (10)$$

$$\delta_2 = D(\mathrm{Fe}^+\text{–OH}_2) - D(\mathrm{OFe}^+\text{–OH}_2) \qquad (11)$$

In a chemical sense, $\delta_1$ reflects for the expected decrease of the Fe–OH bond strength when going from the formal iron(II) compound $FeOH^+$ to the formal iron(III) species $Fe(OH)_2^+$. Likewise, $\delta_2$ represents the extra stabilization anticipated for coordination of the dipolar water ligand to the $FeO^+$ unit in which the effective charge at the metal center exceeds that in bare $Fe^+$ due to the electron withdrawing oxo ligand. Accordingly, $\delta_1$ is likely to be positive, whereas $\delta_2$ presumably is negative. Consequently, inclusion of the correction terms is expected to lower the energy difference between both isomers compared to the neglect of cooperative effects, that is $\delta_1 = \delta_2 = 0$. Next, these corrections terms are estimated on an empirical basis in order to deduce the more stable isomer.

For the first correction term, the strategy chosen by Kellogg and Irikura is adopted [23]. The thermochemistry of neutral and cationic iron chlorides in the gas phase is known accurately [49–51] and may thus be used to estimate $\delta_1$. The cations $FeOH^+$ and $FeCl^+$ both have quintet ground states [50,53] and similar bond strengths, i.e., $D(\mathrm{Fe}^+\text{–OH}) = 86.0 \pm 2.3$ kcal/mol (see above) and $D_0(\mathrm{Fe}^+\text{–Cl}) = 80 \pm 3$ kcal/mol [51]. As the bonding situation in iron hydroxides is assumed to correlate with that of iron chlorides [50], we may accordingly use $D(\mathrm{ClFe}^+\text{–Cl}) = 54 \pm 5$ kcal/mol [51] to estimate $D_0(\mathrm{HOFe}^+\text{–OH})$ either via additive or multiplicative approaches. Eqs. (12) and (13) lead to $\delta_1 = 26 \pm 6$ and $28 \pm 6$ kcal/mol, respectively, where we adopt $27 \pm 7$ kcal/mol as the average.

$$\begin{aligned}D(\mathrm{HOFe}^+\text{–OH}) &\\ &= D(\mathrm{Fe}^+\text{–OH}) + D(\mathrm{ClFe}^+\text{–Cl}) - D(\mathrm{Fe}^+\text{–Cl})\\ &= 60 \pm 6\,\mathrm{kcal/mol} \qquad (12)\end{aligned}$$

$$\begin{aligned}D(\mathrm{HOFe}^+\text{–OH}) &\\ &= D(\mathrm{Fe}^+\text{–OH}) \cdot \frac{D(\mathrm{ClFe}^+\text{–Cl})}{D(\mathrm{Fe}^+\text{–Cl})} = 58 \pm 6\,\mathrm{kcal/mol} \qquad (13)\end{aligned}$$

As far as $\delta_2$ is concerned, no concise experimental thermochemistry of $OFe(L)^+$ complexes with coordinative, closed-shell ligands L is available so far. Prompted by the rich chemistry of $FeO^+$ cation [52a,b], however, several computational studies have been performed of which we select the most recent and reliable ones. Thus, $D(\mathrm{OFe}^+\text{–H}_2) = 16.2$ kcal/mol has been computed for the complex of $FeO^+$ with dihydrogen [53] compared to an experimental value of $D(\mathrm{Fe}^+\text{–H}_2) = 10.8 \pm 0.7$ kcal/mol [54] for the bare metal ion. Similarly, the computed $D(\mathrm{OFe}^+\text{–CH}_4) =$ 19.6 kcal/mol [55] slightly exceeds the experimental figure of $D(\mathrm{Fe}^+\text{–CH}_4) = 13.7 \pm 0.8$ kcal/mol [31]. In the case of carbon monoxide as a ligand, however, the computed values $D(\mathrm{OFe}^+\text{–CO}) = 27.0$ and 31.8 kcal/mol [56] are close to the experimental value of the bare metal $D(\mathrm{Fe}^+\text{–CO}) = 31.3 \pm 1.9$ kcal/mol [31]. The theoretically predicted $D(\mathrm{OFe}^+\text{–C}_6\mathrm{H}_6) =$ 60 kcal/mol [57] again somewhat exceeds the most recent experimental value for the bare metal ion $D(\mathrm{Fe^+{-}C_6H_6}) = 49.7 \pm 2.5$ kcal/mol [58]. The arithmetic average of the differences between $D_0(\mathrm{OFe^+{-}L})$ and $D_0(\mathrm{Fe^+{-}L})$ might be considered as a very first approximation, thus resulting in $\delta_2 = -4 \pm 6$ kcal/mol. This analysis neglects, however, the particular properties of the dipolar water ligand compared to the σ- and π-donors $H_2$, $CH_4$, CO, and $C_6H_6$. Therefore, $\delta_2$ is expected to be actually more negative.

