ACTIVATION OF METHANE BY FEO$^+$: DETERMINING REACTION PATHWAYS THROUGH TEMPERATURE-DEPENDENT KINETICS AND STATISTICAL MODELING (POSTPRINT)

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The temperature dependences of the rate constants and product branching ratios for the reactions of FeO+ with CH4 and CD4 have been measured from 123 to 700 K. The rate constants are 9.5 × 10⁻¹¹ and 5.1 × 10⁻¹¹ cm³ s⁻¹ for the CH4 and CD4 reactions, respectively. At low temperatures, the CH3OH/CD3OD product channel dominates, while at higher temperatures, FeOH+/FeOD+ + CH3/CD3 becomes the majority channel. The data were found to provide unique insight into the reaction mechanisms as well as energetic benchmarks for the reaction surface. Stationary point energies along the reaction pathway determined by ab initio calculations seemed to be only approximate and were allowed to vary in the statistical model. The model shows a crossing from the ground-state sextet surface to the excited quartet surface with large efficiency, indicating that both states are involved.

The reaction bottleneck for the reaction is found to be the quartet barrier, for CH4 modeled as −22 kJ mol⁻¹ relative to the sextet reactants. Contrary to previous rationalizations, neither less favorable spin-crossing at increased energies nor the opening of additional reaction channels is needed to explain the temperature dependence of the product branching fractions. It is found that a proper treatment of state-specific rotations is crucial. The modeled energy for the FeOH+ + CH3 reaction is −7 kJ mol⁻¹, which reproduces the experimental data of both reactions well over the extended temperature and energy ranges.

The reaction shows spin-switching during the reaction, for CH4 modeled as −22 kJ mol⁻¹ relative to the sextet reactants. Contrary to previous rationalizations, neither less favorable spin-crossing at increased energies nor the opening of additional reaction channels is needed to explain the temperature dependence of the product branching fractions. It is found that a proper treatment of state-specific rotations is crucial. The modeled energy for the FeOH+ + CH3 reaction is −7 kJ mol⁻¹, which reproduces the experimental data of both reactions well over the extended temperature and energy ranges.

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Activation of Methane by FeO⁺: Determining Reaction Pathways through Temperature-Dependent Kinetics and Statistical Modeling

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ABSTRACT: The temperature dependences of the rate constants and product branching ratios for the reactions of FeO⁺ with CH₄ and CD₄ have been measured from 123 to 700 K. The 300 K rate constants are 9.5 × 10⁻¹¹ and 5.1 × 10⁻¹¹ cm³ s⁻¹ for the CH₄ and CD₄ reactions, respectively. At low temperatures, the Fe⁺ + CH₃OH/CD₃OD product channel dominates, while at higher temperatures, FeOH⁺/FeOD⁺ + CH₃/CD₃ becomes the majority channel. The data were found to connect well with previous experiments at higher translational energies. The kinetics were simulated using a statistical adiabatic channel model (vibrations are adiabatic during approach of the reactants), which reproduced the experimental data of both reactions well over the extended temperature and energy ranges. Stationary point energies along the reaction pathway determined by ab initio calculations seemed to be only approximate and were allowed to vary in the statistical model. The model shows a crossing from the ground-state sextet surface to the excited quartet surface with large e⁻ energies for the Fe⁺ + CH₃OH/CD₃OD channel. Contrary to previous rationalizations, neither less favorable spin-crossing at increased energies nor the opening of additional reaction channels is needed to explain the temperature dependence of the product branching fractions. It is found that a proper treatment of state-specific rotations is crucial. The modeled energy for the FeOH⁺ + CH₃ channel (~1 kJ mol⁻¹) agrees with the experimental thermochemical value, while the modeled energy of the Fe⁺ + CH₃OH channel (~10 kJ mol⁻¹) corresponds to the quartet iron product, provided that spin-switching near the products is inefficient. Alternative possibilities for spin switching during the reaction are considered. The modeling provides unique insight into the reaction mechanisms as well as energetic benchmarks for the reaction surface.

INTRODUCTION

There is significant interest in procuring and employing natural gas as a viable alternative to petroleum for both energy and chemical feed stocks. One of the primary impediments to natural gas utilization is that methane (~90% of natural gas) is not easily liquefiable, resulting in increased transportation costs and risks. As such, an efficient conversion of methane to methanol is desirable. The most common approach is the indirect production of methanol from methane; synthesis gas (syngas) is produced by steam reforming (eq 1), followed by eq 2 to 5.

\[
\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \\
\Delta H^\circ = -90.2 \pm 0.2 \text{ kJ mol}^{-1}
\]  

This approach is energy intensive as the initial reaction is endothermic, requiring high temperatures and pressures to proceed. The investment required for this approach is significant, which typically limits its use to areas where large natural gas deposits are in very close proximity, neglecting the many smaller natural gas deposits in more isolated areas.

A preferable approach is direct oxidation of methane to methanol.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \\
\Delta H^\circ = 205.8 \pm 0.6 \text{ kJ mol}^{-1}
\]  

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2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CH}_3\text{OH}

\Delta H^\circ = -252.3 \pm 0.6 \text{ kJ mol}^{-1} \tag{3}

While this reaction is exothermic, it is kinetically hindered and requires a catalyst for efficient utilization. A great deal of research has focused on both finding cheap and efficient catalysts for eq 3 and also understanding the mechanistic underpinnings of the catalyzed half-reactions. Taking a cue from nature and the \text{C}–\text{H} bond oxidizing enzyme methane monooxygenase, whose active site includes an oxygen bridged di-iron center,\textsuperscript{11} numerous experimental and computational studies have focused on reactions of \text{FeO}^+ with methane and other alkanes.\textsuperscript{8,12–24} Initially reported as a nonreaction,\textsuperscript{24} it was later shown by Schwarz et al.\textsuperscript{23} that \text{FeO}^+ reacts at thermal energies with \text{CH}_4 (k = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1})\textsuperscript{25}

