Rate Coefficients and Branching Ratio for Multi-Channel Hydrogen Abstractions from CH$_3$OH by F$^+$

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The hydrogen abstraction reaction F+CH$_3$OH has two possible reaction pathways: HF+CH$_3$O and HF+CH$_2$OH. Despite the absence of intrinsic barriers for both channels, the former has a branching ratio comparable to the latter, which is far from the statistical limit of 0.25 (one out of four available H atoms). Furthermore, the measured branching ratio of the two abstraction channels spans a large range and is not quantitatively reproduced by previous theoretical predictions based on the transition-state theory with the stationary point information calculated at the levels of Møller-Plesset perturbation theory and G2. This work reports a theoretical investigation on the kinetics and the associated branching ratio of the two competing channels of the title reaction using a quasi-classical trajectory approach on an accurate full-dimensional potential energy surface (PES) fitted by the permutation invariant polynomial-neural network approach to ca. 1.21x10$^{5}$ points calculated at the explicitly correlated (F12a) version of coupled cluster singles doubles and perturbative triples (CCSD(T)) level with the aug-cc-pVDZ basis set. The calculated room temperature rate coefficient and branching ratio of the HF+CH$_3$O channel are in good agreement with the available experimental data. Furthermore, our theory predicts that rate coefficients have a slightly negative temperature dependence, consistent with barrierless nature of the reaction.

Key words: Reaction dynamics, Rate coefficient, Product branching ratio

I. INTRODUCTION

Many chemical reactions involving large organic molecules often have multiple reaction pathways, leading to different products. The competition among different reaction pathways is of great importance in understanding product selectivity in chemical processes [1–4]. Theoretically, an accurate determination of the product branching ratio is difficult because, unlike rate coefficients, they may not be completely determined by transition states as dynamics can play a significant role. It is challenging to study reaction dynamics of these systems because of the large dimensionality and considerably more complex multichannel potential energy surfaces (PESs). Indeed, few detailed studies of the product branching in multichannel reactions have been undertaken. To gain deeper insights into complex reactive systems, we in this work examine the hydrogen abstraction from methanol by fluorine atoms, F + CH$_3$OH products. Methanol, the simplest oxygenated polyatomic organic molecule with two functional groups, is an ideal candidate for studying branching ratios and stereodynamics in its reactions with atomic radicals [1]. The current reaction is unique because of the two possible parallel and unequal reaction pathways, namely, hydrogen abstraction from the hydroxyl group of methanol to form methoxy radicals, CH$_3$O,

F(2P) + CH$_3$OH $\rightarrow$ HF + CH$_3$O (R1a)

and from the methyl group to form hydroxymethyl radical, CH$_2$OH,

F(2P) + CH$_3$OH $\rightarrow$ HF + CH$_2$OH (R1b)

Neither abstraction pathway has an intrinsic barrier, although there exist submerged transition states (TSs), which may form reaction bottlenecks with large impact parameters. There are also significant pre- and post-reaction complexes, as shown in FIG. 1, which may affect the dynamics. Over the past few decades, a substantial body of experimental and theoretical work has been reported on the kinetics, branching ratio of the two channels, and dynamics for reactions of F atoms with CH$_3$OH and various deuterated isotopologues, CD$_3$OH, CH$_3$OD, and CD$_2$OD [5–27]. Both reaction channels are highly exothermic, with $\approx$28.40 and $\approx$37.74 kcal/mol for (R1a) and (R1b), re-
respectively [24, 25], and the reaction is very fast because of the lack of intrinsic barriers along the two competing channels [21, 24, 25]. Thermodynamically, R1b is favored due to its larger exothermicity. Statistically, it is also favored as it has three possible hydrogen abstraction channels. Interestingly, the measured branching ratio for R1a, defined as $k_{1a}/(k_{1a}+k_{1b})$, is anomalously high, between 0.4 and 0.6 [10, 15–18, 20, 22, 27]. The latest study of Fittschen and coworkers reported a value of $(0.503±0.013)$ [27]. Although many of these values are with large experimental uncertainties, they are all greater than 1/4, expected from the statistical limit (one H out of four possible ones).