Using these corrections, the thermochemical estimates derived according to Eqs. (8) and (9) are $\Delta_f H(\mathrm{Fe(OH)_2}^+) = 155 \pm 7$ kcal/mol and $\Delta_f H(\mathrm{OFe(OH)_2}^+) = 168 \pm 7$ kcal/mol, suggesting a clear preference for the iron dihydroxide cation as the more stable isomer. This estimation is in accordance with recent computational studies which predict $\mathrm{Fe(OH)_2}^+$ to be 13.3 kcal/mol more stable than the isomeric $\mathrm{OFe(OH_2)}^+$ cation, both having sextet ground states [59]. We will return to the usefulness of these additivity approaches further below.

## 4. Results and discussion

As outlined above, the thermochemistry of the $FeOH^+$ cation and of neutral $Fe(OH)_2$ is settled reasonably well, whereas the properties of their corresponding counterparts FeOH and $\mathrm{Fe(OH)_2}^+$ lack precision. Consequently, a determination of the respective ionization energies may help to resolve the situation.

### 4.1. Iron hydroxide $FeOH^{0/+}$

According to the present knowledge, IE(FeOH) is in the order of 7–8 eV (see above). In order to refine the thermochemistry by bracketing of IE(FeOH), thermalized $FeOH^+$ ions were allowed to react with selected arene ligands L under ICR conditions. In the present context, the major interest concerns the occurrence of the electron transfer (ET) according to reaction (14); the competing associations in analogy to reaction (1) as well as bond activations of the arenes by $FeOH^+$ are only mentioned briefly [35].

$$\mathrm{FeOH^+ + L \rightarrow L^{\bullet +} + FeOH} \qquad (14)$$

In the case of aniline ($L = C_6H_5NH_2$), ET only amounts to about 2% of the products. The major pathways lead to $FeC_6H_6N^+$ (40%) and $FeC_5H_4N^+$ (20%), corresponding to formal losses of $H_2O$ and $CH_3OH$, respectively, as well as adduct formation (35%) analog to reaction (1). While losses of $H_2O$ and $CH_3OH$ leading to $FeC_7H_8N^+$ (55%) and $FeC_6H_6N^+$ (5%), respectively, also prevail with *ortho*-toluidine ($L = o\text{-}CH_3C_6H_4NH_2$), ET to yield the ionized arylamine competes efficiently (25%). In addition, formal hydride abstraction from the amine by the $FeOH^+$ cation to afford a $C_7H_9N^+$ species (15%) is observed, which may be coupled with the ET route [60]. Finally, electron transfer (70%) and hydride abstraction (30%) are exclusively observed in the reaction of $FeOH^+$ with *N*,*N*-dimethylaniline ($L = C_6H_5N(CH_3)_2$). Using the criteria outlined by Bouchoux et al. [61], the increase of the ET channel from 2% for aniline (IE = 7.72 eV) to 25% for *ortho*-toluidine (IE = 7.47 eV) and 70% for *N*,*N*-dimethylaniline (IE = 7.12 eV) suggests that the IE of neutral FeOH is in the order of 7.4 ± 0.3 eV. Strictly speaking, however, this value is to be regarded as a lower limit because the small efficiency of ET with aniline does not necessarily mean that this channel is endothermic because other reactions compete [62]. Conceptually, the basic problem in this approach is that only the forward electron transfer, but not the reversal, i.e., formation of $FeOH^+$, can be observed experimentally.

