FURTHER INSIGHT INTO THE REACTION FeO$^+$ + H$_2$ → FE$^+$ + H$_2$O: TEMPERATURE DEPENDENT KINETICS, ISOTOPE EFFECTS, AND STATISTICAL MODELING (POSTPRINT)

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Subject Terms: multireference perturbation-theory; transition-metal cations; adiabatic channel model; gas-phase; 2-state reactivity; configuration-interaction; rate constants; bare FeO$^+$; H-H; C-H.
Further Insight into the Reaction $\text{FeO}^+ + \text{H}_2 \rightarrow \text{Fe}^+ + \text{H}_2\text{O}$: Temperature Dependent Kinetics, Isotope Effects, and Statistical Modeling

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ABSTRACT: The reactions of $\text{FeO}^+$ with $\text{H}_2$, $\text{D}_2$, and HD were studied in detail from 170 to 670 K by employing a variable temperature selected ion flow tube apparatus. High level electronic structure calculations were performed and compared to previous theoretical treatments. Statistical modeling of the temperature and isotope dependent rate constants was found to reproduce all data, suggesting the reaction could be well explained by efficient crossing from the sextet to quartet surface, with a rigid near thermoneutral barrier accounting for both the inefficiency and strong negative temperature dependence of the reactions over the measured range of thermal energies. The modeling equally well reproduced earlier guided ion beam results up to translational temperatures of about 4000 K.

INTRODUCTION

The reaction between iron oxide cation and molecular hydrogen$^{1,2}$

$$\text{FeO}^+(\Sigma^+^+) + \text{H}_2(\Sigma^+) \rightarrow \text{Fe}^+(\Sigma^+^+) + \text{H}_2\text{O}(\Sigma^+) \quad \Delta H_f^0(0K) = -151 \pm 6 \text{ kJ mol}^{-1}$$

$$\rightarrow \text{Fe}^+(\Sigma^+^+) + \text{H}_2\text{O}(\Pi^+) \quad \Delta H_f^0(0K) = -127 \pm 6 \text{ kJ mol}^{-1}$$

$$\rightarrow \text{FeOH}^+ + \text{H} \quad \Delta H_f^0(0K) = -2 \pm 16 \text{ kJ mol}^{-1}$$

is a simple example of bond activation by a transition metal oxide cation$^{3−5}$ (for energetics, see below). It is highly exothermic and spin-allowed. Nevertheless, near room temperature, it has a small rate constant ($k \sim 10^{−11} \text{ cm}^3 \text{s}^{-1}$) with a negative temperature dependence ($k \propto T$). These intriguing properties attracted great attention$^6$ and made it a prototype for the understanding of "two-state reactivity" (TSR).$^7−9$ Although the sextet potential energy surface of reaction 1.1 was shown to have too high a barrier to explain the observed reaction,$^{10}$ a spin conversion to a quartet surface with a much smaller barrier allows the system to circumvent the high sextet barrier and a second spin conversion may lead back to the sextet product shown in eq 1.1. The basic question then arises whether the small value of $k$ is primarily due to a small spin-conversion probability, or to the barrier on the quartet surface. Likewise, the origin of the negative temperature coefficient has to be understood. It might arise from the complex-forming character of the reaction, where such a phenomenon is typical,$^{11}$ from the decreasing spin-conversion probability with increasing energy,$^{12}$ or from other effects.

Since its early days,$^{13}$ experimental studies have provided a wealth of data on this reaction.$^{3,13−16}$ At the same time, considerable quantum-chemical effort has been invested to characterize the energy profile of the reaction and its intermediate structures.$^{9,17−21}$ Though this has led to convincing insight into the pathway of this reaction and of many other bond activation reactions induced by transition metal oxide cations,$^{3,8,16}$ the quantitative understanding of the rate constant is still in a rudimentary state. The most advanced approach by ref 19 applied nonadiabatic transition state theory in an effort to determine whether the barrier crossing or the spin conversion was truly rate-determining. In spite of being still in a simple form, this work was able to achieve reasonable...
agreement with the room temperature rate constant, concluding the barrier crossing to be rate-determining. The aim of the present work is to expand upon this, employing a combination of advanced statistical modeling, electronic structure calculations, as well as a significantly broader set of experimental data. We are motivated to analyze reaction 1.1 after our successful modeling of the bond activation of methane by FeO⁺:

\[
\text{FeO}^+ + \text{CH}_4 \rightarrow \text{FeOH}^+ + \text{CH}_3
\]

\[
\text{→ Fe}^+ + \text{CH}_3\text{OH}
\] (1.2)

in which we applied the statistical adiabatic channel model (SACM) to the primary complex formation and general statistical rate theory to the subsequent intrinsic dynamics. It was important to account for the multidimensional character of the potential energy surface and, in particular, the conservation of total angular momentum during the reaction (i.e., to account for rotational effects). On the other hand, the details of spin conversion did not have a large effect because such processes were not rate-determining in the sequence of intrinsic steps. These features may not be universal such that it is of interest to test whether reaction 1.1 can also be described by carefully formulated statistical theory and to determine if crossing of the quartet barrier rather than spin conversion is also rate-determining for this reaction. Although many details of the potential energy surface of the reaction are not yet known to chemical accuracy, it appears worthwhile to investigate these questions on a level similar to our work on reaction 1.2.