\text{FeO}^+ + \text{CH}_4 \rightarrow \text{Fe}^+ + \text{CH}_3\text{OH} \quad \Delta H^\circ = -35.5 \pm 6 \text{ kJ mol}^{-1} \tag{4}

\text{FeOH}^+ + \text{CH}_3 \quad \Delta H^\circ = -1.4 \pm 15 \text{ kJ mol}^{-1} \tag{5}

Several studies employing Fourier transform ion cyclotron (FT-ICR), guided ion beam (GIB), or a selected ion flow tube (SIFT) refined that work and revisited the room-temperature rate constant to \( \sim 8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \), the error being attributed to insufficient internal calibration.\textsuperscript{21} While the techniques found reasonable agreement with respect to the reaction rate constant, the reported product branching varied with the apparatus, with the FT-ICR and GIB showing the \text{FeOH}^+ + \text{CH}_3 channel to dominate while the SIFT shows the \text{Fe}^+ + \text{CH}_3\text{OH} to be the principal reaction channel. Furthermore, the GIB experiment displayed a negative energy dependence to the total rate constant below about 1 eV, as well as a significant energy dependence to the product branching. Calculations of the ground-state potential energy surface (PES) for this reaction predicted a significant barrier, inconsistent with the observed kinetics. The PES corresponding to the excited quartet states of \text{FeO}^+ with \text{CH}_4, however, is calculated to be much more consistent with the experiments, suggesting that the interplay of spin states during the reaction is paramount in explaining the reactivity, a case of “two-state” reactivity.\textsuperscript{22,26,27}

The two-state reactivity concept, as developed to explain discordant observations of thermal reactivity for systems whose ground-state surface is computed to have significant kinetic barriers, has been found to be applicable to many organometallic systems.\textsuperscript{12,14,16,28–35} One prominent example is the case of cytochrome P-450, an important superfamily of monoxygenases, which catalyze numerous important biochemical functions, including aspects of drug metabolism.\textsuperscript{36,37} Recently, calculations suggest that multiple spin states, and the interconversion between them during the course of the reaction pathway, may be vital in understanding how this enzyme catalyzes hydroxylation and epoxidation.\textsuperscript{38,39} Increasing the quantitative understanding of this type of mechanism is of great interest, and the \text{FeO}^+ + \text{CH}_4 system offers a unique opportunity to do so.

Despite the previous large body of work on \text{FeO}^+ + \text{CH}_4 several fundamental questions about the system remain unresolved. Here, we present measurements of the \text{FeO}^+ + \text{CH}_4 rate constants and branching ratios over a broad range of thermal temperatures, 123–700 K. We supplement these by measuring the same for the isotopic variant \text{CD}_4. Because these experiments occur at low total energies, the data are a sensitive probe of the PESs of the reaction. Because the reactants are thermalized, the internal state distributions are predictable, and the system is sufficiently well-defined that the data can be deciphered to yield detailed information on the energetics and dynamics of the system. To aid in interpretation, we have explored, as have others,\textsuperscript{13,16,20,22} the \text{FeO}^+ + \text{CH}_4 (\text{CD}_4) systems using ab initio and density functional theory (DFT) approaches. Unfortunately, simulations of the reactivity based on the ab initio energetics fail to reproduce the observed magnitude and temperature dependence of the rate constants, suggesting significant uncertainties in the characterization of the transition state region. We surprisingly conclude that chemically accurate energetics for this system comprising just one light transition-metal cation and two second row atoms still are beyond the capabilities of the state-of-the-art computational chemistry. The lack of a reliable ab initio method for this system precludes attempts at direct dynamics calculations and hinders interpretation of the experimental data.

With the computational avenue being problematic, we turn instead to a statistical adiabatic channel approach, using the ab initio information of the stationary points along the reaction path as guides but leaving their energies as fitting parameters. The modeling must fit the magnitude of the total rate constant, the temperature dependence of the total rate constant over a wide range, the product branching ratios at all temperatures, the isotope effect, as well as the GIB energy dependence. As such, the modeling is severely overdetermined, and success in reproducing the data not only suggests that the system proceeds essentially statistically but also provides energetics for which the quantum chemical calculations are not sufficiently accurate, namely, of the rate-limiting transition state and of reaction exothermicities. Successful application of statistical modeling depends significantly on how rotational effects are incorporated. Finally, the calculations show that the reaction follows the adiabatic reaction path between the sextet and quartet surfaces over a broad energy range, lending insight into the nature of what has been described as two-state reactivity.

\section*{Experimental and \textit{ab initio} methods}

All experiments herein were conducted on the variable-temperature selected ion flow tube (VT-SIFT) apparatus described in detail elsewhere.\textsuperscript{40} Briefly, \text{FeO}^+ ions are created in a high-pressure electron impact source supplied with a mix of \text{Fe(CO)}_5 \text{He}, and \text{N}_2\text{O}. The \text{FeO}^+ ions are mass selected using a quadrupole mass filter, with subsequent detection by an electron multiplier. The ions formed are sampled through a 2 mm aperture in a truncated carbon nose cone. The ions are focused by a lens formed and thermalized before introduction of the reactant (\text{CH}_4 or \text{CD}_4) 59 cm before the end of the flow tube. The ions are maintained at 0.4 Torr for all experiments, other than these experiments by resistive heating (300–700 K), pulsed liquid nitrogen (130–300 K), and recirculating methanol chillers (220–300 K). Remaining primary ions and product ions formed are sampled through a 2 mm aperture in a truncated carbon nose cone. The ions are focused by a lens formed and mass analysis using a second quadrupole mass filter, with subsequent detection by an electron multiplier.

