Understanding the Reactivity Bottleneck in the Spin-forbidden Reaction $\text{FeO}^+ + \text{H}_2 \rightarrow \text{Fe}^+ + \text{H}_2\text{O}$.

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This paper is dedicated to Detlef Schröder, without whose many inputs the work described here could not have been performed.

Abstract. New coupled cluster theory calculations, including extrapolation to the complete basis set limit, are reported for key species on the $[\text{Fe},\text{O},\text{H}_2]^+$ potential energy surfaces. Test calculations including Bruecker orbital methods suggest that the single-reference coupled-cluster approach is reliable for this system. The minimum energy crossing point (MECP) between the sextet and quartet states has been found to lie close in energy and structure to the quartet reactant complex $^4\text{FeO}^+\bullet\text{H}_2$. Non-adiabatic transition state theory is used to calculate the rate constant for hydrogen oxidation, and is found to agree reasonably well with experiment, considering the remaining uncertainties in the ab initio energies and the kinetic modelling. The isotope effects are reproduced fairly well also. The transition state theory calculations suggest that the bottleneck to reaction is an adiabatic quartet transition state for insertion of FeO^+ into the H–H bond. Spin state change at the MECP is calculated to be considerably faster, even allowing for errors in the relative energies.

1. Introduction

The iron oxide cation FeO^+ is a remarkable oxidant, capable of transferring oxygen to very unreactive species such as dihydrogen or methane in the gas phase. This ion is also a very simple model for the oxidation chemistry of related iron-oxo species found in bioinorganic chemistry, and increasingly in biomimetic oxidation systems. Despite the very strong thermodynamic oxidizing character of the iron oxide cation, its reactions with hydrogen and methane are relatively slow, and this is due to the complex nature of the potential energy surfaces involved in oxidation. A number of detailed experimental studies have been performed to characterize the thermal rate constant for reaction with hydrogen, and the corresponding reaction cross section as a function of energy. The reaction proceeds even for very low relative energies of reactants, and in fact the cross-section has a negative dependence on relative energy at lower energies, suggesting that the bottle-neck to reaction lies slightly lower in energy than the separated reactants. As well as performing

some of the initial work on this reaction,¹ Detlef Schröder led an important comparative study² that explored differences between results obtained using different experimental methods. This led to the availability of a benchmark study that continues to serve as an indispensable reference in the field.

As well as the experimental papers mentioned above, other groups have carried out detailed studies of this reaction,^{3,4,5} and there have also been a number of computational investigations.^{6,7,8} A variety of electronic structure methods have been used to characterize the relative energy of the reactants and products, and of the various intermediates and transition states involved in reaction. One significant complication is that the reaction appears to involve more than one electronic state – it is the prototype of “Two-State Reactivity”.⁹ The iron oxide cation, and the iron cation product, both have sextet ground states. As the co-reactant and co-product, H₂ and H₂O, both are closed-shell species, the sextet potential energy surface represents the ground states in both the entrance and exit channels. However, from the earliest computational studies of the reaction,¹⁰ it has been evident that the energies of some of the key transition states and intermediates en route to products are much lower on the quartet potential energy surface than on the sextet surface. Hence one or more spin-state change must occur as part of the reaction mechanism, as reaction on the sextet surface alone would be exceedingly slow. In one sense, then, spin-state change *accelerates* the reaction. There is an interesting associated question, though, which is to ask whether the steps in which spin-state change occur represent the bottleneck to reaction, and thereby have a direct effect on the reaction kinetics.

In this paper, new *ab initio* calculations as well as transition state theory calculations are used to explore the identity of the rate-limiting step in the oxidation reaction. In order to describe the spin-forbidden step leading from sextet to quartet, the minimum energy crossing point¹¹ (MECP) between the relevant potential energy surfaces was optimized and a non-adiabatic form of transition state theory^{12,13} used to compute the rate of surface crossing.

2. Computational Details.

The structure of all species was optimized using the B3LYP hybrid density functional as implemented in the Gaussian 09 program package,¹⁴ together with the large flexible 6-311++G(3df,p) basis set on all atoms. Frequency calculations were performed at stationary points at the same level of theory. The MECP was optimized at the same level of theory using the shell scripts developed by one of us^{15,16} in conjunction with Gaussian 09. Briefly, the energy and gradient on the two potential energy surfaces are computed in Gaussian, then combined to derive an effective gradient that vanishes at the MECP. Approximate vibrational frequencies within the seam of crossing have been computed by diagonalizing a

mass-weighted, projected, weighted average¹⁶ of the B3LYP Hessian matrices on both surfaces at the MECP.

Single-point energy calculations using the CCSD(T) form of coupled-cluster theory were then performed to refine the energetics, using the MOLPRO program package.¹⁷ The coupled-cluster calculations were performed using restricted open-shell orbitals optimised using Kohn-Sham theory and the B3LYP functional, as explained in the text. A restricted ansatz to preserve approximate spin-adaptation was also used in the coupled-cluster expansion.¹⁸ Most of the calculations used an approximate relativistic approach whereby the one-electron integrals were computed using the Douglas-Kroll approximation to second order.¹⁹ All valence electrons, as well as the 3s and 3p semi-core electrons on iron, were included in the correlation treatment. For oxygen and hydrogen, the augmented correlation-consistent basis sets aug-cc-pVTZ and aug-cc-pVQZ were used. For iron, augmented correlation-consistent basis sets with additional functions to describe semi-core correlation effects, aug-cc-pwCVTZ and aug-cc-pwCVQZ were used.²⁰ Except for a few non-relativistic test calculations, the re-contracted forms of these basis sets adopted for use with Douglas-Kroll integrals were used throughout. Extrapolation to the complete basis set limit was performed using the $1/X^3$ dependence of the correlation energy on the order of the basis set (cc-pVTZ, $X = 3$; cc-pVQZ, $X = 4$). For these purposes, the correlation energy was defined as the difference between the CCSD(T) energy and the energy of the reference determinant formed from the Kohn-Sham orbitals

Some additional non-relativistic calculations were performed using the Turbomole program package^{21,22} using unrestricted reference wavefunctions and unrestricted coupled-cluster expansions. The basis set used was the same aug-cc-pVTZ combination as used in MOLPRO for non-relativistic calculations.