On the experimental side, the present work extends the database by studying reaction 1.1 with H₂, HD, and D₂ over a wide temperature range, employing a variable temperature selected ion flow tube (VT-SIFT) apparatus. The comparison with guided ion beam (GIB) data over a large range of translational energies then provides a unique opportunity for testing the kinetic modeling. On the theoretical side, an extension of calculations of molecular parameters along the reaction path became necessary. Even with advanced quantum-chemical methods barrier heights are notoriously difficult to ascertain (estimated uncertainties up to 8 kJ mol⁻¹), which is particularly frustrating in this case because that range of uncertainty changes the sign of the barrier. Therefore, we treated the dominant barrier height as a fit parameter in the statistical calculations. In addition, as many further fine details of the potential energy surface are not yet available but play some role, we had to introduce a second effective fit parameter of the potential. The barrier height is most sensitive to the current data and the second parameter to the GIB data reported previously. The fact that we can reproduce the available experimental observables, obtained over wide ranges of temperature and energy, by using only the two fit parameters of the potential appears encouraging. After the successful kinetic analysis of reactions 1.1 and 1.2, one may hope that more complex-forming bond activation processes can be analyzed in an analogous way.

## EXPERIMENTAL METHODS

All measurements were performed on the Air Force Research Laboratory’s variable temperature selected ion flow tube instrument, which has been described in detail elsewhere. Briefly, Fe⁺ ions are created using an electron impact source in the presence of a 10% mixture of Fe(CO)₅ in He, with N₂O additionally supplied in the source for the formation of FeO⁺. Ions are extracted and injected into a quadrupole mass filter where FeO⁺ is mass selected. The ions are then focused before introduction to a laminar flow tube via a Venturi inlet, where ~10⁴ to 10⁵ collisions with a He buffer gas act to thermalize the ions and carry them downstream. Previous work in our laboratory has shown that some excited electronic states of Fe⁺ are inefficiently quenched and may be present in the flow tube. FeO⁺, however, is expected to be fully quenched due to its extra degrees of freedom. In either case, linear decays in parent ion signal on a semilogarithmic scale were observed over several orders of magnitude, indicative of a single rate constant. The temperature of the flow tube is variable over a large range either by resistive heating devices (300–700 K), pulsed liquid nitrogen (120–220 K), or recirculating methanol chillers (220–300 K). Operating pressures of 0.4 Torr of He are maintained in the flow tube throughout all experiments. The neutral reagent (H₂, HD, or D₂) is added 59 cm upstream of the end of the flow tube, with typical reaction times on the order of 4 ms, dependent on helium buffer flow (varied from 10 to 13 std. L min⁻¹), and temperature.

After traveling the length of the flow tube, the core of the flow is sampled through a truncated nosecone with a 2 mm aperture. The remainder of the flow is pumped away by a roots pump through a throttled gate valve that acts to maintain the desired pressure within the flow tube. After the nose cone, the primary ions and product ions are guided by a lens stack to a quadrupole mass filter for analysis and are subsequently detected using an electron multiplier operated in counting mode. Rate constants are derived by monitoring the decay of the primary ion as a function of the neutral reagent flow. Measurements were made from approximately 170 to 670 K and temperature dependences of the rate constants determined. Errors in the rate constants are estimated to be ±25% absolute and ±15% relative to each other.

## THEORETICAL METHODS

### Calculation Techniques

Previous attempts to model the potential energy surfaces of this reaction have mostly been based on density functional theory (DFT) methods and, in particular, the B3LYP functional. This functional has been shown to provide a reasonably good picture for this reaction and other transition-metal containing systems. Our initial approach followed these early efforts, and in fact, the geometrical parameters used in the following statistical model were produced with the B3LYP functional as defined in the CBS-QB3 optimization procedure. In addition, a number of higher level methods were explored to account for electron correlation effects and multireference character. These methods include the complete active space self-consistent field (CASSCF), coupled cluster singles doubles and perturbative triples (CCSD(T)), complete active space second-order perturbation theory (CASPT²), and multireference configuration interaction (MRCI) approaches. The CASSCF, CASPT², and MRCI calculations used the MOLPRO suite of electronic structure programs and the other calculations used the Gaussian 09 package.