The reaction R1a has recently been probed by the photoelectron spectroscopy of the $F^\cdot$(HOCH$_3$)$_3$ anion, whose geometry is similar to the transition state for this neutral reaction [19, 26, 28]. The photoelectron spectrum provides a direct probe of the vibrational structure and metastable resonances that are characteristic of the reactive PES of the neutral reaction. In particular, both experiment and theory, consistent with each other, revealed spectral features associated with a manifold of vibrational Feshbach resonances and bound states in the exit channel well [28]. Despite the large number (15) of degrees of freedom (DOFs), the photodetachment results suggested a relatively local nature of the corresponding neutral reaction, which shares many common features with the simpler $F^\cdot$(H$_2$O) case [29, 30].

In sharp contrast to the large body of experimental work on the title reaction mentioned above, relevant theoretical research is very scarce [21, 24, 25], especially on the reaction kinetics and dynamics, due apparently to the lack of the reliable PES. Based on the information of the stationary points determined at the second-order Møller-Plesset perturbation (MP2) [21, 24] and the G2 levels of theory [24], the reaction kinetics of the title reaction has been investigated for both reaction channels, which yielded the $R1a/(R1a+R1b)$ branching ratio. As shown and discussed below, the calculated branching ratio ranges from 0.55 to 0.70 over the temperature range of 300–1000 K [21, 24], which appears to overestimate the experimental values. Recently, Schaefer and coworkers reinvestigated this reaction at the level of coupled cluster theory with single, double, and perturbative triple excitations (CCSD(T)) associated with the augmented double, triple, and quadruple-zeta basis sets (AVDZ, AVTZ, and AVQZ) [25], which can be considered as a benchmark for the title reaction. The energetics of the title reaction was found to be very different from those obtained at the MP2 and G2 levels of theory and sensitive to the level of theory. Hence, the overestimation of the branching ratio by the earlier theoretical calculations is most likely due to the low levels of theory used in those calculations. In addition, the reaction might be significantly influenced by the pretransition state wells, which are typically not taken into consideration in those transition-state theory studies.

In this work, we present a thorough theoretical study of the kinetics and branching ratio of the title reactive system. In particular, quasi-classical trajectory (QCT) calculations are carried out on a globally accurate full-dimensional PES fit to a large number of high-level ab initio data using the permutation invariant polynomial-neural network (PIP-NN) method [31], which has been successfully employed in simulating the photoelectron spectrum of the $F^\cdot$(CH$_3$OH) anion [28]. Different from the previous transition-state theory studies, the QCT calculations capture all dynamical aspects of the reaction. These calculation results are compared with available experimental data and previous theoretical results. It is our hope that these new theoretical results based on a globally accurate PES can provide a more accurate and reliable understanding of the kinetics and branching ratio of the title system.

II. THEORY AND CALCULATION DETAILS

The title reaction, with seven atoms and fifteen DOFs, remains a challenge for full-dimensionality quantum dynamical calculations [32]. Therefore, the QCT theory was employed with the PIP-NN PES [28], interfaced to the VENUS chemical dynamics program [33]. The QCT approach accounts for the vibrational zero point energy (ZPE) of the reactant, but ignores other quantum effects such as tunneling. The thermal rate coefficients at the temperatures of 200, 300, 500, and 1000 K were calculated using the QCT approach, according to the following equation:

$$k = \frac{2}{4 + 2 \exp \left( -404 / k_B T \right)} \sqrt{\frac{8 k_B T \pi \mu b_{\text{max}}^2}{\pi b_{\text{max}}^2}} \frac{N_{\text{r}}}{N_{\text{total}}}$$

where $k_B$ and $\mu$ are the Boltzmann constant and reduced mass between the two reactants, respectively, and the first term is the electronic factor to account for the spin-orbit splitting of $F^\cdot$(2P$_{1/2,3/2}$) and for the doublet nature of the PES. $b_{\text{max}}$ is the maximum impact parameter, and was sampled according to $b = b_{\text{max}} \zeta^{1/2}$ with $\zeta$ being a uniformly distributed random number between 0.0 and 1.0. $N_{\text{r}}$ and $N_{\text{total}}$ denote the number of reactive trajectories and total number of trajectories, respectively. The $b_{\text{max}}$ was determined using small batches of trajectories with trial values, and is 9.6–10.8 Å for temperatures being 200–1000 K. The translational, vibrational, and rotational degrees of freedom of the reactants were sampled at the specified temperature according to the Boltzmann distribution.