Non-adiabatic transition state theory calculations have been performed using a purpose-built in-house code.¹⁶ All input, apart from the spin-orbit coupling matrix elements taken from the literature as described below, was derived from the present *ab initio* and B3LYP calculations. Isotope-specific rotational constants and frequencies were used where needed.

3. Results

3.1. *Ab initio* Potential Energy Surfaces

There have already been a number of *ab initio* studies of the $\text{FeO}^+ + \text{H}_2 \rightarrow \text{Fe}^+ + \text{H}_2\text{O}$ reaction,^{6,7,10} so the features of the potential energy surfaces are quite well known. The best calculations agree well with experiment concerning the structures and energies. Because of this extensive prior work, only a few notable features of the electronic structure calculations will be mentioned here. The computed potential energy surface obtained here using CCSD(T) energies and B3LYP structures is shown in Fig. 1, with the corresponding

relative energies in Table 1. In the rest of the paper, we will mainly discuss the most reliable energy values, those obtained at the CCSD(T) level with basis set extrapolation – shown in the rightmost column of Table 1.

Figure 1. Schematic potential energy surfaces (in kcal mol⁻¹, with structures of key species) for the FeO⁺ + H₂ reaction, based on CCSD(T)/aug-cc-pVXZ (X = T, Q) calculations with extrapolation to the complete basis set limit.

Table 1. Calculated relative energies (kcal mol⁻¹) for species on the quartet and sextet [Fe,O,H₂]⁺ potential energy surface, at the B3LYP and CCSD(T)/aug-cc-pVXZ (X = T, Q) levels of theory. Results based on extrapolation to the complete basis set limit, noted [T,Q], are shown also. Single point energies at the B3LYP/6-311++G(3df,p) structures, including a correction for zero-point energy. Term symbols are given for iron-containing species; all other species are in their ground state.

Species	E _{rel} (B3LYP) ^(a)	E _{rel} (cc-pVTZ)	E _{rel} (cc-pVQZ)	E _{rel} ([T,Q])
FeO ⁺ (⁶ Σ ⁺) + H ₂	0.0	0.0	0.0	0.0
FeO ⁺ (⁴ Δ) + H ₂	12.4	14.4	13.3	12.6
FeO ⁺ •H ₂ (⁶ A ₁)	-12.6	-12.8	-12.9	-13.0
FeO ⁺ •H ₂ (⁴ A'')	-5.6	-5.9	-7.1	-7.9
MECP (⁴ A''/ ⁶ A')	-5.4 ^(b)	-6.0 ^(b)	-6.8 ^(b)	-7.4 ^(b)
TS1 (⁶ A')	9.7	10.7	10.4	10.1
TS1 (⁴ A'')	0.8	0.6	-0.5	-1.4

HFeOH ⁺ (⁶ A')	-18.9	-33.0	-33.4	-33.5
HFeOH ⁺ (⁴ A'')	-38.3	-33.4	-34.8	-35.7
TS2 (⁶ A')	-11.4	-8.1	-9.0	-9.5
TS2 (⁴ A)	-31.6	-24.6	-26.1	-27.2
Fe ⁺ •OH ₂ (⁶ A ₂)	-65.1	-69.9	-70.7	-71.1 ^(c)
Fe ⁺ •OH ₂ (⁴ A ₂)	-74.2	-65.7	-67.8	-69.1 ^(c)
Fe ⁺ (⁶ D) + H ₂ O	-32.0	-37.5	-37.9	-38.0
Fe ⁺ (⁶ D) + O + H ₂	81.1	75.1	77.0	78.4
Fe ⁺ (⁶ D) + OH + H	82.2	78.0	79.0	79.7
FeOH ⁺ (⁵ A') + H	-7.1	-2.9	-3.9	-4.6 ^(d)
Fe ⁺ (⁴ F) + H ₂ O	-36.9	-27.7	-29.9	-31.3

(a) The B3LYP energies were computed using the 6-311++G(3df,p) basis set. (b) See text for a discussion of the MECP energies. (c) ⁶A₁ and ⁴A₁ states lie a small fraction of a kcal mol⁻¹ higher in energy than the ⁶A₂ and ⁴A₂ states. (d) The ⁵A'' state lies very close in energy, just 0.03 kcal mol⁻¹ higher at the [T,Q] level.

It is to be noted first that the B3LYP calculations agree very well with CCSD(T) for most of the key species, especially the reactant complexes, and the first insertion TS – which is important in retrospect, since many of the discussions of reactivity patterns for this and related systems were based on such B3LYP calculations. Of course, such good performance will not necessarily be mirrored across all iron oxidation systems, e.g. the neglect of dispersion effects may impact quite severely on calculated energies. It should also be noted that the CCSD(T) energies with the smallest basis set, aug-cc-pVTZ, which is still quite a large basis set, are somewhat different from those obtained after basis set extrapolation. Indeed, the results of our CCSD(T) calculations also differ somewhat from some CCSD(T) results reported previously,⁷ using basis sets similar in size to aug-cc-pVTZ.