### Statistical Modeling

We base our kinetic modeling on the schematic diagram of the minimum energy paths (MEP) of the reaction in its sextet and quartet states as shown in Figure 1. At the same time we employ the rotational constants and vibrational frequencies of the stationary points of the MEPs from the DFT calculations given in the previous section and summarized in the Supporting Information. We model only the...
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Approximate rate constants $k_{tot}$ for product formation, leaving branching between $^4$Fe$^+$ and $^6$Fe$^+$ and between Fe$^+$ and FeOH$^+$ for later work, although no FeOH$^+$ is observed in the present thermal measurements. Following the kinetic modeling of ref 22, the thermal rate constant $k_{tot}$ then is expressed by

$$k_{tot} = \frac{1}{\hbar Q} \sum_j (2J + 1) \int W_A W_B W_{TS} W_{TS} W_A + (W_{TS} + W_A) W_B e^{-E_{tot}/kT} dE$$

where $Q$ stands for the product of the relevant electronic, translational, rotational, and vibrational partition functions of the reactants, the $W_A$ are the energy ($E$) and total angular momentum (quantum number $J$) dependent "numbers of open channels" in SACM language (or "numbers of activated complex states") at the positions $i$; $A$ denotes the entrance to the complex from the primary reactants, $B$ the exit toward the products, and $TS$ the intermediate bottleneck. $W_A$ stands for the primary formation of the [FeOH$^+$]$^n$ complex from FeO$^+$ and H$_2$ and $W_A$ for its back-dissociation, which may differ according to the experimental distributions of reactant states; however, the difference in the present case turned out not to be relevant. For completeness, we also present the rate constant $k_{tot}(E_n)$ as a function of the translational energy $E_n$ relevant for GIB experiments (with vibrational temperatures $T_0$),

$$k_{tot}(E_n) = \nu(\sigma) = \frac{\kappa}{\mu} \frac{\pi \hbar^2}{\kappa^2 Q_{vibr}} \sum_j (2J + 1) e^{-E_n/kT_0} \times \frac{W_A W_B W_{TS} W_A + (W_{TS} + W_A) W_B}{W_{TS} W_A + (W_{TS} + W_A) W_B}$$

where $\nu = \kappa/\mu$, $\mu$ is the reduced mass of the reactant pair, and $\kappa = (2\mu E_n)^{1/2}$, $Q_{vibr}$ is the product of the rovibrational partition functions of the reactants and $n$ are their rovibrational states. With a thermal distribution of translational energies, $E_n$, eq 1.4 leads to eq 1.3. When $T$ approaches zero, in the case of a negative energy TS (submerged barrier), one has $W_A \ll W_B$, and $W_A \ll W_{TS}$ such that eq 1.1 approaches

$$k_{tot} (T \rightarrow 0) \approx \frac{kT}{hQ} \sum_j (2J + 1) \int W_A e^{-E/kT} dE$$

which here is the Langevin rate constant $2\pi\sigma(\alpha/\mu)^{1/2}$; see, e.g., ref 38 ($q$ denotes the ionic charge and $\alpha$ is the polarizability of the neutral reactant).

$W_A$ and $W_B$ are numbers of rotational states of reactants and products convoluted with vibrations. For channel A (in this case a linear rotor + linear rotor), $W_{A,rot}(E_f)$ is calculated by phase space theory (PST), leading to

$$W_{A,rot}(E_f) = \sum_{j_1,j_2,j,L} P(j_1,j_2,j,L,E_f)$$

where $j_1$ and $j_2$ are the numbers of rotational angular momenta of the reactant rotors, $j$ corresponds to their combined angular momentum, $L$ to the orbital angular momentum, $J$ to the total angular momentum (we note that, because of the small reduced mass of the FeO$^+$ + H$_2$ system, $J \approx L$ would be a poor approximation; in that respect, the present reaction differs from FeO$^+$ + CH$_4$). $P$ is equal to unity provided that $j_1 + j_2 \geq j$, $j_1 \geq j_1$, $j_2 \geq j_2$, $j + L \geq J$, $L + J \geq j$, $j + j \geq L$, and $B_{j_f}(J_f + 1) + B_{j_i}(J_i + 1) + E_{cent}(L) < E$ (the $B_i$ are the rovibrational constants of the reactants in energy units). Otherwise, $P$ is equal to zero. The centrifugal energy $E_{cent}(L)$ for the assumed charge-dipole + induced dipole potential is given by

$$E_{cent}(L) = \left[ \frac{J(J + 1)\hbar^2 - 2\mu_0 \mu_D^2}{8\mu_0 \mu_D^2} \right]$$

for $L(J + 1)\hbar^2 \geq 2\mu_0 \mu_D$ and zero otherwise ($\mu_0$ denotes the dipole moment of the neutral). For channel B (in this case an atom + symmetric top), $W_{B,rot}(E_f)$ is approximated by

$$W_{B,rot}(E_f) = \sum_{j,k,l} P(j,k,L,E_f)$$

with $P$ equal to unity for $j + L \geq j$, $L \geq j$, $j \geq j$, $L \leq j$, and $B_j(j+1)$ ($A_i - B_i$)$^2 + E_{cent}(L) \leq E$ ($k$ and $j$ denote the rotational quantum numbers and $A_i$ and $B_i$ in energy units, denote the rovibrational constants of the symmetric top). We note that calculations for o- and p-H$_2$ (or D$_2$) were done separately but at 300 K differed only insignificantly. $W_{TS}(E_f)$ is the usual counted number of rovibrational states at the transition state TS (which was treated as a symmetrical top; further refinements proved to be unnecessary). It differs from zero as long as $E_{TS}(J)$ such that $E_{TS}(J) - E_{TS}(J=0) - E_{TS,rot}(J)$ such that $E_{TS}(J=0)$ is the energy of the submerged barrier of TS at 0 K and $E_{TS,rot}(J)$ is the rotational energy of TS.