As an alternative approach, $LFeOH^+$ complexes were generated by electrospray ionization of dilute solutions of $FeSO_4$ in water with traces of arene ligands L added; the choice of L was given by the expected range of IE(FeOH). Similar to the ICR results, low-energy CID of these ions is dominated by dehydration, yet significant amounts of the relevant fragments $FeOH^+$ and $L^{\bullet +}$ evolve as well (Table 3). Thus, as a function of IE(arene), reactions (14a) and (14b) are observed which only differ by the location of the positive charge.

$$\mathrm{LFeOH^+ \rightarrow L^{\bullet +} + FeOH} \qquad (14a)$$

$$\mathrm{LFeOH^+ \rightarrow FeOH^+ + L} \qquad (14b)$$

Table 3
Neutrals lost upon collision-induced dissociation of mass-selected $LFeOH^+$ cations generated by electrospray ionization at various collision energies ($E_{lab}$ in eV)[a]

| Arene (L) | IE(L)[b] | $E_{lab}$ | $-H_2O$ | –FeOH | –HFeOH[c] | –L | Ratio[d] |
|---|---|---|---|---|---|---|---|
| *N*,*N*-Dimethylaniline | 7.12 ± 0.02 | 20[e] | 5 | | 100 | | |
| *ortho*-Toluidine[f] | 7.47 ± 0.04 | 15 | 100 | 6 | 11 | <1 | 12 |
| | | 20 | 100 | 8 | 15 | 1 | 6.0 |
| | | 30 | 100 | 18 | 39 | 5 | 3.8 |
| | | 40 | 100 | 47 | 66 | 14 | 3.4 |
| *meta*-Toluidine[f] | 7.54 ± 0.03 | 15 | 100 | 5 | | 2 | 3.0 |
| | | 20 | 100 | 9 | 1 | 3 | 2.6 |
| | | 30 | 100 | 23 | 7 | 10 | 2.4 |
| | | 40 | 100 | 56 | 24 | 20 | 2.8 |
| Aniline[f] | 7.72 ± 0.002 | 15 | 100 | 5 | | 8 | 0.60 |
| | | 20 | 100 | 6 | | 12 | 0.50 |
| | | 30 | 100 | 13 | | 26 | 0.45 |
| | | 40 | 100 | 58 | 19 | 61 | 0.45 |
| Hydroquinone[f] | 7.94 ± 0.02 | 15 | 100 | <1 | | <1 | 0.05 |
| | | 20 | 100 | <1 | | 1 | 0.08 |
| | | 30 | 100 | 1 | 2 | 6 | 0.12 |
| | | 40 | 100 | 3 | 4 | 13 | 0.22 |

[a] The approximate conversion to the center-of-mass frame is $E_{CM} \approx 0.2 \times E_{lab}$.

[b] Ionization energies of the ligand L taken from [20].

[c] At low collision energies, formation of HFeOH, rather than $Fe + H_2O$ is assumed on thermochemical grounds; see: A.M. Mebel, D.H. Hwang, J. Phys. Chem. A 105 (2001) 7460.

[d] Precise ratio of FeOH and L losses within the experimentally significant digits.

[e] Because the reactions of interest do not occur, only data for $E_{lab} = 20\,eV$ are displayed.

[f] Exclusive loss of $H_2O$ is observed at $E_{lab} = 10\,eV$.

Irrespective of the prevailing dehydration channel, both reactions can directly compete with each other in these experiments. In fact, the ratios $L^{\bullet +}/FeOH^+$ correlate quite nicely with the IEs of the arene ligands investigated. By analogy to Cooks' kinetic method [63], IE(FeOH) is derived from a plot of $\ln(L^{\bullet +}/FeOH^+)$ vs. IE(L) for the various collision energies (Fig. 1). While the internal energy of the dissociating ions and

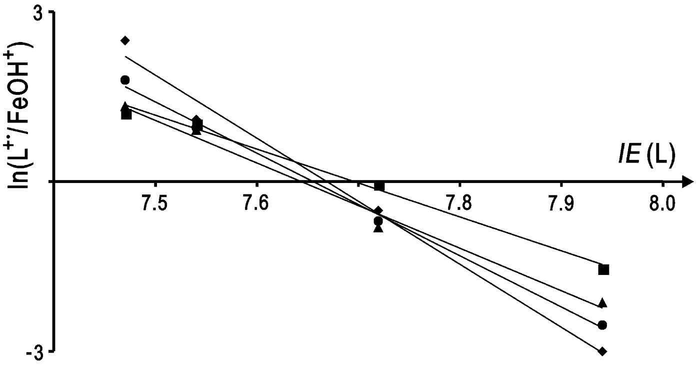

Fig. 1. Logarithmic branching ratio of $L^{\bullet +}$ (loss of FeOH) and $FeOH^+$ (loss of L) fragments upon CID of mass-selected $LFeOH^+$ cations at various collision energies; $E_{lab} = 15\,eV$ (◆), 20 eV (●), 30 eV (▲), 40 eV (■); for the ligands L used, see Table 3.