Rate constants are measured by monitoring the decay of the \text{FeO}^+ signal as a function of reactant concentration. The reaction time is determined by the measured helium velocity,
the known reaction length, as well as the previously determined helium to ion velocity ratio. The measured rate constant is determined by
\[
k = \frac{\ln([\text{FeO}^+]/[\text{FeO}^+])}{[\text{CH}_4] \times t}\]

where \([\text{FeO}^+]_0\) is the \text{FeO}^+ concentration at zero reactant flow and \(t\) is the reaction time. Previous work with \text{Fe}^+ created in this source have shown upward of 20% of the \text{Fe}^+ population to be excited under some source conditions, having a significant effect on the observed product branching. For the current experiment, however, electronically excited \text{FeO}^+ is much more likely to be quenched by collisions in the source as well as the \(10^3 - 10^5\) collisions with helium prior to reaction due to the presence of internal degrees of freedom. As this reaction occurs only at a fraction of the collisional value, any substantial presence of excited \text{FeO}^+ would be evident by curvature in the logarithmic decay of the primary ion with respect to reactant concentration as it is unlikely that excited \text{FeO}^+ reacts with the same rate constant as in the ground state.

Product branching is determined by taking data with little primary ion depletion, less than a factor of 2. The fractional abundance of each product is monitored and extrapolated to zero flow. The low reactant flow is imperative as secondary chemistry, such as the clustering of the \text{FeOH}^+ primary product with methane, can greatly complicate the interpretation of the branching fraction. Mass discrimination and secondary chemistry had little to no impact on these results, as is evident by the total ion count being independent of reactant flow. While the extrapolation of the observed branching to zero flow is an approximation, Anderson et al. have shown that as long as the primary ion depletion is kept small, this method results in the nascent branching fraction within a few percentage points. Errors in the rate constants are estimated to be ±25% absolute and ±15% relative to each other, and errors in the product branching are estimated to be ±10%.

The stationary points along the reaction pathways for the \text{FeO}^+ + \text{CH}_4 \rightarrow \text{Fe}^+ + \text{CH}_3\text{OH} reaction have been determined with the CBS-QB3 method, similar to that reported by Altinay et al. This composite method performs a geometry optimization and frequency calculations at the B3LYP/CBSB7 (6-31G(2d,d,p)) level, followed by a series of additional single-point calculations with larger basis sets and higher levels of theory to extrapolate to what is typically considered a very accurate value for the energy. There is strong evidence that B3LYP performs adequately in structural determination for systems involving transition metals, but the energetics might contain significant errors. To obtain better estimates of energetics, the CBS-QB3 protocol performs single-point calculations at CCSD(T)/6-31+G(d) and MP4SDQ/CBSB4 levels on the B3LYP geometry, and then, the final infinite basis set energy is extrapolated with pair natural orbital energies at the MP2/CBSB3 level. Additionally, a correction for spin contamination is included based on the \(\langle S^2 \rangle\) eigenvalue from MP2/CBSB3. CBS calculations were performed using the GAUSSIAN 09 software suite. The energy values reported are those at 0 K and include the zero-point energy corrections from the B3LYP-derived frequencies. The vibrational frequencies and rotational constants of the stationary points were obtained at the B3LYP level.

In addition to the CBS-QB3 calculations, we have also preformed explicitly correlated CCSD(T)-F12 calculations at the B3LYP geometries of the stationary points. This approach has recently been shown to accelerate convergence with respect to the size of the basis set, and the AVTZ results were found to be close to the CBS limit. CCSD(T) and CCSD(T)-F12 energies were calculated using the MOLPRO 2010 code suite.

### EXPERIMENTAL RESULTS

The total rate constants for the reaction of \text{FeO}^+ with both \text{CH}_4 and \text{CD}_4 from 123 to 700 K are shown in Figure 1a. The rate constant for \text{FeO}^+ with \text{CH}_4 at 300 K (Table 1) was found to agree with the consensus of those previously reported, occurring at about 9% of the collision rate constant (Table 1); the collision rate constant is calculated using quasi-classical trajectory calculations as parametrized by Su and Chesnavich. The reaction with \text{CD}_4 is found to be somewhat less efficient, with only about 5% of collisions leading to reaction at room temperature.

The observed product branching (Table 1 and Figure 1b) at 300 K seems to be somewhat in the middle of the widely varied branching reported in the literature. While both FT-ICR and GIB results show the \text{FeOH}^+ channel to be favored at 300 K (\text{FeOH}^+ / \text{Fe}^+ of 61/39 and 71/29, respectively), the previous SIFT work shows the \text{Fe}^+ channel to account for 81% of the products. In order to address this, we have compared our total and partial rate constants to that of the GIB experiment. The rotational and vibrational energies of the system at 300 K were added to the GIB kinetic energies. The kinetic, rotational, and vibrational energies at each temperature in our experiment were
calculated and the two sets of data compared on a total energy scale (Figure 2a). When comparing the data as a function of translation energy only (Figure 2b), we see excellent agreement, with the exception of the lowest-energy point, which the GIB authors agree has greater absolute error in the cross section as well as larger relative uncertainty energetically. This agreement suggests little importance of vibrations to the reaction rate at these energies and lends credence to the previous GIB and present SIFT results. This observation is of central importance for the formulation of the present statistical approach (vide infra). The FT-ICR-derived branching in the CH$_4$ and CD$_4$ reaction, as well the rate constant for the CH$_4$ reaction (no rate constant for the reaction with CD$_4$ was reported), would also be consistent with our results for ions slightly above room temperature (350−400 K). Incomplete ion thermalization is a potential issue for ICR experiments due to the low-pressure regime in which the experiments take place, and thus, the ICR results can also be thought to agree well with the present results. While the rate constant that we observe for FeO$^+$ + CH$_4$ agrees with the previous SIFT result reported, the disagreement in branching remains anomalous.

