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Gaseous Rust: Thermochemistry of Neutral and Ionic Iron Oxides and Hydroxides in the Gas Phase[†]

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The experimental and theoretical thermochemistry of the gaseous neutral and ionic iron oxides and hydroxides FeO, FeOH, FeO_2, OFeOH, and $Fe(OH)_2$ and of the related cationic water complexes $Fe(H_2O)^+$, $(H_2O)FeOH^+$, and $Fe(H_2O)_2{}^+$ is analyzed comprehensively. A combination of data for the neutral species with those of the gaseous ions in conjunction with some additional measurements provides a refined and internally consistent compilation of thermochemical data for the neutral and ionic species. In terms of heats of formation at 0 K, the best estimates for the gaseous, mononuclear $FeO_mH_n{}^{-/0/+/2+}$ species with $m = 1$, 2 and $n = 0-4$ are $\Delta_fH(FeO^-) = (108 \pm 6)$ kJ/mol, $\Delta_fH(FeO) = (252 \pm 6)$ kJ/mol, $\Delta_fH(FeO^+) = (1088 \pm 6)$ kJ/mol, $\Delta_fH(FeOH) = (129 \pm 15)$ kJ/mol, $\Delta_fH(FeOH^+) = (870 \pm 15)$ kJ/mol, $\Delta_fH(FeO_2{}^-) = (-161 \pm 13)$ kJ/mol, $\Delta_fH(FeO_2) = (67 \pm 12)$ kJ/mol, $\Delta_fH(FeO_2{}^+) = (1062 \pm 25)$ kJ/mol, $\Delta_fH(OFeOH) = (-84 \pm 17)$ kJ/mol, $\Delta_fH(OFeOH^+) = (852 \pm 23)$ kJ/mol, $\Delta_fH(Fe(OH)_2{}^-) = -431$ kJ/mol, $\Delta_fH(Fe(OH)_2) = (-322 \pm 2)$ kJ/mol, and $\Delta_fH(Fe(OH)_2{}^+) = (561 \pm 10)$ kJ/mol for the iron oxides and hydroxides as well as $\Delta_fH(Fe(H_2O)^+) = (809 \pm 5)$ kJ/mol, $\Delta_fH((H_2O)FeOH^+) = 405$ kJ/mol, and $\Delta_fH(Fe(H_2O)_2{}^+) = (406 \pm 6)$ kJ/mol for the cationic water complexes. In addition, charge-stripping data for several of several-iron-containing cations are re-evaluated due to changes in the calibration scheme which lead to $\Delta_fH(FeO^{2+}) = (2795 \pm 28)$ kJ/mol, $\Delta_fH(FeOH^{2+}) = (2447 \pm 30)$ kJ/mol, $\Delta_fH(Fe(H_2O)^{2+}) = (2129 \pm 29)$ kJ/mol, $\Delta_fH((H_2O)FeOH^{2+}) = 1864$ kJ/mol, and $\Delta_fH(Fe(H_2O)_2{}^{2+}) = (1570 \pm 29)$ kJ/mol, respectively. The present compilation thus provides an almost complete picture of the redox chemistry of mononuclear iron oxides and hydroxides in the gas phase, which serves as a foundation for further experimental studies and may be used as a benchmark database for theoretical studies.

Introduction

Besides their obvious relevance in corrosion, iron oxides and hydroxides play several, sometimes unique, roles in various kinds of oxidation reactions. For example, bulk iron oxides are important heterogeneous catalysts in industrial processes, while mononuclear iron oxides are of considerable interest in diverse areas ranging from the elusive iron−oxo species in the family of cytochrome P-450 enzymes[1] to the possible role of iron in ozone depletion in the upper atmosphere.[2] Inspired by the early work of Kappes and Staley[3] and subsequent reactivity studies of Freiser and co-workers,[4] the gas-phase reactivity of iron oxide cations has been investigated in quite some detail since 1990. Most remarkable in these early studies were the C−H bond activation of methane by the FeO^+ cation[5] and the realization of a catalytic cycle for alkane activation with FeO^+ as the key intermediate.[6] The range of substrates which are activated by gaseous FeO^+ in the gas phase is rather rich, including linear and cyclic hydrocarbons,[4–7] various arenes,[8] and heterocontaining compounds such as alcohols,[9] ketones,[10] amines,[11] and even hexafluorobenzene.[12]

In 1994, the reaction of FeO^+ with molecular hydrogen was investigated, and this seemingly simple reaction gave quite puzzling results.[13–15] At this point, a visit of Sason Shaik initiated a rather fruitful interplay between theory and experiment, which first lead to the solution for the problem at hand[16] and, in the following, to the development of two-state reactivity (TSR).[17] Meanwhile, TSR has turned out as a new reactivity concept in organometallics which has found acceptance in many areas of chemistry[18,19] and, meanwhile, even become a paradigm of multiple states.[20] In addition to the insights achieved into molecular reactivity, the experimental and theoretical work in this area provided a wealth of thermochemical information about iron oxide and hydroxide ions in the gas phase as a spin-off, which are compiled and evaluated here.

In 1999, Kellogg and Irikura[21] comprehensively treated the thermochemistry of neutral iron oxides and hydroxides relevant in combustion processes from a theoretical perspective. However, they focused on the gas-phase thermochemistry of the neutral iron compounds, whereas the additional insight which can be gained from the consideration of the ion chemistry of these species in the gas phase has not fully been exploited. It is a matter of fact, however, that even as far as main-group compounds are concerned, the nowadays most accurate energetics are derived from gas-phase data on ionic species.[22,23] In this contribution, the work of Kellogg and Irikura is thus complemented with the implications derived from previous experimental and theoretical studies of the gas-phase ion chemistry of iron oxides and hydroxides in conjunction with additional work aimed to get a hand on the few missing links. By such, an almost comprehensive overview of the redox chemistry of gaseous, mononuclear $FeO_mH_n{}^{-/0/+/2+}$ species ($m = 1, 2$; $n = 0-4$) ranging from monoanions to dications is provided.

Methods Section

While the major focus of this paper is on the evaluation of earlier data, some additional experiments are reported below, which are

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aimed to refine the present knowledge of $FeO_mH_n^{-/0/+/2+}$ compounds in some specific cases. These experimental methods utilize Fourier-transform ion cyclotron resonance (ICR),[24] sector field,[25] and quadrupole-based mass spectrometers.[26,27] Because the methods used for the examination of the gaseous $FeO_mH_n^{-/0/+/2+}$ compounds are very similar to those in our previous publications on these topics, the reader is referred to the original sources given below for detailed descriptions of the experimental conditions. Briefly, in the ICR experiments, mass-selected $^{56}Fe^+$ cations were reacted either with a mixture N_2O/CH_4 to afford $OFeOH^+$ or with β-butyrolactone and dioxygen to yield FeO_2^+. After mass selection, these ions were trapped in the presence of the neutral reagents indicated, and the products were detected as a function of reaction time. In the sector experiments, the iron-containing ions of interest were generated by chemical ionization of $Fe(CO)_5$ in the presence of N_2O, H_2O, and CH_3OH. In the quadrupole experiments, aqueous solutions of iron(II) and iron(III) salts were submitted to electrospray ionization, and the ions of interest were mass selected and submitted to collision-induced dissociation or reacted with neutral molecules under quasi-thermal conditions. In addition, the few complementary computations reported here[28] used precisely the same methods as those in most of our previous studies mentioned below, that is, the B3LYP hybrid functional in conjunction with 6-311*G basis sets.