We note also that our calculations agree well with experiment for key relative energies in the [Fe,O,H₂]⁺ system, as shown in Table 2. In this Table, we also include the energy difference between the ground ⁶Σ⁺ sextet and excited ⁴Δ state of FeO⁺, which is not known accurately from experiment, but has been computed using an accurate MRCI method.²³ As can be seen in the Table, our results are within 3 kcal mol⁻¹ or better from experiment in all cases. The biggest discrepancy concerns the bond energy of FeO⁺ itself, which is somewhat underestimated by the present approach.

Table 2. Experimental and computed energies at 0 K (kcal mol⁻¹) for the [Fe,O,H₂]⁺ system. Computed values include a correction for zero-point energy but not – unless mentioned otherwise – for spin-orbit coupling.

Value	E _{exp}	E _{calc} (CCSD(T)/cc-pV[T,Q]Z)
FeO ⁺ (⁶ Σ ⁺) → Fe ⁺ (⁶ D) + O (³ P)	81.2 ± 0.5 ²⁴	78.4
FeO ⁺ (⁶ Σ ⁺) → ⁴ FeO ⁺ (⁴ Δ)	/	12.6 (14.4 – MRCI ²³)
FeOH ⁺ (⁵ A') → Fe ⁺ (⁶ D) + OH	82.3 ± 5.1 ²⁵	84.3
Fe ⁺ •OH ₂ (⁶ A ₂) → Fe ⁺ (⁶ D) + H ₂ O	30.6 ± 1.2 ²⁶	33.1
Fe ⁺ (⁶ D) → Fe ⁺ (⁴ F)	5.35 ²⁷	6.7 (6.3 ^a)
O (³ P) + H ₂ → H ₂ O	-116.1 ± 0.007 ²⁸	-116.4

(a) Corrected to take spin-orbit effects into account.

The ‘new’ species discussed here is the minimum energy crossing point between the quartet and sextet potential energy surfaces. A low-lying MECP is found with an energy similar to that of the quartet reactant complex ⁴FeO⁺•H₂. The structure is also similar to that of the quartet complex, involving an H₂ molecule interacting with the iron atom of the iron oxide cation, with an O–Fe–H₂ angle between 90 and 180 degrees. As shown in Fig. 1, the minimum energy structure of the ⁴FeO⁺•H₂ complex involves the H₂ molecule lying at right angles to the plane defined by the FeO⁺ moiety and the H₂ centroid. The MECP also adopts this type of structure, albeit with slightly larger O–Fe–H angles. The Fe–O distance is 1.684 Å (vs. 1.644 Å and 1.556 Å for the sextet and quartet complexes, respectively), and the Fe–H distances are both 1.848 Å (vs. 1.991 Å in the sextet complex, and 1.767 Å in the quartet complex). Calculation of the frequencies within the seam of crossing of the MECP¹⁶ returns only real frequencies, indicating that at the B3LYP level of theory, this structure is a minimum within the seam of crossing.

Prior to locating this MECP, a different “MECP” structure was found, with a broadly similar structure, except that the hydrogen molecule is rotated and lies within the overall molecular plane. The Fe–O bond length is 1.584 Å and the Fe–H distances are equal to 1.882 Å and 1.905 Å. Frequency calculations at this “MECP” show one imaginary frequency, corresponding to rotation of the H₂ molecule around the axis running from the iron atom to the H₂ centroid. Clearly, this structure is not a minimum in the seam of crossing at the B3LYP level, and indeed it lies 1.6 kcal mol⁻¹ above the true MECP at the B3LYP level. The reason for reporting this second structure is that the single point CCSD(T) calculations at this structure return a slightly *lower* energy than those at the true B3LYP MECP (–7.4 kcal mol⁻¹, vs. –6.0). This indicates that the B3LYP and CCSD(T) potential energy surfaces are not exactly parallel to one another. In the subsequent analysis, we have used the vibrational frequencies and rotational constants of the B3LYP MECP, but the CCSD(T) energies of the other structure, since this point clearly represents a better approximation to the MECP at the CCSD(T) level of theory. We note that for both MECP structures, the direction orthogonal to the seam of crossing of the potential energy surfaces is largely due to the stretching of the Fe–O bond, which has different equilibrium values for the sextet and

quartet complexes. Overall, the MECP clearly lies in the region of the quartet complex, and is close both in energy and structure to this species.

The CCSD(T) energies for the MECP (and the other 'MECP' structure) are not exactly degenerate for the two states, with a difference of 0.5 and 3 kcal mol⁻¹ respectively. This is because these calculations were computed as 'single points' at the B3LYP structures, and there is no reason why the seam of crossing between sextet and quartet states should lie exactly in the same place at the two levels of theory. The result in the Table is the average of the quartet and sextet energies. This, and the issues with orientation of the H₂ moiety just discussed, leave some uncertainty about the exact energy of the MECP. However, it clearly lies very close in energy to the quartet reactant complex ⁴FeO⁺•H₂, which itself clearly lies significantly below the energy of reactants. This conclusion is unlikely to be modified upon changing the level of theory.