### Ab Initio Calculations

A large number of theoretical studies have been undertaken recently to explore the two-state model. The nature of intersystem crossing in transition metals is a challenging problem for current computational methods. For the FeO$^+$ + CH$_4$ reaction, the reaction pathways have been explored by DFT studies, some augmented with higher-level energy corrections. The qualitative PESs for the quartet and sextet states are depicted in Figure 3. The calculations all indicate a crossing between the quartet and sextet PESs somewhere before the first transition state (TS 1), which allows the system to access a pathway with a submerged barrier via the quartet TS 1, which is then rate-limiting.

The vibrational frequencies and rotational constants of the stationary points employed in the modeling to be discussed for both spin states are collected in the Supporting Information. Our CBS-QB3 energy for quartet TS 1 relative to that for the sextet FeO$^+$ reactant is slightly negative (−7.72 kJ mol$^{-1}$), which is quite similar to those reported earlier by other theoretical calculations. This submerged barrier is consistent with the negative temperature dependence of the rate constants at low temperatures. However, as discussed below, the ab initio value for this reaction bottleneck is probably not quantitatively accurate, evidenced by the much more negative value determined by the statistical fit of the experimental rate constants presented below. With the less negative (or positive)
values for the bottleneck from the ab initio calculations (see below), statistical modeling would obtain a rate constant significantly smaller than that observed experimentally.

In order to gain a better understanding of the energetics, we performed single-point calculations using the CCSD(T) method. Similar calculations have been reported before but with a relatively small basis set.3 Here, the explicitly correlated version of CCSD(T)-F12 was used with the AVTZ basis set, which is expected to provide results with CBS quality.4 The results shown in Table 2 suggests that the previous CCSD(T) results are well-converged with the basis set. More importantly, it shows that the quartet TS 1 is 11.8 kJ mol\(^{-1}\) above the reactant, in worse agreement with the kinetic data.

The data in Table 2 underscore many of the challenges in describing this system theoretically. Hartree–Fock theory, as is expected, fails badly due apparently to the paramount importance of electron correlation. B3LYP, which incorporates electron correlation, tends to do a far better job, as noted in previous studies.46,47 The higher-level composite CBS-QB3 method only marginally improves upon the B3LYP values. In addition, it fails to describe the relative ordering of the two spin–orbit levels of the Fe\(^+\) atom, incorrectly predicting the quartet to be more stable than the sextet by 8.1 kJ mol\(^{-1}\). The CCSD(T)-F12 method does describe asymptotic regions well but fails to predict a submerged TS 1, finding it to be 11.8 kJ mol\(^{-1}\) above the reactant asymptote. Due to the failures of what are often considered reliable methods, we have concluded that an alternative approach is necessary to shed light on the energetics of this reaction.

The inconsistency may have several possible origins. First, the CBS-QB3 and CCSD(T)-F12 calculations used the B3LYP geometry for the stationary points, which might be different at the higher levels of theory. Second, the system may have significant multireference character due to the numerous low-lying excited states. The T1 diagnostic value at the quartet TS 1 is 0.02 for single-reference systems. However, multireference ab initio calculations involving transition metals, particularly with geometry optimization, are computationally formidable.

**Kinetic Modeling.** With the ab initio results being problematic, we instead turned to a kinetic analysis of absolute rates and branching fractions for the FeO\(^+\) + CH\(_4\) reaction from the present measurements and the previously reported GIB data. An important test for the analysis will also be the modeling of experimental isotope effects of the rate constants and branching fractions for FeO\(^+\) + CD\(_4\) as obtained in the present work. Despite the fact that we do not have complete sextet and quartet PESs of the reaction, we can elaborate on statistical rate theory using frequency and structural parameters as calculated using DFT theory. In addition, the problem of the sequence of spin-switchings during the reaction and their influence on the reaction dynamics need to be addressed.

Before doing a statistical modeling of the reactions, one aspect of the data has to be emphasized. The comparison of the present fully thermalized SIFT data with the translationally hot GIB data in Figure 2b clearly indicates that the vibrational energy of the reactants influences the reaction rate in a different way than the translational energy. Therefore, it would not be appropriate to use a model in which both vibrational and translational energies of the reactants can be used to overcome the centrifugal barriers to form complex Int 1. The model used here allows only translational and rotational energies to contribute to the primary capture process, followed by fully statistical dynamics for the later part of the reaction. Therefore, the present approach follows the statistical adiabatic channel model (SACM/CT; for its application to ion–molecule reactions, see, e.g., refs 57–61) for the primary approach of the reactants.

The modeling of the reaction by statistical rate theory requires knowledge of the energies of the stationary points along the minimum-energy path (MEP) of the reaction, with the results being highly sensitive to those values. Furthermore, vibrational frequencies and rotational constants of these structures need to be known (although the modeling is much less sensitive to these values compared to the stationary point energies). The question also arises to what extent, besides the pathway involving an OFe\(^+\)(CH\(_4\)) entrance complex (Int 1) isomerizing to an intermediate (HO–Fe–CH\(_3\))\(^+\) complex (Int 2), a more direct second pathway contributes to the formation of FeOH\(^+\) + CH\(_3\). As this channel is consistently predicted to require higher energies, it was not further included in the present modeling. In our statistical modeling, we rely on the vibrational frequencies and rotational constants as those derived by DFT calculations. As discussed above, energies are not known with sufficient accuracy for use in the modeling, though these calculations provide reasonable measures of the frequencies, and the conclusions of the model are minimally sensitive to these values on the order of their potential errors. Fine tuning the frequencies yields slightly better fits, but we do not report those numbers as the addition of more adjustable parameters would muddle the simple interpretation presented here. CCSD(T) and CBS-QB3 calculations are more precise but, nevertheless, still leave considerable differences between the derived values; see, for example, ref 13. A comprehensive analysis of experimental and thermochemical data from ref 25 has illustrated the remaining uncertainties. This is probably a consequence of the T1 diagnostic showing considerable multireference nature for this system. Therefore, it appeared reasonable to leave the energies of the reactants and the products as fit parameters in the modeling. Furthermore, the