In the evaluation of the thermochemical data, in addition to the references on neutral iron oxides and hydroxides given by Kellogg and Irikura,[21] several reactions of gaseous iron-containing ions were analyzed. In particular, the thermochemical implications of ion/molecule reactions occurring under thermal conditions as well as several other data available in the literature are evaluated. Some limitation is that temperatures are not unequivocally defined in all experiments, and corrections between values for 0 and 298 K energies cannot always be made. Nevertheless, Kellogg and Irikura[21] reported that thermal corrections are minor for the iron oxides and hydroxides, and it is hence assumed that the essential issues of the present contribution remain unaffected by this shortcoming. For this very reason, no further attempts were made to include rovibrational or electronic partition functions of the species described below as the changes are expected to be within the error margins of the thermochemical data derived in this work. Unless noted otherwise, all complementary thermochemical data were taken from the compendium by Lias et al. and/or the NIST database.[29] Note that these sources of auxiliary thermochemistry as well as the most recent data on the energetics of the iron oxides and hydroxides described below may lead to some deviations between the thermochemical data derived in the original papers quoted and the present evaluation. Further, the selection of reference values in cases where multiple sets of data are available is somewhat individual, and those values are chosen which are anticipated to be most reliable. In the evaluation, it is usually assumed that all errors are independent from each other and use error propagation in terms of square roots, that is, $\Delta x = (\sum \Delta x_i^2)^{1/2}$. For weighted averaging, the formulas

$$\bar{x} = \sum_i \frac{x_i}{\Delta x_i^2} \Big/ \sum_i \frac{1}{\Delta x_i^2}$$

and

$$\Delta \bar{x} = \sqrt{1 \Big/ \sum_i \frac{1}{\Delta x_i^2}}$$

are applied. In the bracketing experiments, however, the full error ranges are considered in the averages given below.

Results and Discussion

This section begins with a discussion of the results available about the thermochemistry of $FeO_mH_n^{-/0/+}$ with particular attention to the thermochemical implications of several ion/molecule reactions.[30] This evaluation is complemented by some additional experimental or theoretical work aimed to refine the data set in cases where particular ambiguity remains. A separate subsection is devoted to $FeO_mH_n^{2+}$ dications because recent methodological results require a re-evaluation of the earlier work. Finally, the resulting thermochemical information is compiled in an internally consistent network of the thermochemistry of gaseous iron oxides and hydroxides.

This contribution almost exclusively addresses aspects relevant to the thermochemistry of gaseous iron compounds. It needs to be pointed out right at the outset, however, that it is precisely the gas-phase chemistry of iron in which the role of spin multiplicity is most pronounced and well-documented among the transition metals.[17,31] For example, $Fe^+(^4F)$ is by about 70 times more reactive toward H_2 than the $Fe^+(^6D)$ ground state, although the state splitting is small.[32] On the other hand, the highly excited $Fe^+(^6S)$ state is less reactive than the $Fe^+(^6D)$ ground state due to the particular nature of the $4s^23d^5$ configuration in $Fe^+(^6S)$.[33] Further, spin multiplicity acts as a mechanistic distributor of major importance in the reactions of the FeO^+ cation in the gas phase.[34] In fact, the variations with respect to electronic structures as well as the richness of accessible structural isomers renders iron chemistry as one of the most difficult challenges for contemporary experimental and theoretical methods. For example, the computational predictions for neutral FeO_2 agree for a dioxide structure, while the assignments of the low-lying states vary from singlet $^1A_1$ to triplet $^3B_1$, quintet $^5B_2$, and even a septet $^7A_1$ state.[2b,21,35] In the present study, the nature of the electronic ground states is mostly ignored, but it needs to be stressed that appropriate consideration of all conceivable states is essential for reliable theoretical approaches.

Thermochemistry of $FeO_mH_n^{-/0/+/2+}$ Species. In this subsection, previous literature data on the thermochemistry of $FeO_mH_n^{-/0/+/2+}$ species in the gas phase are evaluated and interpreted with respect to the reactivity of these species. In the course of the evaluation of these reactions in terms of thermochemical properties, also some best estimates for the heats of formation of various species are derived.

Iron Oxide FeO. The thermochemistry of iron oxide is well settled and does not require major discussion. However, one particular aspect which becomes more important further below is addressed here. The most precise and reliable experimental data are often only indirect measures in terms of the relevant heats of formation ($\Delta_f H$).[36] For example, accurate data for FeO are the gas-phase bond dissociation energies $D(Fe-O) = (401 \pm 8)$ kJ/mol[37] and $D(Fe-O) = (424 \pm 15)$ kJ/mol[38] and the theoretical estimate of $D(Fe-O) = (414 \pm 22)$ kJ/mol,[21] from which a weighted average of $D(Fe-O) = (408 \pm 6)$ kJ/mol is derived. For the monocation, an accurate value of $D(Fe^+-O) = (335 \pm 6)$ kJ/mol[36,39] is available. The electron affinity of neutral FeO has been determined with an even larger precision, and a recent ZEKE study gives $EA(FeO) = (1.4944 \pm 0.0006)$ eV.[40] These properties can be combined with atomic properties in thermochemical cycles. For example, $D(Fe-O)$ and $D(Fe^+-O)$ together with $IE(Fe) = 7.9023$ eV result in $IE(FeO) = (8.67 \pm 0.09)$ eV, which agrees well with independently determined appearance energies of (8.71 ± 0.10) eV[41] and (8.8 ± 0.2) eV[42] as well as with $IE(FeO) = (8.8 \pm 0.2)$ eV derived from ion/molecule reactions.[43] Recently, Metz et al.[44] measured a somewhat lower value of IE(FeO) = (8.56 ± 0.01) eV by photoionization of neutral FeO, a truly remarkable step forward with respect to the direct determination of fundamental properties of small transition-metal compounds. With respect to the, in part, still preliminary character of these data and possible contributions of excited states, however, the value is not included in the averaging. Further, IE(FeO^+) has been determined,[43,45] thereby complementing the gas-phase ion chemistry of diatomic FeO from the anion to the dication.

The best estimates for the heats of formation of these species are accordingly $\Delta_f H(FeO^-) = (108 \pm 10)$ kJ/mol, $\Delta_f H(FeO) = (252 \pm 6)$ kJ/mol, and $\Delta_f H(FeO^+) = (1088 \pm 6)$ kJ/mol; the FeO^{2+} dication is addressed further below.

Iron Hydroxide FeOH. As mentioned by Kellogg and Irikura,[21] there exist two conflicting sets of data for the neutral compound, that is, $\Delta_f H(FeOH) = (136 \pm 17)$ kJ/mol determined by Murad[42] versus $\Delta_f H(FeOH) = (69 \pm 20)$ kJ/mol derived by Jensen and Jones,[46] while both studies agree reasonably well for $\Delta_f H(FeO)$. On the basis of a previous study[47] and their own theoretical prediction of $D(Fe-OH)$, Kellogg and Irikura[21] preferred Murad's measurements, while their best estimate of $\Delta_f H(FeOH) = (91 \pm 21)$ kJ/mol is in between both figures. An ab initio study by Rollason and Plane gives $\Delta_f H(FeOH) = (112 \pm 26)$ kJ/mol.[48] While in the past some conflicting values have also been obtained for the cationic species $FeOH^+$, a recent re-evaluation of the experimental data $D(Fe^+-OH) = (366 \pm 12)$ kJ/mol[36] and (357 ± 13) kJ/mol[49] recommended a value of $D(Fe^+-OH) = (345 \pm 14)$ kJ/mol,[50] which agrees well with a reliable ab initio prediction of $D(Fe^+-OH) = (356 \pm 12)$ kJ/mol.[51] Combination of $D(Fe^+-OH) = (345 \pm 14)$ kJ/mol with the recently refined experimental IE(FeOH) = (7.67 ± 0.06) eV[52] leads to $D(Fe-OH) = (323 \pm 15)$ kJ/mol or $\Delta_f H(FeOH) = (129 \pm 15)$ kJ/mol for the neutral species, which is fully consistent with the experimental value of Murad but somewhat out of the error margins in comparison to the theoretical prediction of Kellogg and Irikura, $\Delta_f H(FeOH) = (91 \pm 21)$ kJ/mol,[21] and clearly discounts the earlier value by Jensen and Jones.[46] Further notable is a theoretical study of Cao, which demonstrated that inclusion of relativistic effects is mandatory for the correct description of $FeOH^{0/+}$.[53]