Notwithstanding the general agreement between the reported B3LYP and CCSD(T) relative energies in Table 1, it is not obvious that the CCSD(T) energies are themselves accurate. For the iron containing compounds, CCSD wave functions, with either restricted or unrestricted Hartree-Fock reference determinants, contain very large singles amplitudes: for example, the UHF-CCSD D1-diagnostic²⁹ for FeO⁺ is rather high, at 0.352, and the ROHF-RCCSD T1 diagnostic³⁰ is also high, at 0.135. Such very high degrees of orbital relaxation often indicate that multi-reference or higher-order coupled-cluster methods are necessary to reliably model the electronic structure. The observation of large single excitation amplitudes is the main reason why the results reported above use a Kohn-Sham reference determinant: we have found previously³¹ that the use of such a reference leads to smaller excitation amplitudes in coupled-cluster calculations. Indeed, the singles amplitudes in the corresponding CCSD wave functions using a Kohn-Sham reference determinant, are found to be small: for FeO⁺ the D1-diagnostic is only 0.015 and the T1-diagnostic is only 0.01. Also, the difference between the CCSD(T) and CCSDT total energy of FeO⁺ when using a Kohn-Sham reference determinant is only 0.63 kcal mol⁻¹.

Based on these observations, for these iron-containing compounds the strong orbital relaxation appears to be a consequence of dynamic correlation, not multi-reference character and, moreover, Kohn-Sham orbitals capture a large part of this effect, differing significantly from the Hartree-Fock orbitals.

Further evidence that using Kohn-Sham determinants is both pragmatic and meaningful is presented in Table 3, where we compare results of CCSD(T) calculations using Hartree-Fock and B3LYP reference determinants with the corresponding calculations using Brueckner orbitals, BD(T), which are those that optimise the coupled-cluster doubles wave function.³² These calculations have only been carried out for a few key species. The Brueckner results were obtained using open-shell Brueckner methods available in the Turbomole program package.³³ The results in Table 3 are not directly expected to be exactly comparable to those in Table 1, because they are non-relativistic, and also because unrestricted reference

determinants and unrestricted coupled-cluster wave functions were employed, versus restricted references and restricted coupled-cluster methods in Molpro. For comparison, though, the non-relativistic energies were recomputed using the same basis set and method combinations as in Table 1 and are provided in the last line of Table 3.

Table 3. Calculated non-relativistic relative energies (kcal mol⁻¹) for selected [Fe,O,H₂]⁺ species, using the aug-cc-pVTZ basis set combination unless mentioned otherwise, and including a correction for zero-point energy.

Method	FeO ⁺ + H ₂	Fe ⁺ (⁶ D) + O + H ₂	TS1 (⁴ A'')	Fe ⁺ (⁶ D) + H ₂ O
CCSD(T)	0.0	76.6	3.4	-36.0
BD(T)	0.0	76.0	1.4	-36.6
KS-CCSD(T) ^(a)	0.0	75.9	0.6	-36.7
CCSD(T)-F12	0.0	79.6	2.1	-35.7
BD(T)-F12	0.0	78.6	0.0	-35.7
KS-CCSD(T)-F12 ^(a)	0.0	78.4	-0.7	-36.9
KS-RCCSD(T) ^(b)	0.0	78.9	-1.7	-37.7

(a) These calculations were performed using a Kohn-Sham based reference function.

(b) These calculations were obtained using the MOLPRO program package, as for the [T,Q] values in Table 1 except that the relativistic correction was not included.

Considering the first three rows of Table 3 first, it can be seen that the three choices of reference orbital lead to broadly similar energies. However, the Kohn-Sham based energies are closer to the Brueckner values in all cases, which gives credence to the assertion that the Kohn-Sham orbitals give a better reference determinant than Hartree-Fock orbitals here. The relative energy of the important TS1 species is somewhat higher when using Hartree-Fock orbitals. As will be seen below, the quite high energies obtained for the energy of TS1 with standard CCSD(T) treatments would not be consistent with experiment concerning the observed reactivity.

In the next three rows of Table 3, energies computed using the explicitly-correlated variants³⁴ of the coupled-cluster approaches are shown. In all cases the F12 energy contribution was computed as a post-hoc perturbative correction using the CCSD(2)_{F12} method.^{35,36} The F12 energies provide an independent estimate of the energies at the complete basis set limit. As for the values in the first three rows of the Table, it can be seen that the three reference functions give similar values. Comparing the BD(T)-F12 values in row 5 with the BD(T) values in row 2 gives an estimate of the basis set incompleteness effect when using the aug-cc-pVTZ basis set. This provides a test of the extrapolation procedure used to derive complete basis set limit results in Table 1. Indeed, it can be seen that the BD(T)-F12 and KS-CCSD(T)-F12 energies agree fairly well with the KS-RCCSD(T) values extrapolated to the basis limit. The small differences are presumably due to the use of an unrestricted vs. a restricted ansatz.

One notable difference between the BD(T)-F12 and KS-RCCSD(T) values concerns the height of TS1, which is less negative with the presumably more accurate BD(T)-F12 method, suggesting that the energy of this TS may be slightly underestimated in Table 1. All in all, though, the fact that the computed values with basis set extrapolation or explicit correlation are quite close to one another, and mostly insensitive to details of the correlation treatment suggests that the relative energies in Table 1 are most likely highly accurate, perhaps with errors of the order of 2 kcal mol⁻¹ or less. This is also apparent from the comparison to experimental data in Table 2. We note that our calculations do not account for the effect of spin-orbit coupling on the energies. For the sextet reactant species, such effects will be very small given the Σ state of the FeO⁺ ground state cation. For the quartet TS1, it is possible that spin-orbit coupling would change relative energies by 1 kcal mol⁻¹ or less, i.e. this factor is not the greatest uncertainty in our presented calculations. These effects will be slightly more important for some of the other species in Table 1, e.g. the product iron ion, where spin-orbit splitting of the ⁶D and ⁴F states of Fe⁺ is somewhat greater, with the lowest spin-orbit level lying respectively 1.2 and 1.6 kcal/mol below the J-weighted average of the spin-orbit levels.²⁷