<table>
<thead>
<tr>
<th>stationary point</th>
<th>HF</th>
<th>B3LYP</th>
<th>CBS-QB3 (ref 10)</th>
<th>CCSD(T)-F12/AVTZ</th>
<th>CCSD(T)AVTZ (ref 10)</th>
<th>exp. derived values</th>
<th>current model II determined values</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO(^+)(4) + CH(_4)</td>
<td>−7.68</td>
<td>52.5</td>
<td>24.1 (25)</td>
<td>50.5</td>
<td>49.5 (45)</td>
<td>~34.6(^{64})</td>
<td></td>
</tr>
<tr>
<td>Fe(^+)(6) + CH(_2)OH</td>
<td>−304.9</td>
<td>−29.8</td>
<td>−35.9 (−36)</td>
<td>−36.6</td>
<td>−52.0 (−49)</td>
<td>−35.5 ± 6(^{25})</td>
<td>−34.6</td>
</tr>
<tr>
<td>Fe(^+)(4) + CH(_2)OH</td>
<td>−114.0</td>
<td>−21.7</td>
<td>−39.8 (−6)</td>
<td>−24.4</td>
<td>−30.0 (−31)</td>
<td>−10.6 ± 6(^{25,55})</td>
<td>−9.7</td>
</tr>
<tr>
<td>FeOH(^+)(5) + CH(_3)</td>
<td>−209.7</td>
<td>−21.7</td>
<td>−22.8 (−23)</td>
<td>−6.4</td>
<td>−5.4</td>
<td>−1.4 ± 15(^{25})</td>
<td>−0.6</td>
</tr>
<tr>
<td>TS 1(6)</td>
<td>113.9</td>
<td>44.0</td>
<td>40.1 (40)</td>
<td>56.9</td>
<td>(60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS 1(4)</td>
<td>−4.22</td>
<td>−7.9 (−1)</td>
<td>11.8</td>
<td>(12)</td>
<td>−22.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{5}\)The literature values for CBS-QB3 and CCSD(T) are given in parentheses.
energy of the quartet transition state (TS 1) between the OFeO(CH4) and (HO–Fe–CH3)+ complexes was kept as a third fit parameter. The results of the statistical modeling sensitively depend on these three fit parameters such that the present approach likely provides a better representation of these quantities than the ab initio values. The other values of the energetics are not particularly relevant to the calculations except to get the correct ordering of their positions.

Figure 3 shows the qualitative sextet and quartet pathways of the reaction, such that the figure only serves for an illustration of the reaction mechanism. The long-range interaction potential between FeO+ and CH4 at the entrance to the reaction complex, is of charge-induced dipole character and corresponds to a loose transition state.59 Therefore, we treat the entrance by phase space theory (PST) only. Similar arguments apply to the FeOH+ + CH4 exit channel, which is characterized by the charge-induced dipole interaction. On the other hand, Fe++ + CHOH is characterized by charge-induced + permanent dipole interaction (accounting for the rigidity of the permanent dipole contribution60) such that, in this case, additional rigidity may be generated by short-range valence contributions of the potential combining with the charge dipole. At this stage, this possibility is not further considered. Complex-forming bimolecular reactions require a particularly careful account of rotational effects.58,62,63 It is, therefore, most important not to start with rotationally averaged reactants. Instead, rotationally selected events have to be considered, and averaging should only be performed at the end.

In the following, we consider energy E- and angular momentum (quantum number J)- specific rate constants k(E,J) for dissociation and barrier crossing, as given in statistical unimolecular rate theory64 by

\[ k(E, J) = \frac{W(E, J)}{hp(E, J)} \]  

(7)

with rovibrational numbers of open channels W(E,J) and densities of states \(\rho(E, J)\). Rovibrational numbers of open entrance channels W(E,J) also enter the rate of formation of the complex at the entrance of the reaction.59 While the W(E,J) are identical for forward and backward fluxes over intrinsic transition states like TS 1 (see Figure 3), they may differ for formation, W(E,J), and redissociation, W(E,J), at the entrance to the reaction complex, depending on the experimental situation. This difference will be described by our statistical approach. The molecular parameters used in our calculations are given in the Supporting Information.

We consider reaction complexes with a total internal energy between \(E + dE\) and a total angular momentum (quantum number J). With the number of open entrance channels denoted by \(W(E, J)\), we express the rate constant for formation of the reaction complex by the capture rate constant \(k_{\text{cap}}(E, J)\) as63

\[ k_{\text{cap}}(E, J) = (2J + 1)\tilde{W}_\alpha(E, J) \exp \left( \frac{-E/kT}{hQ} \right) \]  

(8)

We assume either fully thermalized reactants of temperature \(T\) or thermal reactants with (nearly) frozen vibrations in the GIB experiments. Q then stands either for the product of the relevant partition functions for translations, rotations, and vibrations or for translations and rotations only. We note that summation over \(J\) and integration over \(E\) of eq 8 leads to a thermal capture rate constant given by the Langevin rate constant

\[ k_1 = 2\pi \left( \frac{\alpha}{\mu} \right)^{1/2} \]  

(9)

which, for FeO+ + CH4, takes the value \(k_1 = 1.04 \times 10^{-9}\) cm\(^3\) s\(^{-1}\). Entrance channels here are open when the energy \(E\) exceeds the threshold energies \(E_0(L)\) given by

\[ E_0(L) = C_\alpha [L(L + 1)]^{1/2} \]  

(10)

where \(L\) is the quantum number for orbital angular momentum and \(C_\alpha = \hbar^4/8 \mu^2 \alpha^2\); \(\mu\) is the reduced mass of the reacting species, and \(\alpha\) is the isotropic polarizability of the neutral. One can show that the approximation \(L \approx J\) under the present conditions is always fulfilled and that numbers of open channels \(W(E,J)\) here can always be approximated by their high-J limits (for the transition from low-J to high-J expressions, see refs 65 and 66). Expressions for various combinations of atoms and tops (or tops and tops), as used in the present modeling, are also given in the Supporting Information.