At each temperature, 5×10$^4$ trajectories were calculated with its maximal impact parameter ($b_{\text{max}}$) determined using small batches of trajectories with trial values. The statistical errors were all less than 2%. The trajectories were initiated at a separation of 11.0 Å and terminated when reactants were separated again by 11.5 Å for nonreactive processes, or when products were separated by 8 Å for reactive processes. Other
scattering parameters including the spatial orientation of the initial reactants and vibrational phases, were determined using a Monte Carlo approach as implemented in VENUS [33]. The propagation time step was selected to be 0.01 fs with the gradient of the PES with respect to atomic coordinates calculated numerically. The combined fourth-order Runge-Kutta and sixth-order Adams-Moulton algorithms were used for the integration of the trajectories. Almost all trajectories conserved energy within a chosen criterion (1.0×10^{-4} kcal/mol).

III. RESULTS AND DISCUSSION

The full-dimensional global PES for the F+CH\textsubscript{3}OH reactive system has been described in detail in Ref.[28], so only a short summary is given here. The PES was fitted to 1.21×10\textsuperscript{5} points calculated at the explicitly correlated (F12a) version [34] of coupled cluster singles doubles and perturbative triples (CCSD(T)) method with the aug-cc-pVDZ basis set and core electrons frozen. The level of theory was found to yield comparable results to the benchmark \textit{ab initio} results by Schaefer and coworkers [25]. The fitting was done with the permutation invariant polynomial-neural network (PIP-NN) method [35, 36], which has been successfully applied to many reactive systems for fitting PESs [31]. The fitting RMSEs for the training, validation, testing, total sets, and maximum deviation are 0.48, 0.45, 0.58, 0.56, and 10.55 kcal/mol, respectively.

As shown in FIG.1, along the two reaction pathways, R\textsubscript{1a} and R\textsubscript{1b}, there exist relatively deep wells before and after the submerged transition states (TSs), namely, the reactant complexes (RCs) in the entrance channels and product complexes (PCs) in the exit channels. For each channel, the three-dimensional plot (with other coordinates relaxed) as a function of the breaking and forming bond lengths is shown in FIG. 2 and FIG. 3, along with the corresponding two-dimensional contour plot. Along each reaction path, the submerged TS and the complexes before and after the TS can be clearly seen. Note that RC\textsubscript{1} is rather deep due to a three-electron-two-center hemi-bond, similar to the corresponding complex between F and H\textsubscript{2}O [37], while RC\textsubscript{2} is quite shallow as it is dominated by a van der Waals interaction.

FIG. 4 plots the QCT calculated reaction rate coefficients for channels R\textsubscript{1a}, R\textsubscript{1b}, and their sum, as a function of the inverted temperature 1000/T. Available experimental and theoretical results from the literature [15, 16, 20, 21, 24, 27] are also included for comparison. At 300 K, where most experimental data were reported, our total rate coefficient (1.65×10\textsuperscript{-10} cm\textsuperscript{3}mole\textsuperscript{-1}s\textsuperscript{-1}) is in good agreement with the experimental values (1.66×10\textsuperscript{-10}, 1.70×10\textsuperscript{-10}, and 1.27×10\textsuperscript{-10} cm\textsuperscript{3}mole\textsuperscript{-1}s\textsuperscript{-1}) [15, 16, 20, 27]. The agreement is quite good, validating the accuracy of our PES.
The total rate coefficients calculated by Jodkowski et al. [24] based on G2 calculations are also in good agreement with experiments [15, 16, 20, 27], and the current QCT results. However, the results calculated earlier by Glauser and Koszykowski based on MP2 calculations are much smaller at 300 K [21]. This is presumably due to an intrinsic barrier in the MP2 calculation for R1b [21], which is now known to be inaccurate [25]. Our QCT results predict a slight negative temperature dependence for the total rate coefficient, consistent with the barrierless nature of the reaction characterized by submerged saddle points. However, both previous theoretical results gave positive temperature dependences, which are the results of intrinsic barriers, rather than submerged ones [25] found by the lower levels of calculations [21, 24]. Indeed, it has been pointed out that the geometries and energies of the earlier theoretical calculations at the MP2 level are not sufficiently accurate, even for qualitative description [25]. We thus conclude that our new results provide a much more reliable and accurate characterization of the overall kinetics for this reaction.