Further, IE($FeOH^+$) has been determined by charge-stripping of $FeOH^+$ to the $FeOH^{2+}$ dication,[45,54] to which it is returned below. While data for the anionic species $FeOH^-$ has not been reported so far, the thio analogue $FeSH^-$ as well as the carbonyl complexes $(CO)_nFeOH^-$ (n = 3, 4) have been described.[55,56]

The best estimates for the heats of formation are thus $\Delta_f H(FeOH) = (129 \pm 15)$ kJ/mol and $\Delta_f H(FeOH^+) = (870 \pm 15)$ kJ/mol.

Iron Dioxide FeO_2. An essential issue with this species concerns the structural dichotomy of neutral and ionic FeO_2 in the gas phase.[57,58] Thus, the FeO_2^- anion as well as neutral FeO_2 were proposed to exhibit dioxide structures, that is, $O{=}Fe-O^-$ and $O{=}Fe{=}O$, respectively. For the cation, however, the iron−dioxygen complex $Fe(O_2)^+$ and the dioxide FeO_2^+ are close in energy and separated by a surprisingly low barrier. Facile interconversion between both isomers is therefore anticipated for the cation and is indeed indicated by experimental findings.[57] Ion/molecule reactions provide a bracket of $D_0(Fe^+-O_2) = (105 \pm 25)$ kJ/mol which agrees well with a theoretical prediction of $D_e(Fe^+-O_2) = 121$ kJ/mol. Further, IE(FeO_2) = (9.5 ± 0.5) eV has been reported by Hildenbrand.[41] Additional valuable information about FeO_2^+ is due to Rollason and Plane.[2d] Their theoretical approach led to a significantly lower value for the dioxide species, $D_e(Fe^+-O_2) = 30$ kJ/mol, which these authors attributed to the strong effect of dynamic correlation in FeO_2^+ ($^6A_1$) which is only partially covered with the DFT approach used.[59] The calculated frequencies indicate that the difference between $D_e(Fe^+-O_2)$ and $D_0(Fe^+-O_2)$ is only about 1 kJ/mol for the FeO_2^+ ($^6A_1$) ground state.[2b] More recently, Plane and co-workers reported a theoretical value of $D(Fe^+-O_2) = 114$ kJ/mol.[60] The FeO_2^{2+} dication has also been detected,[57] but no quantitative information on the monocation's IE is available. With the average of the experimental value of $D(Fe^+-O_2) = (105 \pm 25)$ kJ/mol[57] and the theoretical predictions of 114 and 121 kJ/mol,[57,60] one arrives at an averaged $D(Fe^+-O_2) = (113 \pm 25)$ kJ/mol and hence an estimate of $\Delta_f H(FeO_2^+) = (1062 \pm 25)$ kJ/mol.

TABLE 1: Heats of Formation of Gaseous FeO_2 at 0 K ($\Delta_f H(FeO_2)$ in kJ/mol) Derived from Various Literature Sources

experiment	63 ± 14,[a] 75 ± 21,[b] 102 ± 20,[c] <140 ± 6[d]
theory	−1[e], 91 ± 20,[f] 145,[g] 233 ± 50[h]

[a] Derived from EA(FeO_2) = (2.358 ± 0.030) eV[66] and $\Delta_f H(FeO_2^-) = 164 \pm 13$ kJ/mol.[64] [b] Ref 41. [c] Value quoted in ref 64. [d] Upper limit given in ref 63. [e] Derived from $D(Fe-O_2) = 415$ kJ/mol. [f] Ref 21. [g] Derived from $D(Fe-O_2) = 268$ kJ/mol.[35] [h] Derived from $D(Fe-O_2) = (180 \pm 50)$ kJ/mol.[2b]

The formation of transient FeO_2 in the gas phase as well as a report on the bulk substance goes back to Addison and co-workers in 1965.[61] Several thermochemical studies of neutral FeO_2 are already compiled in ref 21.[62] There remains to add a previous study of Helmer and Plane who predicted a binding energy of $D(Fe-O_2) = (180 \pm 50)$ kJ/mol[2b] and an upper bound of $\Delta_f H(FeO_2) < (140 \pm 6)$ kJ/mol, which Baranov et al. deduced from the occurrence of reaction 1 under thermal conditions.[63] The various values available for $\Delta_f H(FeO_2)$ are collected in Table 1, and the considerable divergence of the data suggest a critical analysis.

$$FeO^+ + NO_2 \rightarrow NO^+ + FeO_2 \qquad (1)$$

For the anionic species, $\Delta_f H(FeO_2^-) = (-164 \pm 13)$ kJ/mol has been determined by equilibrium measurements.[64] This figure is consistent with the observed bimolecular reactivity of FeO_2^- in the gas phase[65] and the dioxide structure proposed in a previous mass spectrometric study.[57] Further, Wang and co-workers studied photoelectron detachment from the FeO_2^- anion and derived an electron affinity of EA(FeO_2) = (2.358 ± 0.030) eV.[66] Combined with $\Delta_f H(FeO_2^-)$, this yields $\Delta_f H(FeO_2) = (63 \pm 14)$ kJ/mol for the neutral species, which is in excellent agreement with the early experimental value $\Delta_f H(FeO_2) = (75 \pm 21)$ kJ/mol due to Hildenbrand,[41] and the weighted average of both values leads to a final estimate of $\Delta_f H(FeO_2) = (67 \pm 12)$ kJ/mol. Accordingly, the criticism of the photodetachment data in a theoretical study by Cao et al.[35b] appears unjustified.

However, inspection of these results for the neutral and the anionic species reveals a discrepancy in comparison to the cation because $\Delta_f H(FeO_2) = (67 \pm 12)$ kJ/mol and $\Delta_f H(FeO_2^+) = (1062 \pm 25)$ kJ/mol imply IE(FeO_2) = (10.3 ± 0.3) eV, which disagrees with IE(FeO_2) = (9.5 ± 0.5) eV reported by Hildenbrand.[41] To address this issue, gaseous FeO_2^+ has been prepared by ligand exchange of the weakly bound $Fe(CO_2)^+$ cation, which is accessible in the gas phase from bare Fe^+ and β-butyrolactone,[67,68] and after mass selection, so-formed FeO_2^+ was allowed to react with various fluorobenzenes which cover IEs above that of benzene (IE = 9.24378 eV).[29]

$$FeO_2^+ + C_6F_6 \rightarrow C_6F_6^+ + FeO_2 \qquad (2)$$

In fact, even for hexafluorobenzene, $IE(C_6F_6) = (9.90 \pm 0.04)$ eV,[29] occurrence of electron transfer is observed, reaction 2, hence implying a somewhat larger IE than the value given Hildenbrand,[41] for which, accordingly, $IE(FeO_2) = (10.3 \pm 0.3)$ eV derived above from the heats of formation is suggested. Note that in bimolecular ion/molecule processes such as reaction 2, long-lived collision complexes are likely to be involved, and hence, the measurements reflect adiabatic ionization energies, whereas photoionization studies or high-energy collision experiments (see below) mostly refer to vertical transitions.