3.2. Transition State Theory

Next, we performed non-adiabatic transition state theory calculations of the rate constant for this reaction. The B3LYP calculations provide structures and thence rotational constants for the different species, as well as harmonic frequencies, and these are combined with the CCSD(T) extrapolated basis set electronic energies of Table 1 to compute the free energy of the reactants and of the bottlenecks to reaction. Before describing in detail how this is done, it is useful to lay out some of the kinetic assumptions that have been made in the calculations, with reference to the species and potential energy surfaces shown in Fig. 1. First of all, the rate constants of reaction as measured in ref. 2 refer to the rate constant for disappearance of the reactant FeO⁺ ion, and this is what we set out to calculate. Under the very low pressure conditions of some of the experiments, the only observed product is Fe⁺, whereas under other conditions it is conceivable that the strongly bound Fe⁺•OH₂ product complexes might be stabilized. However, for our purposes here, this potential branching behaviour is not important, since it will clearly occur after the rate-limiting step.

Another potential competing channel is formation of FeOH⁺ + H, which, as shown in Table 1, lies lower in energy than reactants. However, as was shown experimentally⁴ and in a previous computational study,⁶ this species is formed over a significant barrier, and experimentally, it is only formed upon high-energy collisions between FeO⁺ and H₂,² so this process is ignored here.

Next, it is clear from the observed rate constant that two-state reactivity must be occurring, i.e. the system cannot be reacting on the reactant sextet potential energy surface. The high barrier on this potential energy surface, of 10.1 kcal mol⁻¹, would correspond to an exceedingly small rate constant, far smaller than is observed experimentally. Hence the

observed reactivity must involve initial formation of ${}^6\text{FeO}^+\bullet\text{H}_2$, followed by spin state change through ${}^4,6\text{MECP}$, and passage over ${}^4\text{TS1}$. This reaction is clearly an example of Two-State Reactivity.^{9,10} This is assumed in all that follows.

We also assume that the reaction occurs on the sextet and quartet potential energy surfaces faster than collision with background gas. It has been noted experimentally that the ${}^6\text{FeO}^+\bullet\text{H}_2$ adduct is not observed to form under the conditions of the reaction, and its further reaction, or dissociation to regenerate reactants, should occur rapidly, without any possibility of change in internal energy relative to the colliding reactants. The FeO^+ and H_2 reactants will be (approximately) thermalised. Neglecting the differential collisional cross sections as a function of the internal energy of the reactants, we therefore assume throughout that the colliding species exist as a distribution of energies defined by a Boltzmann distribution for the separated reactants, i.e. we assume a low-pressure limit.

Each of the three reaction steps mentioned above involves a potential bottleneck to reaction. Consider first addition of H_2 to ${}^6\text{FeO}^+$. Although there is no potential energy barrier for this ion-neutral association reaction, there is a variational transition state corresponding to a maximum in free energy along the approach coordinate. If this was the only bottleneck to reaction, for this reaction of an ion with a non-polar but polarisable molecule, the rate constant would be given by the Langevin theory,³⁷ yielding a rate constant of $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The experimental rate constant² is much smaller than this, so clearly other bottlenecks must exist. The second possible bottleneck is spin-state change at the MECP. This has a low probability, and there is a potential energy barrier to reaching the MECP. Finally, the system must then cross TS1 on the quartet surface. Although this TS is lower in potential energy than separated reactants, it is also lower in entropic terms, and it is known that ‘submerged’ barriers of this type can influence rates of ion-molecule reactions.³⁸ To treat the net reaction efficiency for these three steps, as described below, we use the unified statistical formalism,^{39,40} whereby the net flux towards products can be computed based on properties computed for each of the bottlenecks.

The overall rate constant k for disappearance of reactants at a given temperature T is computed based on statistical rate theory, using the following expression:³⁹

$$k = \frac{1}{hQ_R(T)} \int_0^\infty dE N(E) e^{-E/k_B T} \quad (\text{eq. 1})$$

In this expression, h is Planck’s constant, and $Q_R(T)$ is the partition function of the FeO^+ and H_2 reactants, including rotational and vibrational degrees of freedom as well as the relative translational motion. Within the integral, $N(E)$ is an effective number of states within the bottleneck to reaction that are accessible at a given energy E . Finally, k_B is Boltzmann’s constant. As mentioned above, we assume that the reactants are thermally equilibrated due

to collision with background gases, but that species along the reaction coordinate do not undergo any energy exchange processes with the environment, so that in that respect, our approach deviates quite significantly from a standard fully canonical version of transition state theory.

It is to be noted that equation (1) does not refer to angular momentum. In the absence of intermolecular collisions, FeO^+ reactive encounters with H_2 will conserve orbital angular momentum. Collisions at large impact parameter will have high angular momentum, which will translate to large rotational energies for the compact transition state and MECP. The present approach assumes that the thermal energy of the reactants can be redistributed in any way between the vibrational and rotational degrees of freedom of the TS and MECP. This assumption is not correct, and in a more sophisticated version of the present theory,⁴¹ this effect could be treated at least approximately.