In our QCT calculations, \( k_{R1a} \) is smaller than \( k_{R1b} \). This is in contrast with the earlier theoretical computations [21, 24], which predicted much larger R1a branching ratios. FIG. 5 shows our calculated branching ratio of the channel R1a (HF+CH₃O) as a function of temperature. The results are 0.43, 0.43, 0.43, and 0.40, at \( T = 200, 300, 500, \) and 1000 K, respectively, which are within the experimental values bounded between 0.4–0.6 at 300–1000 K [10, 14–16, 18, 20, 22, 27]. Our value at 300 K (0.43) is in reasonable agreement with the latest measurement of (0.504±0.013) of Fittschen and coworkers [27]. It can be seen that the QCT branching ratios are temperature independent within the range of 200–1000 K, consistent with the experimental measurements [22]. On the contrary, earlier theoretical branching ratios obtained according to transition-state theory calculations with the stationary point information computed at the level of MP2, which are also included in the figure for comparison, are within 0.55–0.70 over the temperature range of 300–1000 K [21, 24]. These results predict a much higher reactivity for the R1a channel, in contrast to the current work and most experimental results. Again, this overestimation is due to the low-level characterization of the transition states for the two channels. In particular, the MP2 work of Glauser and Koszykowski found a barrier of 1.89 kcal/mol for R1b and no barrier for R1a [21]. These are apparently in disagreement with the CCSD(T) benchmark of Schaefer and coworkers [25]. In the G2 work of Jodkowski et al. [24], on the other hand, the barrier for R1a is 1.3 kcal/mol, but it was argued that the larger R1a branching ratio was due to another submerged cyclic saddle point, which was not found in the CCSD(T) calculations [25].

The origin of the non-statistical branching ratio obtained in our QCT calculations can be attributed to the delicate balance between the relative barrier heights of the two channels and the stereodynamics at low collision energies. The latter stems from unique cones of acceptance of the two reactions, which leads to different excitation functions. The detailed analysis of the reaction dynamics, particularly the competition between the two channels, will be presented in a future publication. Finally, we note that the QCT approach does not account for tunneling, which might play a role due to the fact that the submerged barriers will rise above the reactant asymptote at large impact parameters due to the centrifugal barrier. This deficiency might account for the difference between our QCT branching ratio and the experimental value. To properly account for tunneling will require either a tour-de-force quantum dynamics investigation [32] or an approximate treatment such
as ring-polymer molecular dynamics [38]. Both are beyond the scope of this work.

IV. CONCLUSION

Recent years have witnessed extensive experimental advances in measuring kinetics and dynamics of many prototypical reactions involving more than three atoms. However, our ability to determine product branching ratios in multichannel reactions is still quite limited. On the other hand, theoretical treatments of high-dimensional systems are often hindered by the lack of accurate potential energy surfaces. The F+CH₃O reaction represents a prototype with two possible product pathways: HF+CH₃O and HF+CH₂OH. Previous theoretical calculations based on transition-state theory with the stationary point information calculated at the MP2 and G2 levels failed to account quantitatively for the rate coefficients and the measured branching ratio, due apparently to the intrinsic inaccuracy of the electronic structure methods. By using the QCT approach based on an accurate ab initio based full-dimensional PES, the calculated rate coefficients and the associated branching ratio of the competitive channels of the title reaction system have been obtained. The calculated rate coefficients are found to be in good agreement with available experimental measurements. The theoretical data also show slightly negative temperature dependence, consistent with the barrierless nature of the reaction pathways. In addition, the branching ratio of the HF+CH₃O channel is determined to be 0.40–0.43, temperature independent within 200–1000 K. This is in satisfactory agreement with the latest experimental value of (0.504±0.013) at 300 K.

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