Once the complex Int 1 (see Figure 3) is formed with the capture rate constant of eq 8, the system can either back-dissociate or advance over the transition state TS 1 to Int 2. As discussed before, the latter takes place after a sextet–quartet spin-switching (the energy of TS 1 in the sextet apparently is too large to contribute). We tentatively assume that the rate of formation of the final products FeOH+ + CH4 and Fe++ + CHOH after passage of TS 1 is governed by neither the rates of spin-switching nor the rate of passage of TS 2; see below. Instead, we assume that it is determined by the rates of the respective bond fission processes to the final products (we denote these by B and C, while we have denoted the entrance FeO+ + CH4 by A). Below, we explore the two possibilities of efficient or inefficient spin switching. We then consider the fractional populations of the intermediates Int 1 (denoted by \(c_1\)) and Int 2 + Int 3 (denoted by \(c_2\)). We calculate their steady-state values by equilibrating in- and out-fluxes (we denote by TS the transition state TS 1 separating Int 1 and Int 2 + Int 3).

We obtain

\[ \frac{k_{\text{cap}} + c_1 W_{TS}}{h\rho_2} = \frac{c_1 (W_{TS} + W_{A})}{h\rho_1} \]  

(11)

and

\[ \frac{c_1 W_{TS}}{h\rho_1} = \frac{c_1 (W_{TS} + W_{B} + W_{C})}{h\rho_2} \]  

(12)

Combining eqs 8, 11, and 12 leads to the partial rate constants \(k_{\beta,\gamma}(E, J)\) for formation of the products B or C, respectively,

\[ k_{\beta,\gamma}(E, J) = \frac{c_1 W_{\beta,\gamma}}{h\rho_2} \]  

\[ = \left( \frac{1}{hQ} \right) \exp \left( \frac{-E}{kT} \right) \times \frac{(2J + 1)\tilde{W}_{TS} W_{\beta,\gamma}^{W_{\alpha}}}{[W_{TS} W_{A} + (W_{TS} + W_{\alpha})(W_{B} + W_{C})]} \]  

(13)

We note that the densities of states \(\rho_1\) and \(\rho_2\) do not appear in eq 13. Integration over \(E\) and summation over \(J\) finally give the thermally averaged rate constants for formation of B or C

\[ k_{\beta,\gamma} = \int_{\text{th}} \frac{dE}{\rho(E, J)} \int_{\text{th}} dz \]  

(14)
\[ k_{B,C}(T) = \left( \frac{kT}{\hbar} \right) \sum (2J + 1) \int \frac{dE}{kT} \exp \left( \frac{-E}{kT} \right) \]
\[ \times \frac{W_A W_B W_C}{[W_{TS} W_A + (W_{TS} + W_C)(W_B + W_C)]]} \] (14)

Within PST and assuming \( J \approx L \gg 1 \), the numbers of open channels are equal to the numbers of rotational states as given in the Supporting Information, convoluted with the vibrations of the system at the positions \( r \) along the MEP and with the distributable energies \( E_i = E - E_{0i}(J) \). The threshold energies \( E_{0i}(J) \) correspond either to lose activated complexes such as those given, for example, for the entrance A by eq 10 or to rigid activated complexes as TS 1. In the former case, they increase \( \propto [J(J + 1)]^2 \) whereas they increase \( \propto J(J+1) \) in the latter case. The interplay between the \( J \) dependences of the threshold energies \( E_{0i}(J) \) of the various stationary points along the MEP is of crucial importance for the statistical modeling. It governs both the absolute values of the rate constants and the branching fractions, and it cannot be accounted for by working with an average \( J \) from a thermal rotational distribution.

Before calculating \( k_B(T) \) and \( k_C(T) \) and optimizing the energetics, the kinetic relevance of spin-switching needs to be considered. The magnitude of the total rate constant \( k_{\text{tot}} = k_B + k_C \) indicates that sextet–quartet spin-switching in Int 1 must be efficient; the spin-switching time is short compared to the complex lifetime such that the quartet TS 1 is the rate-determining bottleneck of the reaction. After crossing quartet TS1, we consider two possibilities; model I assumes that in Int 2 and Int 3, efficient crossing allows sextet and quartet states to fully equilibrate and thus both contribute, and model II assumes inefficient crossing, and thus, only quartet Int 2 and Int 3 contribute. Some information on the rate of spin-switching can be deduced from the calculations of spin–orbit coupling matrix elements in ref 16, showing a decrease in coupling as one proceeds from Int 1 to Int 3. However, the rate of spin-switching has to be seen in relation to the respective lifetimes of the intermediates, that is, a poorly coupled crossing point still may be efficient given a long enough complex lifetime.