The best estimates for the heats of formation of anionic, neutral, and cationic species are, accordingly, $\Delta_f H(FeO_2^-) = (-161 \pm 13)$ kJ/mol, $\Delta_f H(FeO_2) = (67 \pm 12)$ kJ/mol, and $\Delta_f H(FeO_2^+) = (1062 \pm 25)$ kJ/mol; note that $\Delta_f H(FeO_2^-)$ is recalculated from $\Delta_f H(FeO_2)$ and $EA(FeO_2)$.

Oxo Iron Hydroxide OFeOH. Kellogg and Irikura[21] gave no reference for the experimental thermochemistry of neutral OFeOH, whose vibrational properties have been determined by matrix-isolation spectroscopy.[69] The ionic species $OFeOH^+$ was described in 1991, and not surprisingly, this formal iron(IV) compound is capable of oxidizing hydrocarbons, including methane.[70] At that time, no further thermochemical information on the ionic species was provided. Meanwhile, complementary studies on related ions extend the knowledge, and some further specification is indicated. Most of this information is derived from the rather rich ion chemistry of iron oxide cation FeO^+ in the gas phase;[71] also, the $OFeOH^+$ cation is made via FeO^+ as an intermediate.[70] With regard to neutral OFeOH, the reactions of FeO^+ with potential hydroxide donors are to be considered, and in this respect, the observed occurrence or nonoccurrence of reactions 3–8 is of interest.

$$FeO^+ + HCOOH \rightarrow HCO^+ + OFeOH \qquad (3)$$

$$FeO^+ + CH_3COOH \rightarrow CH_3CO^+ + OFeOH \qquad (4)$$

$$FeO^+ + CH_3OH \rightarrow CH_3^+ + OFeOH \qquad (5)$$

$$FeO^+ + C_2H_5OH \rightarrow C_2H_5^+ + OFeOH \qquad (6)$$

$$FeO^+ + i{-}C_3H_7OH \rightarrow C_3H_7^+ + OFeOH \qquad (7)$$

$$FeO^+ + t{-}C_4H_9OH \rightarrow C_4H_9^+ + OFeOH \qquad (8)$$

The fact that hydroxide transfer to FeO^+ does not take place with formic acid while it is efficient with acetic acid[72] provides a bracket of -117 kJ/mol $< \Delta_f H(OFeOH) < -6$ kJ/mol. Similarly, reactions 5–8 between FeO^+ and simple alkanols imply -211 kJ/mol $< \Delta_f H(OFeOH) < -48$ kJ/mol.[9a] In combination, these brackets suggest $\Delta_f H(OFeOH) = (-82 \pm 34)$ kJ/mol. Note, however, that the nonoccurrence of certain reactions is used in the bracketing, which might lead to errors if there exist barriers which exceed the relevant thermochemical asymptotes. The use of nonoccurring reactions may be justified by the similarity of the reactivity patterns within the homologous rows, however, and it is further confirmed by the good agreement with $\Delta_f H(OFeOH) = (-85 \pm 20)$ kJ/mol predicted in ref 21. Combination of both values provides a weighted average of $\Delta_f H(OFeOH) = (-84 \pm 17)$ kJ/mol.

In addition, the formation as well as the degradation of $OFeOH^+$ in the ion/molecule reactions 9–12 suggests a rather crude bracket of 740 kJ/mol $< \Delta_f H(OFeOH^+) < 921$ kJ/mol or $\Delta_f H(OFeOH^+) = (831 \pm 92)$ kJ/mol.[70,72]

$$FeOH^+ + N_2O \rightarrow OFeOH^+ + N_2 \qquad (9)$$

$$FeO^+ + HNO_3 \rightarrow OFeOH^+ + NO_2 \qquad (10)$$

$$OFeOH^+ + CH_4 \rightarrow FeOH^+ + CH_3OH \qquad (11)$$

$$OFeOH^+ + CH_4 \rightarrow FeOCH_3^+ + H_2O \qquad (12)$$

Reactions 3–8 and 9–12 can be related to each other by the additional observations that the mass-selected $OFeOH^+$ cation generated according to reaction 9 undergoes efficient electron transfer with adamantane (IE = 9.24 eV), benzene (IE = 9.24 eV), and NO (IE = 9.25 eV) and slows electron transfer with NO_2 (IE = 9.75 eV) but not with hexafluorobenzene (IE = 9.90 eV. Similarity of the IEs of NO_2 and OFeOH is further suggested by the competitive formation of NO_2^+ and $OFeOH^+$ upon CID of mass-selected $(HO)Fe(NO_3)^+$ generated via electrospray ionization.[73] These findings thus suggest $IE(OFeOH) = (9.7 \pm 0.2)$ eV,[72] which is consistent with the wider range of $IE(OFeOH) = (9.4 \pm 1.1)$ eV derived from the bracketed heats of formation. About the ionic species $OFeOH^-$ and $OFeOH^{2+}$, no thermochemical information is available so far.

The best estimates for the heats of formation are, accordingly, $\Delta_f H(OFeOH) = (-84 \pm 17)$ kJ/mol and $\Delta_f H(OFeOH^+) = (852 \pm 23)$ kJ/mol, where the latter value stems from combining the heat of formation of the neutral with the IE.

Iron Dihydroxide $Fe(OH)_2$. For the neutral species, a very precise experimental value of $\Delta_f H(Fe(OH)_2) = (-322 \pm 2)$ kJ/mol[74] agrees reasonably well with theoretical predictions of $\Delta_f H(Fe(OH)_2) = (-323 \pm 20)$ kJ/mol[21] and $\Delta_f H(Fe(OH)_2) = (-304 \pm 13)$ kJ/mol.[48] Thus, the experimental figure for the neutral species is adopted and used as a benchmark in the further evaluation below. Cationic iron dihydroxide is formed in the reaction of bare Fe^+ with hydrogen peroxide,[75] 1,2-diols,[76] or nitroalkanes[77] upon association of FeO^+ with water,[63,78] upon oxidation of $Fe(H_2O)^+$ with N_2O,[6] and in the reaction of $HFe(H_2O)^+$ with molecular oxygen.[79] Despite the fact that FeO^+ and $Fe(OH)_2^+$ are both formal iron(III) compounds, the latter is much less reactive than the oxo species. For example, the formation of $Fe(OH)_2^+$ has been identified as the major sink in the FeO^+-catalyzed oxidations of hydrogen and ethane in the gas phase.[6,13] By means of the bracketing technique, $IE(Fe(OH)_2) = (9.15 \pm 0.10)$ eV has been determined,[52] which leads to $\Delta_f H(Fe(OH)_2^+) = (560 \pm 10)$ kJ/mol. The CID behavior of mass-selected $Fe(OH)_2^+$ is consistent with a dihydroxide structure.[52,80] However, the cation has two low-lying isomers, namely, the dihydroxide cation $Fe(OH)_2^+$ and the hydrated oxide $FeO(H_2O)^+$. Theory predicts $Fe(OH)_2^+$ to be 63 kJ/mol more stable than the isomeric $OFe(OH_2)^+$ cation, both having sextet ground states.[81] Further, B3LYP/6-311*G+ calculations predict $IE(Fe(OH)_2) = 9.10$ eV, which agrees well with the experimental value.[28,82]