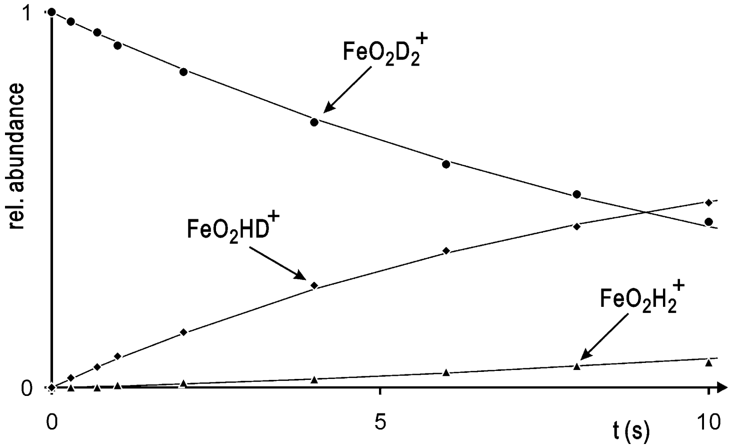

Fig. 2. Temporal evolution of the isotopic ions in the reaction of mass-selected $Fe(OD)_2^+$ with traces of $H_2O$ ($p = 1.2 \times 10^{-9}$ mbar). The $Fe(OD)_2^+$ ion was prepared by reacting mass-selected $Fe^+$ with a pulsed-in mixture of $N_2O/C_2D_6$ (ca. 20:1). The dots are experimental data and the solid lines an explicit kinetic fit of reactions (15) and (16).

thus the $L^{\bullet+}/FeOH^+$ ratio depend on the collision energies, the resulting IE(FeOH) is hardly affected. As an average, IE(FeOH) = 7.67 ± 0.06 eV is obtained, where the error bar already includes the considerable uncertainties of IE(L).[3] With $D(Fe^+\text{–}OH) = 86.0 \pm 2.3$ kcal/mol and IE(FeOH) = 7.67 ± 0.06 eV, we arrive at $D(Fe\text{–}OH) = 80.6 \pm 2.7$ kcal/mol and thus $\Delta_f H(FeOH) = 27.4 \pm 2.7$ kcal/mol. Whereas this result is consistent with the values given by Murad [26] and Gorokhov et al. [29], it is clearly beyond the error margin of $\Delta_f H(FeOH) = 16.5 \pm 5$ kcal/mol derived by Jensen and Jones [27]. Further, the revised IE(FeOH) agrees nicely with the most recent predictions of this quantity based on ab initio calculations [28,34].

### 4.2. Iron dihydroxide $Fe(OH)_2^{0/+}$

As outlined above, a prerequisite for a meaningful interpretation of the reactions of a gaseous $FeO_2H_2^+$ species is some knowledge about the ion's connectivity. According to recent ab initio calculations [59], the two most likely isomers $Fe(OH)_2^+$ and $OFe(OH_2)^+$ are similar in energy (the former is about 13 kcal/mol more stable), while being separated by an appreciable barrier for intramolecular interconversion (53 kcal/mol relative to $Fe(OH)_2^+$). Accordingly, either one or a mixture of both isomers might be probed in experimental investigations of $FeO_2H_2^+$. Among the various routes to produce $FeO_2H_2^+$ cations, we have chosen the reaction of bare $Fe^+$ with a $N_2O/C_2H_6$ mixture as it is most convenient and involves multiple collisions thereby ensuring collisional relaxation [12a,b].