The key property $N(E)$ is the effective number of states within the bottleneck to reaction. This is calculated using the unified statistical formalism,^{39,40} whereby a number of cuts through the potential energy surface, situated at several positions along the reaction coordinate, are treated as dividing surfaces that may contribute to the bottleneck to reaction. Here, there could in principle be three such dividing surfaces: in the vicinity of the variational transition state for complex formation, across the MECP, and around the quartet TS. It is possible to calculate the number of rovibrational states for each of these dividing surfaces, and from these one obtains the overall $N(E)$:

$$\frac{1}{N(E)} = \frac{1}{N_{\text{coll}}(E)} + \frac{1}{N_{\text{MECP}}(E)} + \frac{1}{N_{\text{TS}}(E)} \quad (\text{eq. 2})$$

In this expression, $N_{\text{coll}}(E)$, $N_{\text{MECP}}(E)$, and $N_{\text{TS}}(E)$ are the number of rovibrational states of energy equal or lower to E at the barrierless collision TS, the MECP, and $^4\text{TS1}$, respectively. As emphasized by Miller,³⁹ these numbers of states are equivalent to *fluxes* through the corresponding dividing surfaces. Where the three values are different, it can readily be seen that the overall $N(E)$ is roughly equal to the *smallest* of the three, i.e. the overall bottleneck to reaction is caused by the tightest of the three bottlenecks. However, in cases where two or more of the values are similar, this approach accounts for the impact of each on the reaction probability..

In the present study, we choose to slightly simplify eq. (2), by omitting the first term, $1/N_{\text{coll}}(E)$. This is due to the fact, already mentioned above, that the collision event cannot be the main bottleneck to reaction, as the rate constant is known to be much smaller than the Langevin value. Hence $N_{\text{coll}}(E)$ must be larger than one or both of $N_{\text{MECP}}(E)$ and $N_{\text{TS}}(E)$, and hence will not contribute to the value of the overall $N(E)$. If, as will be shown below to be the case, N_{TS} is also smaller at a given energy than N_{MECP} , i.e. there are fewer available rovibrational states allowing passage through the TS than there are such states at the MECP, then the TS forms a greater impediment to reaction than the MECP. In this case, one

expects that many collision events will involve crossing the MECP, but then failing to cross the TS and reverting to reactants. This situation is illustrated in Fig. 2, showing the three putative bottlenecks to reaction, and showing the fluxes through these dividing surfaces.

Figure 2. Schematic kinetic diagram for reaction of FeO^+ with H_2 , showing the three putative bottlenecks to reaction treated within the unified statistical model. As the reaction is much slower than the Langevin capture rate, $N_{\text{coll}}(E)$ is not explicitly included in the calculations.

$N_{\text{TS}}(E)$ is simply calculated using the steepest descent algorithm of Forst,⁴² based on the rotational constants of the TS and the 5 real vibrational frequencies computed using B3LYP. It also takes into account the electronic degeneracy of the quartet TS and statistical factor⁴³ that accounts for the different possible arrangements of the atoms in the reactants, and the TS. This factor is equal to 2 in the case of reaction with H_2 and with D_2 . In the case of reaction with HD , there are two isotopomeric TSs, and the $N_{\text{TS}}(E)$ for each of them are calculated separately, then added to one another, with the statistical factor equal to one in each case. No attempt is made to include a correction for tunnelling.

$N_{\text{MECP}}(E)$ is calculated as previously described,¹² using the following equation:

$$N_{\text{MECP}}(E) = \int_{E_0}^E dE_h p_{sh}(E_h) \rho_{\text{MECP}}(E - E_h) \quad (\text{eq. 3})$$

In this expression, the total energy of the system E , is assumed to be split into two parts: E_h is the amount of energy that is allocated to the unique degree of freedom corresponding to the motion orthogonal to the seam of crossing between the two potential energy surfaces (the hopping coordinate). The rest of the energy, $E - E_h$, is allocated to all the other degrees of freedom – vibrational modes within the seam of crossing and rotational modes. The integral considers all possible values of E_h . The minimum value for E_h , E_0 , corresponds to no energy in this mode, i.e. in a simplified sense, the system is located at the bottom of the ${}^6\text{FeO}^+ \cdot \text{H}_2$ well on the one-dimensional sketch of Figure 1 (at -13.0 kcal/mol). The maximum value of E_h corresponds to when *all* the internal energy is in this single mode. The probability for

surface-hopping to occur upon passing the seam of crossing between surfaces is denoted $p_{sh}(E_h)$. Finally, $\rho_{MECP}(E-E_h)$ is the density (with respect to the energy variable) of rovibrational states within the seam of crossing at a given energy, calculated using the steepest descent method of Forst.⁴²

As described previously,¹² two different expressions can be used to describe the surface-hopping probability p_{sh} , a Landau-Zener expression and one based on a semiclassical treatment allowing for tunnelling:⁴⁴

$$p_{sh}(E) = 4\pi^2 H_{ab}^2 \left(\frac{2\mu}{\hbar^2 F \Delta F} \right)^{2/3} \text{Ai}^2 \left\{ -E \left(\frac{2\mu \Delta F^2}{\hbar^2 F^4} \right)^{1/3} \right\} \quad (\text{eq. 4})$$

Where H_{ab} is the matrix element coupling the wavefunction of the first state to that of the other state, μ is the effective mass for motion along the hopping coordinate, $\hbar$ is Planck's constant divided by 2π , F is the mean slope of the two potential energy surfaces, ΔF is the difference in these slopes, and Ai is an Airy function. The Airy function is close to zero for positive arguments, i.e. when the energy is negative, that is, for energies in the hopping coordinate lower than $-7.4 \text{ kcal mol}^{-1}$, the energy of the MECP. The decay to zero is not immediate, though, allowing for tunnelling through the MECP.