We calculated $k_{tot}(T)$ alternatively with eq 1.1 and with its simplified form of

$$k_{tot} \approx \frac{kT}{hQ} \sum_j (2J + 1) \int W_{TS} e^{-E/kT} dE$$

which is obtained from eq 1.1 for $W_A \gg W_{TS}$, $W_B \gg W_{TS}$, and $W_A \approx W_{rot}$ corresponding to a bottleneck at TS. For the conditions of the present experiments, the differences were insignificant. We note, however, that eq 1.9 becomes invalid for $T \rightarrow 0$ and, thus, does not approach the Langevin rate constant. Instead, for $T \rightarrow 0$, eq 1.3 has to be used. We also note that differences between eqs 1.3 and 1.9 become significant at $T > 1000$ K where eq 1.3 has to be employed. The simplified eq 1.9 holds down to temperatures of about 50–100 K. Only at temperatures around 1 K the transition from a marked negative temperature coefficient of $k_{tot}(T)$ to the temperature independent Langevin value, $k_{Langevin} = 1.5 \times 10^{-9}$ cm$^3$/s$^{-1}$, takes place.

The range of contributing $J$ needs special considerations. The MEP of Figure 1 generally implies $J = 0$. With increasing $J$
however, the energy of compact structures like TS increases much more strongly than the energy of the separated reactants (and products). In addition, the potential well of the intermediate complex [FeOH$_2^+$] may become increasingly shallow and finally disappear. We have simulated these effects by limiting $J$ by an upper limit $J_{\text{max}}(E)$. In practice, we have chosen $J_{\text{max}}(E) = \min(J_{\text{maxA},J_{\text{maxTS}}})$. Here, $J_{\text{maxA}}$ corresponds to that $J$ where $W_A(E_J) \approx W_A$ becomes zero, and $J_{\text{maxTS}}$ is defined by

$$B_{TS/J_{\text{maxTS}}}(J_{\text{maxTS}}+1) = E - E_{0,TS}(J=0)$$

(1.10)

At small energy, $J_{\text{maxA}}$ corresponds to $E_{\text{contA}}$ and is determined by PST as expressed by $J_{\text{maxPST}}(E)$. With increasing energy, the limiting centrifugal maximum moves into the range of [FeOH$_2^+$] whose well finally disappears. Without further knowledge of the potential (i.e., the depth and shape of the intermediate well) the latter effect is difficult to quantify. In addition, $W_A(E_J)$ will be decreased by rigidity effects from the anisotropy of the potential; see, e.g., ref 39. We mimic these combined effects by employing

$$J_{\text{max}} = \min(J_{\text{maxPST}}(E),J_{\text{max}})$$

(1.11)

where $J_{\text{max}}$ is a constant fit parameter. The sensitivity of the modeled $k_{\text{tot}}$ vs $J_{\text{max}}$ is an indication for the importance of the described effects.

Two further aspects require additional discussion: the role of tunneling and the participation of electronic states. In our modeling as described below, we obtained fitted energies of the TS, which for the reactions of FeO$^+$ with H$_2$, HD, and D$_2$ within the modeling uncertainties just differ by the differences in the TS zero-point energies. As the TS barrier along the MEP is relatively broad (imaginary frequency corresponds to about 1000 cm$^{-1}$), tunneling could only play a role at relatively low temperatures. At the same time, there is, however, also reflection above the barrier, which partly compensates for tunneling. The remainder would form a minor contribution to the fitted TS energy. However, we found no evidence for such a contribution. We have done our final modeling under the assumption that the approaching reactants in the [FeOH$_2^+$] adduct have sufficient time to switch from the sextet to the quartet potential such that the overall spin-conversion probability $P$ is close to unity and that TS is quartet. When the potential well of [FeOH$_2^+$] becomes shallow with increasing $J$, such that the lifetime of this complex becomes too short to allow for efficient spin conversion, $P$ may fall below unity. We did not find evidence for such a behavior. However, such an effect may also be included in the fitted $J_{\text{max}}$ parameter. The conclusion that probabilities for spin conversion do not enter overall rates of sequences of processes is not new. In relation to reactions like 1.1 and 1.2 it was considered in refs 19 and 40–42. One may, in addition, also remember that spin-forbidden thermal dissociation reactions, proceeding by sequences of pressure-proportional collisional activation and pressure-independent spin conversion, only at high pressures are governed by spin conversion; see, e.g., refs 12, 43, and 44. We finally note that the reaction 1.1 with HD instead of H$_2$ has two transition states TS whose energy difference here was fixed at the difference of the TS zero-point energies.