It would have been impossible to reproduce the experimental results in this model using the energetics from CBS-QB3 calculations, which have the energy of quartet TS 1 close to that of the entrance \( {}^6\text{FeO}^+ + \text{CH}_4 \) and a markedly exothermic channel \( \text{FeOH}^+ + \text{CH}_3 \). The overall rate constant would not be as efficient as that observed and would not decrease as sharply with temperature. Furthermore, the product branching modeled would not agree with that observed as the FeOH+ channel would dominate over the entire energy range due to the larger number of rotational degrees of freedom as compared to the Fe+ channel. This changes only when the energy of the exit to \( \text{FeOH}^+ + \text{CH}_3 \) is increased to values much closer to that of the reactants, in better agreement with experimentally established thermochemistry. Instead, we calculate \( k_B(T) \) and \( k_C(T) \) from eq 13 while varying the three energy parameters mentioned above. We then perform mean-least-squares fits of the modeling to the experimental results presented here and in ref 18. The results are shown in Figure 4 (for model II as an example; similar quality of the fit is obtained for model I). In detail, the following energy parameters are fitted (at 0 K, including zero-point energies, energy differences between quartet and sextet Fe+ fixed at 23.9 kJ mol\(^{-1}\))

![Figure 4. Statistical modeling of rate constants for FeO+ + CH₄ from the present work (squares) and from GIB experiments of ref 18 (filled circles). (Green) Total rate constants; (red) rate constants for formation of Fe+ + CH₃OH; (black) rate constants for formation of FeOH+ + CH₃. (Lines) Modeling by model II; see the text.]

model I: \( E(\text{TS} 1) = -22.2, E(\text{FeOH}^+ + \text{CH}_3) = -1.3, \) and \( E(\text{6Fe}^+ / \text{4Fe}^+ + \text{CH}_3\text{OH}) = -15.1/9.8 \text{ kJ mol}^{-1} \)

model II: \( E(\text{TS} 1) = -22.5, E(\text{FeOH}^+ + \text{CH}_3) = -0.6, \) and \( E(\text{6Fe}^+ / \text{4Fe}^+ + \text{CH}_3\text{OH}) = -34.6/-9.7 \text{ kJ mol}^{-1} \)

(15)

We note that the fitted energies for \( E(\text{TS} 1) \) and \( E(\text{FeOH}^+ + \text{CH}_3) \) are insensitive to which model was used. We further note that \( E(\text{FeOH}^+ + \text{CH}_3) = -8(\pm 3) \text{ kJ mol}^{-1} \) and \( E(\text{6Fe}^+ / \text{4Fe}^+ + \text{CH}_3\text{OH}) = -38(\pm 8) \text{ kJ mol}^{-1} \) were estimated in ref 21, while \( E(\text{FeOH}^+ + \text{CH}_3) = -1.4(\pm 1.5) \text{ kJ mol}^{-1} \) and \( E(\text{6Fe}^+ / \text{4Fe}^+ + \text{CH}_3\text{OH}) = -35.5(\pm 6.0) \text{ kJ mol}^{-1} \) follows from ref 25 (with enthalpies of formation at 0 K for \( \text{CH}_4, \text{CH}_3\text{OH} \) of \(-66.633, 150.0, \) and \(-190.11 \text{ kJ mol}^{-1} \), respectively, from ref 5). We observe that the fitted value for \( \text{FeOH}^+ + \text{CH}_3 \) is consistent with these literature data. There is a significant difference for \( \text{6Fe}^+ / \text{4Fe}^+ + \text{CH}_3\text{OH} \) energies of model I, which will be discussed below, while the derived energies from model II are in close agreement with the experimentally derived thermochemistry. We finally mention that \( J \) was limited to the range of 0–250 because the potential well of Int 1 ceases to exist beyond \( J_{\text{max}} = 250 \) (\( J_{\text{max}} = 275 \) for the deuterated system). We also mention that the slightly higher experimental rate constants for formation of \( \text{Fe}^+ \) below 200 K could not be reproduced by the modeling that produced the best fit to the \( \text{CH}_4 \) data only.

The good general agreement between statistical modeling and experiments over the broad range of transitional temperatures at first sight may appear surprising as \( S_\text{N2} \) reactions, also proceeding through ion–dipole complex formation, have been suggested to involve nonstatistical dynamics. \(^{67}\) It would be interesting to repeat such calculations with \( J \)-selected dynamics. However, the present calculations have been done for individual rotational states of the reactants with proper care for angular momentum couplings. Rotational averaging then was done only at the end of the calculations.

Comparing models I and II, we note that upon fitting to the experimental branching ratios, model I leads to unphysical energies for the \( \text{6Fe}^+/\text{4Fe}^+ + \text{CH}_3\text{OH} \) channels, while model II describes the energetics in close agreement with experimental
values. One, therefore, would be tempted to prefer model II, that is, contributions exclusively from the quartet states to the reaction upon crossing of TS 1. While this conclusion would be in agreement with those made based on spin–orbit coupling matrix elements, this conclusion is premature for the following reason. Our statistical modeling was done with loose activated complexes at both the FeOH+ and Fe’ exits. This may be adequate for the isotropic charge-induced dipole long-range potential of the FeOH+ + CH3 exit, but it may not apply to the Fe’ + CH3OH exit with its anisotropic charge-permanent (and induced) dipole long-range potential with possible contamination from an anisotropic short-range valence potential. The anisotropic components would introduce “rigidity” into the calculation of \( W_c(E,J) \). We have explored introducing global rigidity factors into the determination of \( W_c(E,J) \). The fits to the experimental data then moved the apparent energy of the Fe’ exit energy from model II in the direction of model I, indicating that branching into \( ^6 \)Fe’ and \( ^6 \)Fe products, with partial contributions from both quartet and sextet states after crossing TS 1, cannot be ruled out. Nevertheless, we consider model II to be more realistic (and its results are included in Table 2).