One aspect that needs some care is which value of H_{ab} to use. In our work, this is taken from the detailed spin-orbit coupling calculations of Danovich and Shaik.⁴⁵ However, for coupling a sextet state to a quartet state, there are in fact $(2S_a+1)(2S_b+1) = 24$ different coupling matrix elements to take into account. In principle, one could treat each of the six substates of the reactant separately, and each of the substates of the quartet product state separately also. For each pair of states one could then compute the effective number of states of eq. (3), using the appropriate values for H_{ab} in eq. (4). Then, the overall effective number of states at the MECP considering all 24 combinations of substates would simply be the sum of all the corresponding N_{MECP} values. The presence of the electronic partition function of 6 in the denominator of eq. (1) accounts for the fact that the six near-degenerate substates of the sextet reactant are each only a fraction of the total reactant state. Some of the substates are more reactive than others, but their population will be maintained roughly equal to one another over the reaction duration, due to spin-substate changes occurring during the long periods between collisions and during the many non-reactive collisions.

A simpler approach, used here, is based on recognizing that in eq. (4), surface-hopping probability is proportional to H_{ab}^2 , and this is the only place where H_{ab} intervenes. Hence the sum of the integrated density of state N_{MECP} functions can be obtained by computing a single such sum N_{MECP} in eq. (3), using an effective coupling matrix element H_{ab}^{eff} given by the square root of the sum of all 24 individual coupling matrix elements. Previously,¹⁶ we have used an effective coupling matrix element H_{ab}^{rms} in eq. (4) that is the root-mean-square of the individual matrix elements, i.e. the square root of the sum of their squares, divided by $(2S_a+1)(2S_b+1)$. In the present case, using H_{ab}^{rms} instead of H_{ab}^{eff} would lead to a difference in

N_{MECP} by a factor of $(2S_a+1)(2S_b+1) = 24$. This discrepancy does not arise for systems where the two coupled states have lower spin multiplicity so is not relevant for our previous work.

In this work, we use the square root of the sum of the matrix elements, based on the computed rms value from the paper by Danovich and Shaik. These authors computed matrix elements at several different structures, including the quartet $\text{FeO}^+\bullet\text{H}_2$ complex and $^4\text{TS1}$, obtaining $H_{\text{ab}}^{\text{rms}}$ values of 41 and 39 cm^{-1} . As these values are similar, and the sensitivity of the calculated N_{MECP} values and rate constants to the coupling matrix element is smaller than the sensitivity to other parameters such as the energy of TS1, we have simply used the latter value throughout in the present work.

We first show the calculated values of N_{MECP} and N_{TS} obtained as a function of reactant internal energy, for the case of reaction with H_2 , see Figure 3.

Figure 3. Calculated integrated number of states at $^4\text{TS1}$ and at the MECP as a function of internal energy.

As can be seen, the integrated number of states at the TS is lower than that at the MECP at all relevant energies. This is basically due to the fact that the MECP lies much lower in

energy than the TS, hence at any given internal energy, the available energy that can be spread between the different rotational and vibrational modes of the MECP is much higher than that available at the TS. One counterbalancing effect is that of the surface-hopping probability of eq. (4). This is smaller than one, in fact on average, it is equal to ca. 0.1 at lower energies, and to ca. 0.05 at higher energies. In other words, approach to the seam of crossing only leads to a successful ‘hop’ onto the other potential energy surface in roughly 1 case out of ten or twenty. Without this effect, N_{MECP} in Fig. 3 would be even larger.

Given this difference between N_{TS} and N_{MECP} , the *overall* number of states $N(E)$ used to calculate rate constants in eq. 1, which is given by equation (2), $1/N(E) = 1/N_{\text{TS}}(E) + 1/N_{\text{MECP}}(E)$ is largely determined by N_{TS} , i.e. it is mainly $^4\text{TS1}$ which represents a bottleneck to reaction. The spin-forbidden nature of the reaction has only a very minor effect on the calculated rate constant according to the present model. This conclusion is of course dependent on the accuracy of the calculated potential energy surfaces, and of the accuracy of the statistical rate theory used. If the energy of the MECP and of $^4\text{TS1}$ were closer together than found in the calculations here (where they lie at -7.4 and -1.4 kcal mol $^{-1}$), then passage through the MECP would start to play a greater role in determining the overall rate constant.

The calculated rate constants are shown in Table 4, together with the experimental data measured in various mass spectrometric experiments in ref. 2. As can be seen, while the computed rate constant is still well below the Langevin rate constant³⁷ (1.5×10^{-9} cm 3 s $^{-1}$, i.e. our computed reaction efficiency is of 0.05), the calculated data are somewhat too large, by a factor of ca. seven. This is relatively encouraging, given that the rate constant is very sensitive to the energy of $^4\text{TS1}$, and, despite the high level of electronic structure theory used here, as discussed in section 3.1, there remain uncertainties on the energies of ± 2 kcal mol $^{-1}$. In fact, as discussed based on the data in Table 3, it seems likely that the energy of $^4\text{TS1}$ is underestimated in our calculations, by 1 kcal mol $^{-1}$ or more. Repeating the calculations of N_{TS} , $N(E)$, and k for the case of H_2 after shifting the energy of TS1 up by 1 kcal mol $^{-1}$ leads to a k_{calc} (300 K) of 24×10^{-12} cm 3 s $^{-1}$, much closer to experiment. We note the observation that the cross-section for formation of Fe^+ is found² to decrease with increasing collision energy at low collision energies; this is consistent with the negative relative energy for TS1 found in this study.