## RESULTS AND DISCUSSION

### Experimental Results

The room temperature rate constants measured for the reactions of FeO$^+$ with H$_2$, D$_2$, and HD are shown in Table 1, along with the observed temperature dependences. The reactions are found to proceed very inefficiently, agreeing well with previously published room temperature rate constants obtained by ICR and SIFT apparatuses. The reaction of FeO$^+$ with D$_2$ was observed to react with a rate constant twice as high as that determined by the GIB experiment, just outside of the combined error limits of the two experiments. The authors of the GIB experiment, however, admit the lowest energy data points from which the room temperature rate constant is derived may have larger experimental error due to transmission inefficiencies at very low energies. The rate constants are found to vary strongly with temperature for each of the three reactions, scaling as $\sim T^{-1}$. As was observed in the GIB experiment, the negative energy dependence of the rate constant signifies no barrier in excess of the reactant energies. The results from the present work are shown in Figure 2.

### Computational Results

In Figure 1, the schematic potential energy surfaces (PESs) for both the sextet and quartet states of the system are shown. To assess the large number of PESs found in the literature and produced in this work, a few benchmark values are chosen: the splitting between

<table>
<thead>
<tr>
<th>reaction</th>
<th>$k$ (300 K)</th>
<th>$k$ (lit. values)</th>
<th>efficiency ($k/\kappa_{\text{lang}}$)</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO$^+$ + H$_2$ → Fe$^+$ + H$_2$O</td>
<td>10</td>
<td>10 ± 4$^b$</td>
<td>0.0666</td>
<td>$T^{-1.0^1}$</td>
</tr>
<tr>
<td>FeO$^+$ + D$_2$ → Fe$^+$ + D$_2$O</td>
<td>5.1</td>
<td>6.9 ± 2.8$^b$</td>
<td>0.007</td>
<td>$T^{-1.0^1}$</td>
</tr>
<tr>
<td>FeO$^+$ + HD → Fe$^+$ + HDO</td>
<td>8.7</td>
<td>8.1 ± 3.2$^b$</td>
<td>0.0047</td>
<td>$T^{-1.0^1}$</td>
</tr>
</tbody>
</table>

$^a$Errors in the rate constants are estimated at 10% relative and 25% absolute. $^b$ICR derived rate from reference 16. $^c$SIFT derived rate from reference 16. $^d$GIB derived rate from reference 16.

![Figure 2](https://example.com/figure2.png)

Figure 2. Rate constants (circles) and statistical modeling (full lines) for the reactions of FeO$^+$ with H$_2$, HD, and D$_2$ (black, red, and green, respectively). The modeled values shown are for $E_{TS} = -0.33$ kJ mol$^{-1}$ and $J_{\text{max}} = 40$ for H$_2$, $E_{TS} = -0.48$ and $J_{\text{max}} = 49$ for HD, and $E_{TS} = -1.81$ kJ mol$^{-1}$ and $J_{\text{max}} = 40$ for D$_2$. 

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Table 2. Various Calculated and Previously Reported Energies of Key Features of the PESs in kJ/mol

<table>
<thead>
<tr>
<th>method</th>
<th>basis</th>
<th>Fe⁺ (6−4)</th>
<th>FeO⁺ (6−4)</th>
<th>³TS1 − ³INT1</th>
<th>³TS1</th>
<th>ΔEₘₚₐₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>expt</td>
<td></td>
<td>24.1</td>
<td>47.3</td>
<td>−154</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>TZVP</td>
<td>28.0</td>
<td>61.8</td>
<td>102.3</td>
<td>14.5</td>
<td>−159.2</td>
</tr>
<tr>
<td>CBS-QB3</td>
<td>cc-PVDZ/SDD</td>
<td>88.8</td>
<td>−41.5</td>
<td>110.0</td>
<td>34.7</td>
<td>−194.9</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>cc-PVTZ/SDD at above geometry</td>
<td>88.8</td>
<td>52.1</td>
<td>104.2</td>
<td>22.2</td>
<td>−217.1</td>
</tr>
<tr>
<td>CASSCF</td>
<td>aug-cc-pVTZ/cc-pVTZ for H</td>
<td>105.2</td>
<td></td>
<td>44.4</td>
<td></td>
<td>−258.6</td>
</tr>
<tr>
<td>CASPT2</td>
<td>aug-cc-pVTZ/cc-pVTZ for H</td>
<td>95.5</td>
<td></td>
<td>56.0</td>
<td></td>
<td>−158.2</td>
</tr>
<tr>
<td>MRCI</td>
<td>AVTZ</td>
<td>99.4</td>
<td></td>
<td>12.5</td>
<td></td>
<td>−167.9</td>
</tr>
<tr>
<td>a</td>
<td>B3LYP (BP86)</td>
<td>−10.6</td>
<td>33.8</td>
<td>99.4 (117.7)</td>
<td>0.0</td>
<td>−161.1</td>
</tr>
<tr>
<td>b</td>
<td>DMC</td>
<td>30.9</td>
<td>21.2</td>
<td>107.1</td>
<td>5.8</td>
<td>−208.4</td>
</tr>
<tr>
<td>c</td>
<td>CCSD(T)/B3LYP</td>
<td>28.0</td>
<td></td>
<td>96.5</td>
<td>−5.8</td>
<td>−159.2</td>
</tr>
</tbody>
</table>

*Reference 18. ¹Reference 20. ²Reference 19. ³Reference 47. ⁴Reference 48. ⁵Derived from refs 1 and 2.