In order to probe the ion structure, $N_2O/C_2D_6$ was employed to generate $FeO_2D_2^+$. Upon reaction of $FeO_2D_2^+$ with unlabeled water, degenerate H/D exchanges according to reactions (15) and (16) take place (Fig. 2).

$$FeO_2D_2^+ + H_2O \rightarrow FeO_2HD^+ + HDO \qquad (15a)$$

$$FeO_2D_2^+ + H_2O \rightarrow FeO_2H_2^+ + D_2O \qquad (15b)$$

$$FeO_2HD^+ + H_2O \rightarrow FeO_2H_2^+ + HDO \qquad (16)$$

With respect to the quest for ion structure, the initial progression of the reaction kinetics of H/D exchange in the $FeO_2D_2^+/H_2O$ system is particularly relevant. Thus, for the dihydroxide cation, $Fe(OD)_2^+$, one

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[3] A referee suggested to acknowledge the effect of the different collision energies in the center-of-mass frame. With regard to the rather good agreement of the IEs derived from the spectra at $E_{lab}$ = 15, 20, 30, and 40 eV, respectively, as well as the considerable error margins of the literature IEs of the ligands L, this is considered supererogatory, however.

expects sequential H/D exchanges occurring either in one collision (reactions (15a) and (15b)) or in a consecutive process (first reaction (15a), then reaction (16)). Due to statistical considerations, the probability of reaction (15a) vs. (15b) is 4:1 for a genuine dihydroxide, provided that complete equilibration of H and D atoms is achieved. Instead, preferential exchange of both deuterium atoms (reaction (15b)) is expected if the hydrated iron-oxide cation $OFe(OD_2)^+$ were generated from the $Fe^+/N_2O/C_2D_6$ system. Kinetic modeling of the experimental data (Fig. 2) implies a clear preference for the presence of the more stable $Fe(OD)_2{}^+$ isomer. Thus, the rates of reactions (15a), (15b), and (16) behave as 20:1:4. Note that the small fraction of reaction (15b) by no means indicates the presence of the $OFe(OD_2)^+$ isomer because it is easily accounted for by consecutive H/D exchanges during the lifetime of the intermediate collision complex [42,59]. Hence, we conclude that the $Fe^+/N_2O/C_2H_6$ system provides access to the $Fe(OH)_2{}^+$ isomer.

By analogy to the strategy of Kellogg and Irikura [23], exchange of the hydroxy groups by halide ligands and vice versa was examined next. Upon reacting $Fe(OH)_2{}^+$ with the vapor phase over concentrated hydrochloric acid, rapid and irreversible formation of iron-chloride cations is observed (reactions (17) and (18)), although the presence of water could also drive the reverse reactions.

$$Fe(OH)_2{}^+ + HCl \rightarrow Fe(OH)Cl^+ + H_2O \qquad (17)$$

$$Fe(OH)Cl^+ + HCl \rightarrow FeCl_2{}^+ + H_2O \qquad (18)$$

In a complementary experiment, $FeCl_2{}^+$ generated independently from $Fe^+$ and pulsed-in 1,2-dichloroethane (also see [64]) fails to undergo complete Cl/OH exchange forming $Fe(OH)_2{}^+$ in the presence of water. While a trace amount of $Fe(OH)Cl^+$ is observed, the major reactions correspond to simple associations forming $FeCl_2(H_2O)_n{}^+$ ($n = 1, 2$). These observations lead to a lower limit of $\Delta_f H(Fe-(OH)_2{}^+) > 133 \pm 4$ kcal/mol (Table 1). This boundary is within $\Delta_f H(Fe(OH)_2{}^+) = 138 \pm 3$ kcal/mol derived from reaction (3), and thus confirms the anticipated formation of the acetaldehyde/$Fe^+$ complex in this ion/molecule reaction of $Fe(OH)_2{}^+$ with ethanol [43].

Instead, $FeF_2{}^+$ generated by sequential F-atom transfer from $NF_3$ to $Fe^+$, already reacts rapidly even with the background water present in the mass spectrometer to afford $Fe(OH)F^+$ and subsequently $Fe(OH)_2{}^+$ (reactions (19) and (20)).

$$FeF_2{}^+ + H_2O \rightarrow Fe(OH)F^+ + HF \qquad (19)$$

$$Fe(OH)F^+ + H_2O \rightarrow Fe(OH)_2{}^+ + HF \qquad (20)$$

Combined with $\Delta_f H(FeF_2{}^+) = 151 \pm 7$ kcal/mol [65,66] which is consistent with the sequential formation of $FeF_2{}^+$ from $Fe^+$ and $NF_3$ (Table 1), we arrive at an upper bound of $\Delta_f H(Fe(OH)_2{}^+) < 169 \pm 7$ kcal/mol. Combination of reactions (17)–(20) thus suggest the bracket $133 \pm 4$ kcal/mol $< \Delta_f H(Fe(OH)_2{}^+) = 169 \pm 7$ kcal/mol or $\Delta_f H(Fe(OH)_2{}^+) = 151 \pm 22$ kcal/mol; still far from being accurate.