Here, we address the uniqueness of the fitting of the three energy parameters. First, one should note that the total rate constant \( k_0 + k_c \) only depends on the single parameter \( E(TS 1) \), while the branching ratio essentially only depends on the energy difference \( E(\text{FeOH}^+ + \text{CH}_3) - E(\text{Fe}^+ + \text{CH}_3 \text{OH}) \). One may reduce the uncertainty of the fitted energy values by inspecting isotopic effects. Before doing this, one may test the appropriateness of statistical theory by predicting the rate constants and branching fractions for FeO+ + CD4 on the basis of the modeling for FeO+ + CH4 with appropriately modified molecular parameters (vibrational frequencies and rotational constants such as those given in the Supporting Information). Figure 5 shows the results, again given for model II (the fit for model I looks quite similar). Without touching the energy parameters (apart from modifying the vibrational zero-point energies), the good agreement between experimental and modeling results can be taken as strong support for the conclusion about the statistical character of the reaction dynamics. The statistical modeling and its fitting of the energy parameters, however, can still be improved slightly if all CH4 and CD4 data points are used. The result is illustrated in Figure 5.

We finally extended our modeling to higher translational temperatures than those shown in Figure 4. The results in Figure 6 are compared with the experimental data from ref 21.

![Figure 6](image-url) As Figure 4 but extended to higher translational temperatures with the GIB data from ref 18. The three high-temperature lines from top to bottom correspond to maximum angular momentum quantum numbers \( J_{\text{max}} = 300, 250, \text{and } 200; \) see the text.

As mentioned before, increasing translational energies give rise to increasing values of angular momentum quantum numbers \( L \approx J \) such that potential wells of the intermediates cease to exist and complex formation does not happen. This effect depends on more details of the potential than available here. Therefore, we mimic the effect by limiting \( J \) to certain maximum values \( J_{\text{max}} \) which appear realistic (the potential minimum of INT 1, e.g., disappears for values of \( J \) of about 250). Figure 6 shows the results for varying \( J_{\text{max}} \). While the FeOH+ channel is only mildly influenced, there is a strong effect on the Fe+ channel. One should note, however, that the translational distributions of the GIB experiments at the highest energies are markedly nonthermal, such that comparisons with the modeled curves in Figure 6 may be inappropriate. For a more detailed treatment in this range, one would need more information on the translational as well as rotational distributions of the GIB experiments. In addition, finer details of the entrance well potential would be required to fix \( J_{\text{max}} \). This is outside of the scope of the present analysis.

### DISCUSSION

Perhaps the most interesting result of the present work is the relative simplicity of the model used to predict the data so well, over such a wide temperature and energy range. Previous discussion of the large energy dependence of the branching observed for this reaction has focused on the assumed energy dependence of the curve-crossing probability. This would apply if the lifetime of the complex would be similar to the curve-crossing lifetime; as the energy increases, the lifetime of this
complex becomes too short to allow for efficient crossing. It then followed that proceeding to products along the sextet pathway highly favored the FeOH\textsuperscript{+} channel as it is entropically favored because it involves a single bond fission and both products have rotations. Additionally, there is a direct hydrogen abstraction pathway available to the sextet state leading only to FeOH\textsuperscript{+} formation, though this pathway has long been neglected as it has been calculated to have an endothermic barrier. Our calculations consistently place this barrier lower than the sextet barrier of the concerted pathway, suggesting that it could play a role at higher energies or temperatures. Both the energy-dependent spin switching and the direct hydrogen abstraction mechanisms were unnecessary in the present modeling. The curve crossing prior to TS 1 was found to be efficient for the entire energy range modeled, over 1 eV. While the higher energies may be expected to have some contribution from other pathways and perhaps the crossing probability is less efficient at the higher energies, the quality of the fit without these possibilities shows their influence to be minimal in this energy range.

Given the lack of efficient, yet accurate, computational techniques for transition-metal systems such as this, it is important to broaden the experimental benchmark data available for their development. The present work achieves this by refining the thermodynamic value for the FeOH\textsuperscript{+} + CH\textsubscript{3} channel from previous experimentally derived values. Additionally, the current work has provided quantification for the rate-limiting transition state barrier on the quartet surface, previous understanding of which was highly qualitative. Thorough understanding of fundamental reaction mechanisms in numerous aspects of organometallic chemistry is currently inhibited by an inability to precisely map out the energetic landscape of the reaction. For example, modeling of the crossing efficiency in cases of two-state reactivity such as this would greatly benefit from an approximation of the complex lifetime in the vicinity of the crossing, as well as its energy dependence. These quantities are highly dependent, however, on the relative energetics of the complex as well as the neighboring transition states, which state-of-the-art calculation methods have had little success in describing energetically. The ability to build even semiquantitative models, as well as potentially pursuing direct dynamics simulations to allow for better understanding of fundamental reaction mechanisms such as two-state reactivity, will only be possible with the development of computational techniques that impart some level of confidence in their energetic determinations.

CONCLUSIONS

We have presented the temperature dependence of the reaction of Fe\textsuperscript{+} + CH\textsubscript{3} and its deuterated analogue from 123 to 700 K. Kinetic modeling of the rate constants and branching ratios for these reactions has led to new insight into this reaction mechanism as well as the role of two-state reactivity. Contrary to previous descriptions of this reaction, we find efficient spin inversion in the initial product complex for energies upward of 1 eV. The quartet TS 1 was found to be the reaction bottleneck, with a value 22 kJ mol\textsuperscript{-1} below the reactants. The FeOH\textsuperscript{+} + CH\textsubscript{3} channel was found to be about 1 kJ mol\textsuperscript{-1} exothermic relative to the reactants, well within the uncertainty in the experimentally derived thermodynamic value, whereas the Fe\textsuperscript{+} + CH\textsubscript{2}OH channel modeled energy depended on the efficiency of the curve crossing as well as on some details of the potential near the products of the reaction. In addition to providing a previously unavailable computational benchmark for the quartet transition state energy for this important reaction, these results emphasize the complexity of spin inversion in cases of two-state reactivity such as this. Assumptions based solely on spin–orbit coupling or the assumed energy dependence of the intermediate lifetime are potentially misleading.

ASSOCIATED CONTENT

Supporting Information

Parameters employed in the modeling including stationary point vibrational and rotational constants, as well as expressions for determining the number of rotational states. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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