Table 3. Bond Lengths (Å) and Angles (deg) of ⁴TS1 Calculated at Various Methods

<table>
<thead>
<tr>
<th>⁴TS1</th>
<th>R₁Fe−O</th>
<th>R₂H−Fe</th>
<th>R₂H−H</th>
<th>A₁O₁Fe−H</th>
<th>A₂O₂H−H</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBS-QB3</td>
<td>1.603</td>
<td>0.916</td>
<td>1.703</td>
<td>1.665</td>
<td>52.2</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>1.656</td>
<td>0.922</td>
<td>1.760</td>
<td>1.704</td>
<td>48.6</td>
</tr>
<tr>
<td>CASSCF</td>
<td>1.759</td>
<td>0.944</td>
<td>1.925</td>
<td>1.825</td>
<td>40.9</td>
</tr>
<tr>
<td>DFT⁶</td>
<td>1.61</td>
<td>1.01</td>
<td></td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>B3LYP⁸</td>
<td>1.62</td>
<td>0.93</td>
<td></td>
<td>1.689</td>
<td></td>
</tr>
<tr>
<td>B3LYP¹</td>
<td>1.612</td>
<td>0.916</td>
<td></td>
<td>1.687</td>
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the ground state sextet and the first quartet of Fe⁺ and FeO⁺, the barrier height of ⁴TS1 relative to the sextet reactant asymptote, and the barrier height of ⁴TS1 relative to ⁴INT, which provides information about the performance of various electronic structure methods in predicting the barrier height in a single electronic state and the overall exothermicity of the reaction (ΔEₘₚₐₜ) from sextet reactants to sextet products. These values are summarized in Table 2 for B3LYP, CBS-QB3, CCSD(T), CASSCF, CASPT2, and MRCI, as well as previously reported studies using B3LYP, diffusion Monte Carlo (DMC), and CCSD(T) single-point results at B3LYP geometries. CASSCF was performed with 13 active electrons in the sextet and quartet states. As far as overall exothermicity of the reaction (ΔErxn) from sextet reactants to sextet products. These values and is comparable to CCSD(T)/cc-PVTZ and DMC. The lowest barriers are found in MRCI and B3LYP values at +12.5 and +14.5 kJ/mol, respectively. The highest barriers are found in CASPT2 and MRCI are due to a choice of an active space too small to accurately capture the correlation and the multireference character of the wave functions. Unfortunately, a larger active space is prohibitively costly, but we believe that this is the most appropriate methodology for an accurate description of the reaction path.

Because a possible source of error in the height of ⁴TS1 is due to errors in the calculated splitting of the two spin states of FeO⁺, the absolute barrier height along the sextet potential energy surface can provide insight into the accuracy of the method independent of the splitting. In general, most methods find the height of ⁴TS1 to be around 96.5 kJ/mol above ⁴INT, and the largest values correspond to methods that overestimate the ⁴TS1 barrier. The lowest value, of 96.5 kJ/mol at CCSD(T)/B3LYP, also corresponds to the lowest barrier found for ⁴TS1. This methodology was also very accurate for the sextet-quartet splitting of Fe⁺ and FeO⁺ species.

In Table 3 we have compared the geometry of ⁴TS1 obtained using CBS-QB3, CCSD(T), and CASSCF. In general, the transition-state structure becomes progressively looser in that all bond lengths increase in this order. The CBS-QB3 and CCSD(T) results are more similar to each other than CASSCF, in which bond lengths can be as much as 0.2 Å longer. The CBS-QB3 values are closest to previously published geometries, albeit this is not to be unexpected considering these previous studies are also DFT based.
Despite a known problem in calculating the splitting of nearly degenerate spin states in Fe(II) compounds with sulfur ligands,\textsuperscript{30} B3LYP is known to perform quite well in determining bond dissociation energies of MO complexes with respect to other DFT functionals.\textsuperscript{31} It has also been found to provide reasonable geometries\textsuperscript{32} and is commonly used to provide starting geometries for more accurate single-point evaluations, as is the case in ref 19. In this spirit we have chosen to utilize the geometries, rotational constants and vibrational frequencies as found in the CBS-QB3 method, which is B3LYP with the reasonably large 6-311G basis with Fe, O, and H receiving 2d, d, and p polarization functions, respectively. The molecular parameters obtained and used in the statistical modeling are given in the Supporting Information.