Significant improvement can be achieved by consideration of IE($Fe(OH)_2$) as an additional quantity. As $\Delta_f H$ of neutral $Fe(OH)_2$ appears to be settled well (see above), bracketing of IE($Fe(OH)_2$) by the same strategy used in the ICR experiments for the estimation of IE(FeOH) might permit to crosslink the thermochemistry of the neutral and cationic species. Instead of arylamines, however, benzene and chlorobenzene are used as they fall in the range of IEs relevant here and show much simpler product patterns. In the reaction of mass-selected $Fe(OH)_2{}^+$ with benzene (IE = 9.24 eV), loss of water prevails (80%) to afford an $FeC_6H_6O^+$ species [67–69], whereas electron transfer (20%) is a minor pathway (reactions (21a) and (21b) with X = H). The opposite is observed with chlorobenzene (IE = 9.06 eV) in that reaction (21b) predominates over (21a) for X = Cl (85:15). By analogy to the results for $FeOH^+$, it appears justified to neglect the competing dehydration channel (21a) in the evaluation of the IE using reaction (21b).

$$Fe(OH)_2{}^+ + C_6H_5X \rightarrow FeC_6H_5XO^+ + H_2O \qquad (21a)$$

$$Fe(OH)_2{}^+ + C_6H_5X \rightarrow C_6H_5X^+ + Fe(OH)_2 \qquad (21b)$$

This fortunate and simple situation suggests IE($Fe(OH)_2$) $= 9.15 \pm 0.1$ eV, where the small error margin is based on thermokinetic criteria as suggested by Bouchoux et al. [61]. This value is in good agreement with a theoretical prediction of IE$(Fe(OH)_2)$ = 9.10 eV at the B3LYP/6-311+G* level of theory.[4] Combining $\Delta_f H(Fe(OH)_2) = -75.7 \pm 2.7$ kcal/mol and IE$(Fe(OH)_2)$ = 9.15 ± 0.1 eV, we arrive at $\Delta_f H(Fe(OH)_2{}^+) = 135.3 \pm 3.5$ kcal/mol, consistent with the bracket $133 \pm 4$ kcal/mol $< \Delta_f H(Fe(OH)_2{}^+) < 169 \pm 7$ kcal/mol derived above from the reactions of $FeX_n{}^+$ with water (X = F, Cl). Indirect support for $\Delta_f H(Fe(OH)_2{}^+)$ being situated close to the lower bracket comes from the observation of $Fe(OH)Cl^+$ in the reaction of $FeCl_2{}^+$ with water: exchange of one chloro ligand by a hydroxy group is almost thermoneutral whereas formation of $Fe(OH)_2{}^+$ is endothermic.

## 5. Thermochemistry of $Fe(OH)_n{}^{0/+}$ ($n$=1, 2)

Combination of the data derived in the present work provides a consistent set of thermochemical data for the iron hydroxides $Fe(OH)_n{}^{0/+}$ ($n = 1, 2$) in the gas phase (Table 4). Note, however, that $\Delta_f H(Fe(OH)_2) = -75.7 \pm 2.7$ kcal/mol is used as a anchor point for which no independent experimental confirmation by gas-phase studies is available so far.