The $Fe(OH)_2^-$ anion has been observed several times[65,83,84] but not examined in much detail. Thus, except its obvious existence as a long-lived species, that is, $EA(Fe(OH)_2) > 0$, no valuable thermochemical information can be derived from the ion/molecule reactions reported so far. For example, from a thermochemical point of view, the values derived above imply that the experimentally observed[84] dehydrogenation of methanol according to reaction 13 could still occur if the electron were unbound in $Fe(OH)_2^-$.

$$FeO_2^- + CH_3OH \rightarrow Fe(OH)_2^- + CH_2O \qquad (13)$$

With $EA(Fe(OH)_2) = 1.12$ eV suggested by B3LYP calculations,[82] $\Delta_f H(Fe(OH)_2^-) = -431$ kJ/mol can be derived, however. Further, B3LYP data predicts IE($Fe(OH_2)^+$) = 17.52 eV, while the experimental determination of *I*E($Fe(OH)_2{}^+$) by means of charge-stripping is hampered by isobaric interferences.[45] Interestingly, the order of stability of the singly charged $[Fe,O_2,H_2]^+$ isomers, $\Delta_fH(Fe(OH)_2{}^+) < \Delta_fH(OFe(OH_2)^+) < \Delta_fH(Fe(H_2O_2)^+)$, is reversed for the doubly charged ions in that $Fe(H_2O_2)^{2+}$ corresponds to the most stable species on the dication surface.[85]

The best estimates for the heats of formation are, accordingly, $\Delta_fH(Fe(OH)_2{}^-) = -431$ kJ/mol, $\Delta_fH(Fe(OH)_2) = (-322 \pm 2)$ kJ/mol, and $\Delta_fH(Fe(OH)_2{}^+) = (561 \pm 10)$ kJ/mol; no error margin is given for the value of the anion which is derived from B3LYP data.

Cationic Water Complexes $Fe(H_2O)_n{}^+$ and $(H_2O)FeOH^+$. The sequential hydration energies of the bare Fe^+ ion are well-established, and the most accurate values are $D(Fe^+-H_2O) = (128 \pm 5)$ kJ/mol and $D((H_2O)Fe^+-H_2O) = (164 \pm 4)$ kJ/mol, respectively, for the first two water ligands.[36,86] While the inserted $HFeOH^+$ isomer has, so far, not been generated experimentally, theory predicts it to be by about 100 kJ/mol less stable than the $Fe(H_2O)^+$ cation.[16,51] In contrast, theory has been used to predict a $\Delta_fH(HFeOH)$ of about 35 kJ/mol for the neutral insertion isomer,[48,87] whereas neutralization of the $Fe(H_2O)^+$ cation was unsuccessful.[88] In fact, the neutral $Fe(H_2O)$ isomer is likely to be unbound ($\Sigma\Delta_fH(Fe + H_2O) = 175$ kJ/mol). The anionic bare and ligated insertion species $HFeOH^-$ and $(CO)(H)FeOH^-$ have also been described.[56b,83] Further, the dications $Fe(H_2O)^{2+}$ and $Fe(H_2O)_2{}^{2+}$ have been generated via charge-stripping experiments,[45] and the multiply solvated dications $Fe(H_2O)_n{}^{2+}$ ($n = 6 - 10$) can be made via electrospray ionization (see below).[89]

The $(H_2O)FeOH^+$ cation is abundant in the flame ionization of iron.[90,91] In addition, it has been observed in the reactions of Fe^+ with nitroalkanes,[77] upon the association of $FeOH^+$ cation with water,[92] in the reactions of $OFeOH^+$ with alkanes,[70] and upon photofragmentation of $Fe(H_2O)_n{}^+$ cations.[93] H/D and $^{16}O/^{18}O$ labeling studies demonstrate that both ligands can equilibrate via a rate-determining hydrogen migration.[78,94] Valuable thermochemical information can be derived from the observation of reaction 14[94] in conjunction with $D_0(Fe^+-CH_3OH) = (144 \pm 9)$ kJ/mol.[95]

$$Fe(CH_3OH)^+ + H_2O \rightarrow (H_2O)FeOH^+ + CH_3^{\bullet} \qquad (14)$$

Occurrence of reaction 14 at room temperature requires $\Delta_fH((H_2O)FeOH^+) < (453 \pm 15)$ kJ/mol. Loss of a methyl radical instead of a closed-shell product in reaction 14 may appear surprising at the first sight, but the formation of similar ligated $FeOH^+$ cations concomitant with losses of radicals has been described previously in the reactions of $Fe(CH_3OH)^+$ with methanol[96] and of FeO^+ with propane[4a] or methanol.[9a] These reactions indicate a particular stability of $(H_2O)FeOH^+$ in which iron adopts the favorable +II oxidation state with additional stabilization by water as a σ-donor ligand.[97] While a lower limit for $\Delta_fH((H_2O)FeOH^+)$ is not available so far, the upper bound derived from reaction 14 already implies that $D(HOFe^+-H_2O) > (155 \pm 19)$ kJ/mol is significantly larger than $D(Fe^+-H_2O) = (128 \pm 5)$ kJ/mol[36] and $D(HFe^+-H_2O) = (137 \pm 14)$ kJ/mol,[98] thereby corroborating an increase of $D(HOFe^+-H_2O)$ compared to $D(Fe^+-H_2O)$. Moreover, water can replace ligands such as L = C_2H_4 and CH_2O in $LFeOH^+$ complexes,[6,9a] whereas these ligands are more strongly bound to the bare metal in the corresponding $Fe(L)^+$ ions.[36,99] These qualitative arguments are supported by a theoretical prediction of $D(HOFe^+-H_2O) = 226$ kJ/mol,[81] which is significantly larger than the binding energies of water ligands to Fe^+.

The best estimates for the heats of formation of the cationic water complexes are $\Delta_fH(Fe(H_2O)^+) = (809 \pm 5)$ kJ/mol, $\Delta_fH((H_2O)FeOH^+) = 405$ kJ/mol, and $\Delta_fH(Fe(H_2O)_2{}^+) = (406 \pm 6)$ kJ/mol.

Miscellaneous FeO_mH_n Species. Some limited information is available for the higher oxides FeO_3 and FeO_4 and their anions $FeO_3{}^-$ and $FeO_4{}^-$;[48,57,66,100] as far as connectivity is concerned, O−O bond formation is likely in these species, particularly in the latter. Further, the hydrated iron hydride cation $HFe(H_2O)^+$ has been examined by Tjelta and Armentrout who determined $D(H_2OFe^+-H) = (215 \pm 14)$ kJ/mol and $D(HFe^+-H_2O) = (137 \pm 14)$ kJ/mol.[98,101]