**Statistical Modeling.** The results of our modeling of the present thermal rate constants $k_{\text{tot}}(T)$ over the range 173–673 K, as well as the experimental points from the present work, are illustrated in Figure 2. The curve for H$_2$ is fitted with $E_{\text{B,TS}}(J=0) = -0.33$ kJ mol$^{-1}$ and $J_{\text{max}} = 40$, whereas TS energies of $-0.48$ and $-2.03$ kJ mol$^{-1}$ and $J_{\text{max}} = 49$ were obtained for HD, and $-1.81$ kJ mol$^{-1}$ and $J_{\text{max}} = 40$ for D$_2$. Plots of $k_{\text{tot}}(T_{\text{trans}})$ for the FeO$^+$ reaction with D$_2$ are shown in Figure 3, including GIB data at translational temperature up to 4000 K.\textsuperscript{16} The present data (as well as the SIFT and ICR data from ref 16) differ by more than the combined error limits from the GIB data in the overlapping range. At energies above 300 K, the SIFT experiment has more rotational and vibrational energy available than the GIB experiment where reactant internal energies remain at 300 K, though this is unlikely to be the entire cause of the discrepancy, which may be due to a systematic error in one or both of the experiments. To test the robustness of the modeling, we have tried scaling both sets of data. Scaling the GIB data by a factor of 1.5, we see excellent agreement with predictions from the above model. Conversely, if we instead scale the present data down by a factor of 1.5, the model would fit the entire energy range well with a TS energy of $-0.71$ kJ/mol and a $J_{\text{max}}$ of 34. Finally, if we instead fit to the entire data set ignoring the GIB data below 1000 K we find a reasonable fit to the data with a TS energy of $-2.25$ kJ/mol and a $J_{\text{max}}$ of 33. These fits are shown in Figure 3. As any reasoning as to the cause of the discrepancy between the GIB data and that of the SIFT and ICR measurements is purely speculative, we note that the fitted values of both the TS energy and the value of $J_{\text{max}}$ are essentially independent of this discrepancy. Furthermore, we note that the TS energy is primarily a function of the current thermal data, whereas the $J_{\text{max}}$ parameter is primarily determined by the higher energy range data (GIB), highlighting the complementary nature of the two experiments; the fitted curves of Figure 2 depend weakly on $J_{\text{max}}$ up to about 700 K. Figure 4 illustrates the sensitivity of the fit on the two parameters. Like for the FeO$^+$ + CH$_4$ reaction in ref 22, the restriction of the range of contributing $J$ increasingly matters only with increasing $T_{\text{trans}}$ such that the GIB data could not be reproduced with $J_{\text{max}} = \infty$ at all. Increasing $J_{\text{max}}$ for D$_2$ beyond the fitted value of 40, analogous to the GIB data for FeO$^+$ + CH$_4$ from ref 22, would result in a more pronounced upturn of the modeled $k_{\text{tot}}(T_{\text{trans}})$ with increasing temperature. The increasing sensitivity of $k_{\text{tot}}(T_{\text{trans}})$ on $J_{\text{max}}$ at large $T_{\text{trans}}$ appears understandable because rotations then increasingly modify the effective potential in the [FeOH$_2$]$^+$ adduct range until the well of this complex ceases to exist.

The fitted TS energies from Figures 2–4 are all near zero, but slightly negative. Within the estimated uncertainty of 8 kJ mol$^{-1}$ of present quantum chemical calculations, they agree with the quantum chemical values given above and particularly well with the result from ref 19. As $k_{\text{tot}}(T)$ sensitively depends on the TS energies and the dependence on $J_{\text{max}}$ for D$_2$ beyond the fitted value of 40, analogous to the GIB data for FeO$^+$ + CH$_4$ from ref 22, would result in a more pronounced upturn of the modeled $k_{\text{tot}}(T_{\text{trans}})$ with increasing temperature. The increasing sensitivity of $k_{\text{tot}}(T_{\text{trans}})$ on $J_{\text{max}}$ at large $T_{\text{trans}}$ appears understandable because rotations then increasingly modify the effective potential in the [FeOH$_2$]$^+$ adduct range until the well of this complex ceases to exist.

![Figure 3](image1.png)  
**Figure 3.** Experimental and modeled rate constants as a function of translational temperature (for both SIFT and GIB data, from 163 to 4000 K) for the reaction of FeO$^+$ + D$_2$.

![Figure 4](image2.png)  
**Figure 4.** Model dependence on $J_{\text{max}}$ for the reactions of FeO$^+$ with H$_2$, HD, and D$_2$ (experimental points and full lines for $J_{\text{max}} = 40$, 49, 40 as in Figure 2; dashed lines for $J_{\text{max}} = \infty$ and $E_{\text{TS}} = -0.07$ kJ mol$^{-1}$ for H$_2$, $-0.36$ and $-1.91$ kJ mol$^{-1}$ for HD, and $-1.38$ kJ mol$^{-1}$ for D$_2$).
calculations would be −0.74 and −2.30 for FeO+ + HD and −2.24 for FeO+ + D2. As the zero-point energy-corrected TS energies from the experiments and the quantum chemical calculations (anharmonicity and other uncertainties neglected) differ by no more than 0.43 kJ mol−1, we find our modeling as well reproduces the expected isotope effects as one would hope. We also observe that the temperature dependence of the experimental isotope effects is very well reproduced by the present modeling, Figures 2 and 4.