Table 4
Thermochemical properties ($\Delta_f H$ and $D$ in kcal/mol, IE in eV) of $Fe(OH)_n{}^{0/+}$ ($n$ = 1, 2)

| | FeOH | Fe(OH)$_2$ |
|---|---|---|
| $\Delta_f H_{neutral}$ | 27.4 ± 2.7[a] | −75.7 ± 2.7[b] |
| $D$(XFe–OH) | 80.6 ± 2.7[a] | 112.4 ± 3.8[a] |
| $D$(XFeO–H) | 80.4 ± 4.3[a] | 107.0 ± 5.5[a,c] |
| IE(FeOH) | 7.67 ± 0.06[d] | 9.15 ± 0.1[d] |
| $\Delta_f H_{ion}$ | 204.2 ± 2.3[a] | 135.3 ± 3.5[a] |
| $D(XFe^+–OH)$ | 86.0 ± 2.3[b] | 78.2 ± 4.2[a] |
| $D(XFeO^+–H)$ | 107.2 ± 2.6[a] | 118.1 ± 11.1[a,e] |

[a] Derived from the other properties given here and those in Table 1.
[b] Anchor point, see text.
[c] Determined using $\Delta_f H(OFeOH) = -20.3 \pm 4.8$ kcal/mol from [23].
[d] This work.
[e] Based upon using a bracket of 190 kcal/mol $< \Delta_f H(OFeOH^+) <$ 211 kcal/mol (D. Schröder, Dissertation, TU Berlin D83, 1992).

At first, the bond energies given in Table 4 are inspected with respect to possible correlations with the formal valence of the metal. The Fe–OH bonds do not show a clear trend, i.e., 80 kcal/mol for the formal iron(I) compound FeOH, 86 and 112 kcal/mol for the iron(II) compounds $FeOH^+$ and $Fe(OH)_2$, and 78 kcal/mol for the iron(III) compound $Fe(OH)_2{}^+$. Obviously, the changes associated with the respective bond cleavages cannot be described by valence alone. Instead, the O–H bond strengths nicely correlate with valence. Thus, only 80 kcal/mol are required for bond cleavage of neutral FeOH to the iron(II) species FeO, the transitions $FeOH^+ \rightarrow FeO^+ + H$ and $Fe(OH)_2 \rightarrow OFeOH + H$, both iron(II) → iron(III), require about 107 kcal/mol, and the generation of a formal iron(IV) species, $Fe(OH)_2{}^+ \rightarrow OFeOH^+ + H$, is even less favorable (118 kcal/mol).

Next, let us address the frequently used assumption that OH behaves as a pseudohalide in MX compounds [23,29]. According to the corresponding electronegativities EN(F) = 4.0, EN(OH) = 3.4, and EN(Cl) = 3.0 (Pauling scale), the properties of metal hydroxides are therefore expected to be in-between those of fluorides and chlorides. For the neutral compounds, this simple scheme fits reasonably well (lower part of Fig. 3) though the hydroxides are somewhat closer to the chlorides than expected from consideration of the ENs. For the cations, however, the analogy breaks down. The effect is not so pronounced for the $FeX^+$ cations where the expected trend $D(Fe^+–F) > D(Fe^+–OH) > D(Fe^+–Cl)$ still holds true. Nevertheless, the IEs show an unexpected minimum for FeOH. In the $FeX_2{}^+$ species, however, X = OH is significantly more strongly bound than X = F and Cl. Quite obviously, the origin can be traced back to the low IE of $Fe(OH)_2$ in comparison to $FeF_2$ and $FeCl_2$. A chemically insightful explanation of this phenomenon is that the positive charge in $FeF_2{}^+$ and $FeCl_2{}^+$

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[4] Computational results (B3LYP/6-311+G*): $Fe(OH)_2$ ($^5A_1$, $C_{2v}$): $E_{tot} = -1415.45674763$ H, $r_{FeO} = 1.79$ Å, $a_{OFeO} = 175°$, $a_{FeOH} = 139°$; $Fe(OH)_2{}^+$ ($^6A_1$, $C_{2v}$): $E_{tot} = -1415.12233858$ H, $r_{FeO} = 1.71$ Å, $a_{OFeO} = 154°$, $a_{FeOH} = 177°$; $Fe(OH)_2{}^+$ ($^4A'$, $C_1$): $E_{tot} = -1415.10048814$ H, $r_{FeO} = 1.70/1.72$ Å, $a_{OFeO} = 180°$, $a_{FeOH} = 153/178°$.