The calculated rate constants are also sensitive to the magnitude of the coupling matrix element used in eq. (4) (doubling H_{ab} leads to a quadrupling of the rate constant), and, somewhat less so, to the other parameters in eq. (4). The treatment of the vibrational frequencies, and the magnitude of the latter, also have some importance. The use of a statistical model for rate constants, and the details of this statistical model, also play a role. For example, our present model assumes that after formation of the reactant complex $^6\text{FeO}^+\bullet\text{H}_2$, and also after spin state change, the system undergoes immediate vibrational energy redistribution and also that the vibrational and rotational degrees of freedom

exchange energy. As discussed above, the latter assumption is known not to be correct,⁴¹ as the energy associated with the orbital angular momentum of the two reacting species will not be available for vibrational degrees of freedom. A more accurate treatment of angular momentum would most likely lead to a decrease in the rate constant, associated with the ‘tight’ nature of the TS. Finally, the present calculations neglect the effect of tunnelling through ⁴TS1.

Table 4. Calculated rate constants ($/10^{-12} \text{ cm}^3 \text{ s}^{-1}$) for reaction of FeO^+ with H_2 , HD and D_2 , at 300 K. Experimental values,² also at room temperature, measured using ion-cyclotron resonance (ICR), guided-ion beam (GIB) and selected-ion flow tube (SIFT) mass spectrometry methods are provided for comparison.

Reactants	H_2	HD	D_2
$k_{\text{calc}} (300 \text{ K})$	70	50	33
$k_{\text{exp,ICR}}$	10 ± 4	8.1 ± 3.2	6.9 ± 2.8
$k_{\text{exp,GIB}}$			2.5 ± 1.0
$k_{\text{exp,SIFT}}$	8.8 ± 2.6	7.7 ± 2.3	4.2 ± 1.3

Considering these significant remaining uncertainties, the agreement between experiment and theory shown in Table 4 is reasonably good. The calculations also roughly capture the magnitude of the isotope effect ($k_{\text{H}_2}:k_{\text{HD}}:k_{\text{D}_2}$ vary as 1.00:0.71:0.47 in the calculations, and 1.00:0.88:0.48 in the SIFT experiments). Also, inclusion of tunnelling in the calculations, without any further increase in their accuracy, would probably result in a greater disagreement with experiment concerning the isotope effects. We should also note that a similar calculation of the $\text{H}_2:\text{D}_2$ isotope effect was reported previously, in which ⁴TS1 was assumed to be rate-limiting. Using B3LYP vibrational frequencies and rotational constants, $k_{\text{H}_2}:k_{\text{HD}}:k_{\text{D}_2}$ was predicted to vary as 1.00:0.49, very similar to what is found here.⁶

The present calculations only address the thermal rate constant at room temperature. While obtaining a reasonable value for this requires significant effort, it is clear that a more stringent test of the theory would be to compute energy-dependent rate constants for a broad range of energies. These values are available from experiment,² and in principle a modified version of eqs. 1 and 3 could be used to perform such a calculation. However, this goes beyond the scope of the present work.

One of the key conclusions of this work is that the rate of oxidation of molecular hydrogen by the iron oxide cation is limited mainly by an adiabatic transition state for insertion of quartet FeO^+ into the H–H bond. As noted above in the context of Figure 3, this conclusion arises because the MECP lies significantly lower in energy than TS, and close in energy to the quartet reactant complex $^4\text{FeO}^+\bullet\text{H}_2$. As discussed in section 3.1, this low energy for the MECP is not, in principle, any more dubious than the other calculated energies in this paper. There are good reasons to expect that this MECP should lie low in energy. Nevertheless, to test the effect of changes in this energy, the calculation was repeated after raising the

energy of the MECP by 3 kcal mol⁻¹, i.e. to -4.4 kcal mol⁻¹. This yields N_{TS} and N_{MECP} values that are closer together, though N_{TS} is still clearly smaller, and the calculated rate constant is barely changed, at 68×10^{-12} cm³ s⁻¹ vs. 70 in Table 4. A still larger increase in energy for the MECP seems implausible based on the discussion in section 3.1.

4. Conclusions

In this work, new *ab initio* calculations have been carried out at key points on the quartet and sextet [Fe,O,H₂]⁺ potential energy surfaces. These very large basis set CCSD(T) calculations, extrapolated to the complete basis set limit, provide benchmark energies for the stationary points of interest. The use of Kohn-Sham orbitals for the reference state in the CCSD calculations leads to small single excitation amplitudes. Test calculations using open-shell Brueckner methods and using explicit electron correlation (F12) establish that the computed energies are well converged both in terms of the basis set and the correlation treatment.

As well as these new electronic structure calculations, the minimum energy crossing point between the two surfaces in the vicinity of the quartet reactant complex ⁴FeO⁺•H₂ has been located for the first time. This MECP lies close in structure and in energy to the quartet reactant complex, suggesting that spin state change in this reactant complex is likely to be relatively facile compared to subsequent passage over the adiabatic TS1, which lies significantly higher in energy.

This is confirmed by non-adiabatic transition state theory calculations, which predict that the bottleneck to reaction is indeed the quartet TS1, which only just lies lower in energy than reactants. Agreement with experiment for both the calculated rate constant for reaction with H₂, and for the rate constants with the isotopomers HD and D₂ is reasonable, considering the uncertainties in such calculations. While the electronic structure calculations retain some uncertainties, it is necessary to make large and a priori unjustified changes to the relative energy of the MECP and ⁴TS1 in order to make the former, rather than the latter, the key bottleneck to reaction. It has been suggested⁴⁶ that reactions involving changes in spin state will often occur in a stepwise manner, with spin state change and bond-making and breaking occurring in separate steps, with the latter being rate-limiting. More and more observations support this suggestion,⁴⁷ and the present study suggests that the title reaction is a further example. Given the importance of spin states on reactivity patterns, especially for oxometal complexes,⁴⁸ the present in-depth study of one of the very simplest reactions of an oxometal species can provide useful general insight.

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