We return our attention to the primary question still being debated about this reaction: is the reactivity governed by the transition state crossing or by the spin conversion? It has long been assumed that the low efficiency and negative temperature dependence of this reaction suggested the spin conversion was rate-determining. Reference 19 recently concluded the TS state to be the bottleneck, employing a semiclassical calculation of the spin conversion. As discussed above, the models shown here use the assumption that the TS crossing is rate limiting, and the spin conversion takes place faster than the TS crossing. Though the current data do not allow for enough constraint to vary the effective probability, P, of spin conversion as an additional fitting parameter, a limiting case of a spin-conversion-limited reaction is quite illustrative. In this case P would equal 0.1, as the reaction approaches 10% of the collision rate at low temperatures. The best fit of the data employing a rate limiting 10% curve crossing probability is shown in Figure 5. The TS barrier then would have to be much lower (−14.8 kJ mol−1) to account for the magnitude of the rate constant, but this would also result in a steeper temperature dependence, which less well reflects the data. (For even lower P, the TS barrier would have to be even lower.) From this example, we would conclude (in agreement with ref 19) that the quartet TS crossing is indeed rate limiting for this reaction. However, we cannot exclude a minor contribution from a mechanism with rate-determining spin conversion.

In summary, the present kinetic modeling based on detailed statistical rate theory is able to reproduce the available experiments surprisingly well. This allows one also to extrapolate the existing data over very wide ranges of temperatures. We find no evidence for nonstatistical intrinsic dynamics. We also do not see conditions where spin-conversion probabilities enter the rate constant (although the spin conversion may play a role in high J reaction events and be hidden in the fitted Jmax values, see above). One has to emphasize the crucial importance of rotational effects in the kinetic modeling. In this respect the present work goes far beyond the statistical modeling given in ref 19 where rotational effects were not considered. Meanwhile, it was estimated in ref 19 that spin conversion within the [FeOHH]+ complex is about 2 orders of magnitude faster than the TS barrier crossing. This conclusion is in agreement with the present results. Likewise, the order of the isotope effect at 300 K calculated in ref 19 corresponds to that modeled here. However, this cannot be represented by conventional transition state theory, dealing with a single transition state only, which was not designed for as complicated reactions as the present system. One may finally ask what in the present case determines the temperature coefficient of kint(T), which experimentally below 400 K was found to be about T−1. Although the Langevin equation based on eq 1.3 leads to a temperature independent rate constant, the situation looks different for the now relevant eq 1.7. Neglecting vibrational partition functions, the factor kT/hQ is proportional to T−3/2. Again neglecting vibration of TS (and neglecting the small energy difference between the entrance channel A and TS), the sum Σ(2J + 1)WTS(EJ) is proportional to T−3/2, which leads to kint ∝ T−1. Other factors apparently only contribute to a smaller extent. Unlike other complex-forming bimolecular reactions based on eq 1.1, where the ratio WTS/(WA + Wb) combined with “rotational channel switching” dominates the temperature dependence, here the energy dependence of WTS suffices to rationalize the temperature coefficient of kint.

CONCLUSIONS

We have measured the rate constants for reactions of FeO+ with H2, HD, and D2 from 173 to 673 K for the first time. Statistical modeling of these data has allowed for several key insights into this fundamental reaction. Contrary to many earlier interpretations of this reaction, the crossing from the sextet potential surface to the quartet surface has enough time to occur in the FeOHH+ adduct, such that the quartet transition state is rate limiting. Nevertheless, it should be recognized that our work supports the general concept of the TSR mechanism that the reaction occurs because the transition to the quartet state allows the system to circumvent the high barrier on the initial sextet potential. We also determine quartet TS energies of −0.33 kJ mol−1 for the reaction with H2, −0.48 and −2.03 kJ mol−1 for the two HD transition states, and −1.81 kJ mol−1 for the D2 reaction. These independently modeled values are consistent with expectations based on zero-point energy differences, lending added credibility to the model. Attempts to model the reaction as limited by the spin conversion resulted in a much lower transition state barrier, but a temperature dependence that poorly represented the data. The calculations illustrate the difficulties in modeling these reactions. The combination of multiple near-degenerate electronic states, the multireference nature of the system (particularly at the transition states where bond breaking and formation are occurring) and electron correlation all present in this system prove to be challenging for current quantum chemical models. By building on the strength of DFT to provide reasonable geometries for a statistical model, we are able to probe these elusive energetic details. The integration of statistical modeling, quantum chemical calculations, and kinetic measurements over
a wide energy range, with significant emphasis on the near thermal range, has provided unique insight into the reaction mechanism for this important reaction, as well as provided theoretical benchmarks for the rate limiting transition state, otherwise inaccessible experimentally.

**ASSOCIATED CONTENT**

2 Supporting Information

Parameters employed in the modeling including stationary point vibrational and rotational constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


NOTE ADDED IN PROOF

Most recently another high level quantum chemical calculation has been reported leading to an energy of $-1.6 \text{ kJ mol}^{-1}$ for T$^*$TS1. This value is in very good agreement with the value derived from statistical modeling of the present experiments of $-0.33 \text{ kJ mol}^{-1}$.
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