$FeO_mH_n{}^{2+}$ Dications. Several iron oxide and iron hydroxide dications have been generated by charge-stripping (CS) of the corresponding monocations.[43,45,54,57] For most of these species, ionization energies have been determined by energy-resolved CS experiments. As detailed elsewhere, however, due to some recent results about the double ionization of toluene, whose molecular ion $C_7H_8{}^+$ has widely been used as a convenient reference in energy-resolved CS experiments within the last 30 years, a reanalysis of the earlier data is indicated.[102] Specifically, consideration of the Franck−Condon envelopes in the photodouble ionization threshold of toluene led to the conclusion that the previously used reference value of IE($C_7H_8{}^+$) = 15.7 eV[103] is by almost 1 eV too high, in that the correct value amounts to IE($C_7H_8{}^+$) = (14.8 ± 0.1) eV;[104] note that the revised value has recently been confirmed in independent experiments.[105] Because toluene also served for the calibration of the energy-resolved CS experiments in refs 43 and 45, the resulting energetics of the $FeO_mH_n{}^{2+}$ dications need to be revised accordingly. At least in a precise manner, such an effort requires reanalysis of the raw data because absolute energy differences rather than the relative values are considered in energy-resolved CS, and a proportional rescaling of the IEs for the adjusted IE($C_7H_8{}^+$) is thus only a first-order approximation. In the case of $FeO_mH_n{}^{2+}$, however, the original raw data were still available. Further, the Franck−Condon analysis of the toluene dication also revealed that the double ionization thresholds determined in energy-resolved CS refer to adiabatic transitions, even though the CS process itself occurs as a vertical transition.[104,106] The origin of this seeming paradox is associated with the evaluation of Q_{min} values by extrapolation of the high-energy onset of the charge-stripping peaks to the baseline, which leads to adiabatic values, if the corresponding 0 → 0 transition has a non-negligible cross section.[107]

The results of this re-evaluation and earlier theoretical data are summarized in Table 2. In general, the agreement between the revised experimental data and the theoretical predictions is reasonable. Given the slight tendency of the DFT method employed to overestimate first ionization energies,[108] a similar trend may thus be expected for ionization to dications. In conjunction with the thermochemical data of the monocations derived above, these ionization energies allow one to assess the energetics of the dicationic $FeO_mH_n{}^{2+}$. Most interesting in this respect is the so-called thermochemical stability of the gaseous dications,[106,109,110] that is, the question if the doubly charged ions are stable with respect to dissociation into two monocations. Thus, $\Delta_fH(FeO^+) = (1088 \pm 6)$ kJ/mol derived above and IE(FeO^+) = (17.68 ± 0.28) eV given in Table 2 accordingly lead to $\Delta_fH(FeO^{2+}) = (2795 \pm 28)$ kJ/mol, which is slightly above the charge-separation asymptote for $Fe^+ + O^+$ ($\Sigma\Delta_fH = 2737$ kJ/mol); nevertheless, the FeO^{2+} can be observed as a

TABLE 2: Q_{min} Values[a] Given in Ref 45 and Derived Adiabatic Ionization Energies of $FeO_mH_n^+$ Monocations (IE_a in eV) after Correction of Previous Charge-Stripping Measurements with Respect to More Recent General Findings about Energy-Resolved Charge-Stripping Spectra (see text), the IE_a Calculated Using Density Functional Theory from Ref 45, and the Deviation between the Corrected Experimental and the Theoretical Values

	Q_{min}	$IE_{a,corr}$	$IE_{a,DFT}$	$\Delta IE_{exp/calc}$
Fe^+	15.39 ± 0.26[b]	16.1877[c]	16.52	0.33
FeO^+	18.63 ± 0.26[d]	17.68 ± 0.28	18.75	1.07
$FeOH^+$	17.30 ± 0.26[e]	16.34 ± 0.27	17.23	0.89
$Fe(H_2O)^+$	14.41 ± 0.28	13.68 ± 0.30	13.84	0.16
$Fe(OH)_2^+$	*13.93 ± 0.81*[f]	*13.40 ± 0.80*[f]	17.52	g
$(H_2O)FeOH^+$	15.84 ± 0.39	15.12 ± 0.34	15.80	0.68
$Fe(H_2O)_2^+$	12.63 ± 0.30	12.06 ± 0.29	12.42	0.36

[a] The Q_{min} value is the experimentally measured kinetic energy loss of the dication beam relative to the monocation. Note that the quoted values from ref 45 are anchored on the old, incorrect second ionization energy of toluene used for calibration. [b] The experimental value is underestimated; most likely, there is an interference of electronically excited Fe^+ monocations; see ref 45. [c] Spectroscopic value, see: http://physics.nist.gov/PhysRefData/ASD/index.html. [d] A previous Q_{min} of (18.3 ± 0.3) eV has been reported in ref 43. [e] A previous Q_{min} of (17.0 ± 0.4) eV has been reported in ref 54. [f] Experimental values are underestimated due to isotopic interferences as well as the possible presence of isomers; see ref 45. [g] Not considered, see footnote [f].

metastable dication because charge separation is kinetically hindered by a Coulomb barrier.[109] For $FeOH^{2+}$, the data analogously imply $\Delta_fH(FeOH^{2+}) = (2447 \pm 30)$ kJ/mol and thus indicate the thermochemical stability of $FeOH^{2+}$ with respect to the conceivable Coulomb explosions into $Fe^+ + OH^+$ ($\Sigma\Delta_fH = 2471$ kJ/mol) and $FeO^+ + H^+$ ($\Sigma\Delta_fH = 2617$ kJ/mol); the latter value implies that the FeO^+ monocation has a positive proton affinity of $PA(FeO^+) = (170 \pm 30)$ kJ/mol. With increasing size, however, the number of low-lying charge-separation asymptotes increases, and despite the relatively low ionization energy of $Fe(H_2O)^+$ (Table 2), the heat of formation of the hydrated iron dication, $\Delta_fH(Fe(H_2O)^{2+}) = (2129 \pm 29)$ kJ/mol, is close the charge-separated species $Fe^+ + H_2O^+$ ($\Sigma\Delta_fH = 2155$ kJ/mol). Due to overlapping features in the charge-stripping experiments, only a theoretical prediction of $IE(Fe(OH)_2^+) = 17.52$ eV is available from which $\Delta_fH(Fe(OH)_2^{2+}) = 2252$ kJ/mol is derived, which is significantly above the charge-separation asymptotes for $FeO^+ + H_2O^+$ ($\Sigma\Delta_fH = 2068$ kJ/mol) and $FeOH^+ + OH^+$ ($\Sigma\Delta_fH = 2165$ kJ/mol). Note that the decreased stability of $Fe(OH)_2^{2+}$ is also consistent with the general notion that iron(IV) compounds are unfavorable. The hydrated iron hydroxide dication, $(H_2O)FeOH^{2+}$, $\Delta_fH = 1864$ kJ/mol, is not thermochemically stable with respect to the channels $FeOH^+ + H_2O^+$ ($\Sigma\Delta_fH = 1849$ kJ/mol) and $FeO^+ + H_3O^+$ ($\Sigma\Delta_fH = 1687$ kJ/mol), where the particularly large exothermicity of charge separation in the latter case is associated with formation of the hydronium ion H_3O^+. Finally, the revised CS data for doubly hydrated Fe^{2+} imply $\Delta_fH(Fe(H_2O)_2^{2+}) = (1570 \pm 29)$ kJ/mol, for which the charge separation into $(H_2O)FeOH^+ + H^+$ ($\Sigma\Delta_fH = 1933$ kJ/mol) indicates a sizable proton affinity of $PA((H_2O)FeOH^+) = (363 \pm 29)$ kJ/mol. However, intramolecular proton transfer in $Fe(H_2O)_2^{2+}$ followed by Coulomb explosion into $FeOH^+ + H_3O^+$ ($\Sigma\Delta_fH = 1468$ kJ/mol) is quite exothermic because two relatively stable monocations are formed as products in reaction 15.[111] Thus, none of the $FeO_mH_n^{2+}$ dications considered here shows a particularly pronounced thermochemical stability, and most of them are metastable with respect to charge separation.