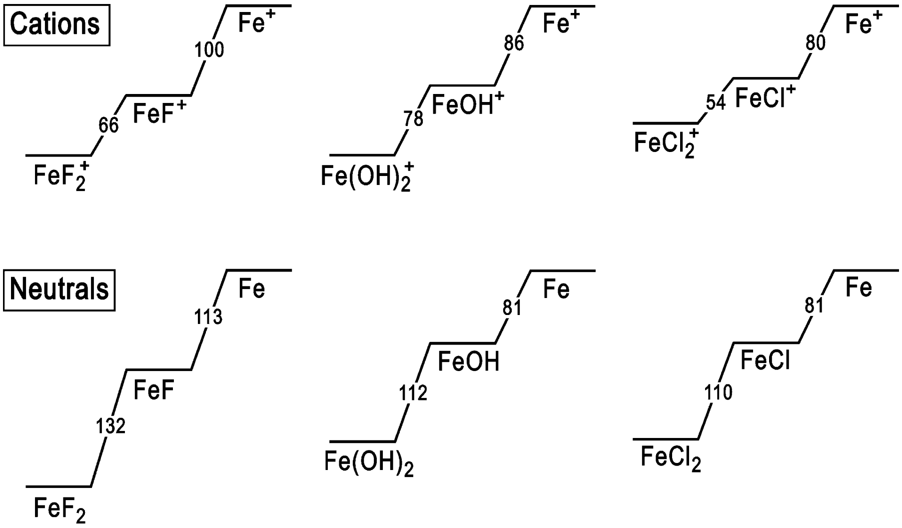

Fig. 3. Thermochemistry of $FeX_n{}^{0/+}$ (X = F, OH, Cl; $n = 1, 2$) in the gas phase (numbers refer to bond energies given in kcal/mol).

is mostly located at the metal, whereas $Fe(OH)_2{}^+$ might have a significant contribution of a structure best described as a protonated iron oxohydroxide $HOFeO{\cdot}H^+$. Consequently, a considerable fraction of the positive charge can be distributed to the hydrogen atoms in $Fe(OH)_2{}^+$, whereas such a charge-resonance stabilization is not available for the halides.

Finally, we return to the estimates derived from the additivity approach (see above). Without considering the additional corrections term ($\delta_1 = 0$), Eq. (8) predicts $\Delta_f H(Fe(OH)_2{}^+) = 128 \pm 3$ kcal/mol which is not too badly deviating from the final value $\Delta_f H(Fe(OH)_2{}^+) = 135.3 \pm 3.5$ kcal/mol derived here. Surprisingly, the agreement is much worse when the correction term $\delta_1$ derived from the corresponding chlorides is included ($\Delta_f H(Fe(OH)_2{}^+) = 155 \pm 7$ kcal/mol). Quite obviously, the anticipated similarity of the bonding situations in the chlorides and the hydroxides does not apply for the cationic species $Fe(OH)_2{}^+$ and $FeCl_2{}^+$ (see above). According to theory [18,59], the computed stability difference $\Delta E$ of the isomers $Fe(OH)_2{}^+$ and $OFe(OH_2)^+$ is 13.3 kcal/mol in favor of the former. With $\delta_1 = \delta_2 = 0$, the additivity scheme agrees poorly ($\Delta E = 44$ kcal/mol), whereas the predicted $\Delta E = 13$ kcal/mol for $\delta_1 = 27$ kcal/mol and $\delta_2 = -4$ kcal/mol (see above) appears to match quite nicely. Upon more careful inspection, however, this is only due to cancellation of errors in that the correction term $\delta_1$ leads to an overestimation of $\Delta_f H(Fe(OH)_2{}^+)$, while the significant difference of $D(Fe^+{-}OH_2) = 30.6$ kcal/mol [31] and $D(OFe^+{-}OH_2) = 53.1$ kcal/mol [59] is not reproduced by $\delta_2$.

## 6. Conclusions

Reactions of iron-hydroxide ions with arenes allow the improvement of the thermochemistry of iron hydroxides in the gas phase. In this respect, it turns out particularly valuable to consider complete Born–Haber cycles of neutral and ionic species in order to combine the methods available in gas-phase chemistry [21]. The values derived here are relevant for the understanding of oxidation reaction occurring in the gas phase and may assist the understanding of combustion processes, atmospheric phenomena, and the corrosion of bulk iron. In a more general perspective, the present results demonstrate that the often used additivity approaches may lead to misleading results not only when cooperative effects are neglected, but also the estimation of such effects from other related species needs judicious application.

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