$$Fe(H_2O)_2^{2+} \rightarrow FeOH^+ + H_3O^+ \qquad (15)$$

While the focus of this contribution lies on $FeO_mH_n^{-/0/+/2+}$ species with $m = 1$ and 2, it is noted that iron(II) dications $Fe(H_2O)_n^{2+}$ with a larger number of water ligands are easily accessible via electrospray ionization of aqueous iron(II) salts.[89,112] Shartsburg and Siu have shown that the critical number of water ligands (n_{crit}) for the occurrence of intramolecular proton transfer in analogy to reaction 15 amounts to $n_{crit} = 5$ in the case of iron(II) and that n_{crit} shows a direct correlation with the second ionization energies of the metals.[113,114] No experimental information about the thermochemistry is available for the multiply hydrated dications.[115]

Comparison with the Predictions by Kellogg and Irikura. Before combining all experimental and theoretical findings in terms of a thermochemical network, let us briefly comment on the accuracy of the predictions made by Kellogg and Irikura.[21]

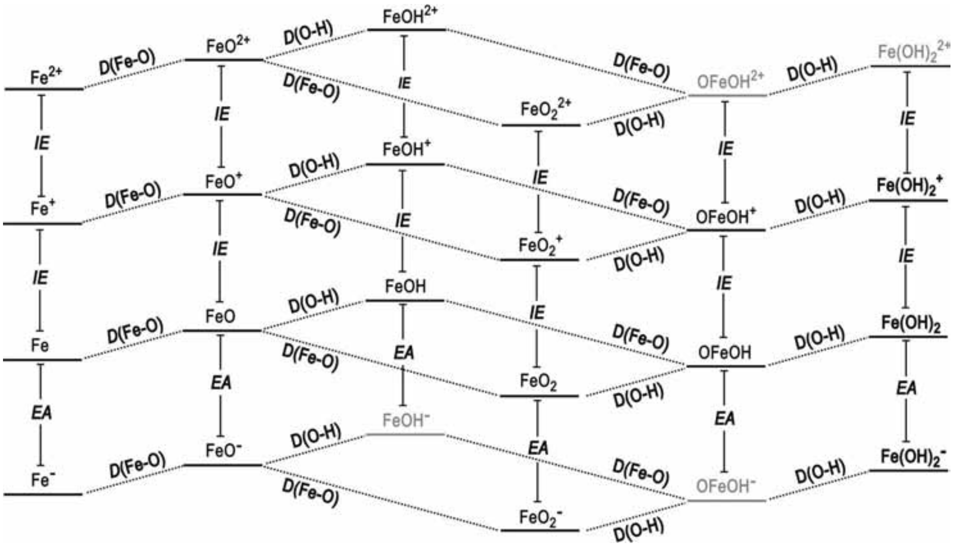

Figure 1. Schematic network of the thermochemical cycles connecting neutral and ionic mononuclear iron oxide and hydroxide in the gas phase. D(X−Y): dissociation energy of the X−Y bond. EA: electron affinity. IE: ionization energy. Species so far not observed experimentally are given in gray. Note that the distances are not proportional to the true energy values and that the cationic water complexes are left out here.

TABLE 3: Recommended Thermochemical Values (heats of formation and bond dissociation energies in kJ/mol; electron affinities and ionization energies in eV)[a,b,c] Resulting from the Comprehensive Evaluation of All Data in a Thermochemical Network[d]

	$\Delta_f H$	EA	IE	$D(\mathrm{X{-}Y})$
Fe	**413 ± 1.3**[e]	**0.151**[f]	**7.9023**[g]	
Fe^+	1176 ± 1.3		**16.1877**[g]	
FeO^-	108 ± 6			$D(\mathrm{Fe^{-}{-}O})$ = 537 ± 6
FeO	252 ± 6	**1.4944 ± 0.0006**	8.67 ± 0.09 8.56 ± 0.01[h]	$D(\mathrm{Fe{-}O})$ = **408 ± 6**
FeO^+	1088 ± 6		**17.68 ± 0.28**	$D(\mathrm{Fe^{+}{-}O})$ = **334 ± 6**
FeO^{2+}	2795 ± 28			$D(\mathrm{Fe^{2+}{-}O})$ = 190 ± 28
FeOH	129 ± 15		**7.67 ± 0.06**	$D(\mathrm{Fe{-}OH})$ = 323 ± 15
$FeOH^+$	870 ± 15		**16.34 ± 0.27**	$D(\mathrm{Fe^{+}{-}OH})$ = **345 ± 15**
$FeOH^{2+}$	2447 ± 30			$D(\mathrm{Fe^{2+}{-}OH})$ = 330 ± 30
FeO_2^-	−161 ± 13			$D(\mathrm{OFe^{-}{-}O})$ = 516 ± 14
FeO_2	**67 ± 12**	**2.358 ± 0.030**	10.3 ± 0.3	$D(\mathrm{OFe{-}O})$ = 432 ± 13
FeO_2^+	1062 ± 25			$D(\mathrm{OFe^{+}{-}O})$ = 273 ± 26 $D(\mathrm{Fe^{+}{-}O_2})$ = **113 ± 25**
OFeOH	**−84 ± 17**		**9.7 ± 0.2**	$D(\mathrm{OFe{-}OH})$ = 375 ± 19 $D(\mathrm{HOFe{-}O})$ = 460 ± 13
$OFeOH^+$	852 ± 23			$D(\mathrm{OFe^{+}{-}OH})$ = 276 ± 27 $D(\mathrm{HOFe{-}O})$ = 265 ± 24
$Fe(OH)_2^-$	*−431*			
$Fe(OH)_2$	**−322 ± 2**	*1.12*	**9.15 ± 0.10**	$D(\mathrm{HOFe{-}OH})$ = 490 ± 15
$Fe(OH)_2^+$	561 ± 10		*17.52*	$D(\mathrm{HOFe^{+}{-}OH})$ = 348 ± 18
$Fe(OH)_2^{2+}$	*2252*			$D(\mathrm{HOFe^{2+}{-}OH})$ = *234*
$Fe(H_2O)^+$	809 ± 5		**13.68 ± 0.30**	$D(\mathrm{Fe^{+}{-}OH_2})$ = **128 ± 5**
$Fe(H_2O)^{2+}$	2129 ± 29			$D(\mathrm{Fe^{2+}{-}OH_2})$ = 370 ± 29
$(H_2O)FeOH^+$	*405*		**15.12 ± 0.34**	$D(\mathrm{HOFe^{+}{-}OH_2})$ = *226*
$(H_2O)FeOH^{2+}$	*1864*			$D(\mathrm{HOFe^{2+}{-}OH_2})$ = *344* $D(\mathrm{H_2OFe^{2+}{-}OH})$ = *304*
$Fe(H_2O)_2^+$	406 ± 6		**12.06 ± 0.29**	$D(\mathrm{H_2OFe^{+}{-}OH_2})$ = **164 ± 4**
$Fe(H_2O)_2^+$	1570 ± 29			$D(\mathrm{H_2OFe^{2+}{-}OH_2})$ = 320 ± 30

[a] Complementary thermochemical data used: $\Delta_f H(\mathrm{H}) = 216.1$ kJ/mol,[22] $\Delta_f H(\mathrm{OH}) = 39.1$ kJ/mol,[22] $\Delta_f H(\mathrm{H_2O}) = -238.92$ kJ/mol,[29] $\Delta_f H(\mathrm{H_3O^+}) = 598.4$ kJ/mol,[29] IE(O) = 13.618 eV,[29] IE(OH) = 13.017 eV,[29] IE(H_2O) = 12.621 eV.[29] [b] If not mentioned otherwise, all other values are derived in the text. [c] If not mentioned otherwise, all values refer to 0 K; also note that according to the evaluation of Kellogg and Irikura,[21] thermal corrections to entropy are minor for gaseous iron oxides and hydroxides. [d] The values which were used as anchors in the network are given in bold; values which only rely on theoretical predictions are given in italics and without error bars. [e] Taken from ref 21. [f] Ref 29. [g] Spectroscopic value, see: http://physics.nist.gov/PhysRefData/ASD/index.html. [h] Direct measurement of IE(FeO);[44] see the text.

Despite some obvious shortcomings in the computational approaches, frankly stated by the authors of ref 21, the best theoretical estimates agree favorably well with the thermochemical data available so far. In particular, the predicted $\Delta_f H(\mathrm{OFeOH}) = (-85 \pm 20)$ kJ/mol nicely coincides with $\Delta_f H(\mathrm{OFeOH}) = (-82 \pm 34)$ kJ/mol derived from bracketing experiments, even though one might expect that electron correlation is substantial and quite difficult to treat comprehensively in this iron(III) oxide.[57–59,116] In fact, most of the predictions made by Kellogg and Irikura[21] are significantly better than previous theoretical values. The origin of this accuracy is primarily attributed to the well-balanced theoretical treatment chosen in ref 21, that is, a combination of B3LYP and CCSD(T) with suitable basis sets in conjunction with considering reaction enthalpies rather than bond dissociation energies. For example, the calculated heats of formation given in ref 21 for OFeOH differ from −14 kJ/mol for the reduction from iron(III) to iron(0) in reaction 16 to −112 kJ/mol for the comproportionation of iron(I) and iron(III) to iron(II) in reaction 17, while the final estimate is within the uncertainty of the present analysis.

$$\mathrm{OFeOH + H_2 + H \rightarrow Fe + 2H_2O} \qquad (16)$$

$$\mathrm{OFeOH + FeCl + 3HCl \rightarrow 2FeCl_2 + 2H_2O} \qquad (17)$$

Moreover, the anchoring of the calculated energetics to those of the corresponding iron chlorides is likely to eliminate several errors which could arise from the limited description of these iron compounds at the levels of theory used. As indicated in ref 21, the pleasing accuracy of the theoretical estimates must therefore be attributed to a cancelation of errors in averaging over the different oxidation states.

The essence of this nice agreement between experiment and theory bears two facets. On the one hand, it is remarkable that, nowadays, computational methods can be used to predict the thermochemistry of gaseous iron compounds with useful "chemical" accuracy.[108] Considering the range of different oxidation states covered by Kellogg and Irikura,[21] the agreement is somewhat fortuitous but appears as a general property of the well-balanced approach chosen. On the other hand, this result is somewhat discouraging for case studies as it implies that only a comprehensive treatment of a wide set of transition-metal compounds at various levels of theory can provide a reliable assessment. Consequently, the theoretical prediction of a single quantity in a case study, for example, a certain bond dissociation energy, may be associated with unbalanced treatments of either side and, in turn, may lead to considerable errors.

Thermochemical Network. Finally, all data compiled in this work are used to construct an internally consistent network of thermochemical data for iron oxides and hydroxides.[117] An approach to a more or less two-dimensional network is shown in Figure 1 in which Fe−O and O−H bond strengths, ionization energies, and electron affinities are linked to each other. Additional connections arise from consideration of reaction enthalpies and proton affinities.

Table 3 collects this information together with the relevant data used for anchoring. The strategy in the evaluation was the following: In addition to some basic data of atoms and simple compounds (e.g., water, OH, etc.) used as inputs, those values discussed above that appeared particularly reliable were used as absolute anchors (marked in bold in Table 3. Then, the other values were derived via Born−Haber cycles. Except those few values explicitly questioned above, all previous data about the thermochemistry of the gaseous $FeO_mH_n^{-/0/+/2+}$ compounds discussed here agree with the final numbers derived within their experimental errors.

To illustrate the power of the resulting network, let us consider PA(OFeOH) = (804 ± 17) kJ/mol, proposed earlier on the basis of reactivity studies.[9a] Together with $\Delta_fH(H^+)$ = 1528.3 kJ/mol,[29] the above values of Δ_fH(OFeOH) = (−84 ± 12) kJ/mol and $\Delta_fH(Fe(OH)_2^+)$ = (561 ± 10) kJ/mol imply a considerably larger value of PA(OFeOH) = (883 ± 16) kJ/mol, however. The origin of the discrepancy appears quite obvious because a set of very exothermic processes was considered in ref 9a, that is, the competing reactions 18 and 19 for $n = 2-4$.

$$FeO^+ + C_nH_{2n+1}OH \rightarrow C_nH_{2n+1}^+ + OFeOH \qquad (18)$$

$$FeO^+ + C_nH_{2n+1}OH \rightarrow Fe(OH)_2^+ + C_nH_{2n} \qquad (19)$$

Specifically, the prevalence of $C_4H_9^+$ over $Fe(OH)_2^+$ in the reaction of FeO^+ with *t*-butanol ($n = 4$) was interpreted as an indication that PA(OFeOH) < PA(i-C_4H_8) = 802.1 kJ/mol.[29] The present data reveal, however, that both reactions are very exothermic, that is, $\Delta_rH(18)$ = (146 ± 14) kJ/mol and $\Delta_rH(19)$ = (232 ± 12) kJ/mol for *t*-butanol ($n = 4$), respectively.[29] As reaction 18 can occur directly via formal hydroxide abstraction whereas reaction 19 requires an additional proton migration, it is a very plausible explanation that consideration of the product yields of the competing reactions 18 and 19 in terms of equilibrium thermochemistry, that is, that the product branching can serve as a measure for ΔPA, is unjustified. Instead, reaction 18 simply is preferred because it involves less rearrangement in comparison to reaction 19, and the exothermicities are large in both cases.

Conclusions

The thermochemistry of iron oxides and hydroxides is of relevance to in corrosion, oxidation catalysis, combustion, ligation phenomena, and even in the earth's atmosphere. It goes without saying that any thermochemical analysis—either in terms of theoretical or experimental aspects—would very much profit from more precise determinations of absolute binding and ionization energies, for example, by accurate dissociation threshold measurements or photoelectron spectroscopy. Upon examining the thermochemical information presented so far, however, it appears that at least for the $FeO_mH_n^{-/0/+/2+}$ compounds described here, the accomplished experimental and theoretical efforts already provide a reasonably satisfying picture of the ion energetics, which forms a solid basis for future experimental studies on the reactivity of gaseous iron oxides and hydroxides and also provides a comprehensive compilation of data for the benchmarking of theoretical methods in transition-metal chemistry.

Nevertheless, a refinement of some properties would be desirable. For example, more information on $OFeOH^{-/0/+/2+}$ would be useful, but this species is difficult to handle at the neutral as well as the cationic stage due to its inherently high reactivity. Further, at least one absolute determination of $D(XFe^+-L)$ where L and X include L = H_2O, CH_2O, C_2H_4, or perhaps C_6H_6 and X = F, OH, Cl, or, less good, Br, Br, I, and OCH_3, would be useful. Such a value would then allow one to assess the relevant thermochemistry of other ligated iron ions by using the broad repertoire of experimental tools for the determination of relative energetics ranging from equilibrium measurements to the kinetic method. Particularly useful for further benchmarking would be direct photoionization studies of small $FeO_mH_n^{-/0/+}$ species, and the preliminary data reported in ref 44 appear quite promising in this respect.

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