Mode Selectivity for a “Central” Barrier Reaction: Eight-Dimensional Quantum Studies of the $O(^3P) + CH_4 \rightarrow OH + CH_3$ Reaction on an Ab Initio Potential Energy Surface

Rui Liu,† Minghui Yang,*† Gábor Czakó,*‡ Joel M. Bowman,§ Jun Li,⊥ and Hua Guo*⊥

†Key Laboratory of Magnetic Resonance in Biological Systems, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Centre for Magnetic Resonance, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China
‡Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös University, H-1518, Budapest 112, P.O. Box 32, Hungary
§Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States
⊥Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States

Supporting Information

ABSTRACT: The dynamics of a combustion reaction, namely, $O(^3P) + CH_4 \rightarrow OH + CH_3$, is investigated with an eight-dimensional quantum model that includes representatives of all vibrational modes of $CH_4$ and with a full-dimensional quasi-classical trajectory (QCT) method. The calculated excitation functions for the ground vibrational state $CH_4$ agree well with experiment. Both quantum and QCT results suggest that excitation of the stretching modes of $CH_4$ enhances the reaction, while the bending and umbrella modes have a smaller impact on reactivity, again consistent with experimental findings. However, none of the vibrational excitations has comparable efficiency in promoting the reaction as translational energy.

SECTION: Kinetics and Dynamics

Polanyi’s rules have been a guiding light for understanding mode and bond selectivity in gas-phase bimolecular reactions. On the basis of observations in atom–diatom reactions, Polanyi summarized in 1972 the role played by various forms of energy in promoting reactivity. For a reaction with an “early” (reactant-like) barrier, for example, translational energy is more effective than vibrational energy. On the other hand, vibrational energy has higher efficacy in promoting reaction with a “late” (product-like) barrier. The extension of the Polanyi’s rules to reactions involving polyatomic molecules is not straightforward. Indeed, the capacity of various reactant vibrational modes for promoting reactivity is likely to be different. Nevertheless, these rules have been largely upheld for such reactive systems, but exceptions have been reported recently for the $F/Cl + CHD_3$ reactions. The latter have been attributed to prereaction van der Waals complexes along the reaction path, although the latest quantum dynamical study on the $Cl + CHD_3$ reaction suggested that the violation of the Polanyi’s rules is restricted to a small energy range. However, most previous systems have either early or late barriers, and few have a “central” barrier, which is neither reactant-like nor product-like. In order to establish general rules of thumb for these complicated reactions, it is important to investigate such reactions.

The $O(^3P) + CH_4 \rightarrow OH + CH_3$ reaction, which represents an important initial step in hydrocarbon combustion, provides an ideal platform for studying reactions with a central barrier. Its near thermoneutrality ($\Delta H^0 = 2.48$ kcal/mol) leads to a transition state that is neither reactant-like nor product-like. At the saddle point, approximately 14 kcal/mol above the $O(^3P) + CH_4$ potential minimum, the breaking $C–H$ and forming $O–H$ bonds are stretched by 0.2 Å relative to the corresponding bond lengths in the reactant $CH_4$ and the product $OH$. As a result, it presents a unique middle point between the much studied $F$ and $Cl + CH_4$ reactions, which have clear early and late barriers, respectively. In some sense, the title reaction is similar to the much studied $H + CH_4 \rightarrow H_2 + CH_3$ reaction, although the former is of the heavy–light–heavy (HLH) type with a much smaller skew angle.

The title reaction has been extensively investigated experimentally. Recent molecular beam experiments have measured the excitation function, as well as differential cross sections. The experimental data are consistent with a simple abstraction mechanism. In particular, the excitation function of the $O + CH_4$ reaction has a threshold of $\sim 8$ kcal/mol and increases monotonically with the collision energy. In addition, the excitation of the $C–H$ vibration in $CHD_3$ results in significantly enhanced reactivity for the $OH +
integral cross section (ICS) was computed using the approximation.44 In addition, the QM ICSs have been calculations reported here were carried out with and Liu.25 However, due to possible large quantum e-
dynamics methods.29 Recently, the first ab initio full-dimen-
sional global PES has been developed by fitting a large number of accurate energy points,15 using a permutationally invariant polynomial method.42 The minimum-energy path for the reaction is depicted in Figure 1, with the geometries and
energies of stationary points. QCT studies of the O + CHD3 reaction have been reported on this PES by two of us,15 and the results are in good accord with the recent experiment by Wang and Liu.25 However, due to possible large quantum effects (which are indeed found), such as tunneling and zero-point energy (ZPE), in this system, it is highly desirable to understand the reaction dynamics with a QM model. In this Letter, we report the first eight-dimensional (8D) QM reactive scattering calculations for this prototypical reaction on the new PES, along with full-dimensional QCT results.
The 8D QM model is similar to the pioneering work of Palma and Clary,35 in which the Cn symmetry of the CZ3 moiety in the X + YCZ3 → XY + CZ3 reaction is maintained while other degrees of freedom are explicitly treated. This 8D model represents a realistic reduced-dimensional model for such a reaction because it includes representatives of all CH4 vibrational modes, particularly the asymmetric stretching mode ignored in the 7D model.38 A coordinate transform was recently introduced to render the CH4 vibrational Hamiltonian more physically transparent and easier to discretize.43 This new 8D Hamiltonian has already been applied to the H + CH4 reaction with good agreement with experiment.43 The QM calculations reported here were carried out with J = 0, and the integral cross section (ICS) was computed using the J-shifting approximation.44 In addition, the QM ICSs have been multiplied by a factor of 4 to account for all possible reaction channels. The details of the QM model and parameters used in the calculations are given in the Supporting Information (SI). On the other hand, the QCT calculations are standard, as described in our earlier work.43 Neither ZPE correction nor product state resolution is imposed as a detailed analysis of the state-to-state QCT calculations will be reported in a subsequent publication. All ICSs are multiplied by the electronic factor of 2/3 to account for the spin–orbit degeneracy of the reactants.

Figure 2 compares the calculated and measured ICSs for the ground vibrational state of CH4, and the agreement is excellent.

The QM ICS correctly predicted a reaction threshold of ~8 kcal/mol as well as the unique concave-up energy dependence observed in the experiment.28 The reaction threshold is significantly lower than the classical and ZPE-corrected barriers (14 and 11 kcal/mol), signifying substantial tunneling. The QCT results are also in good agreement with the experiment, although slightly larger than the QM counterparts, which might be due to a number of factors such as the difference in dimensionality. The excellent overall agreement with experiment confirms again the accuracy of the PES.

To examine mode selectivity, the ICSs for several vibrational excited states of CH4 are plotted in Figure 3 in both collision and total energy. For the latter, the QM vibrational frequencies of CH4 are from our reduced-dimensional model, which are compared in the SI with those in the full-dimensional model, while the normal-mode frequencies on the PES were used in the QCT results. The vibrational state of CH4 is denoted by (n1, n2, n3, n4) where the quantum numbers are for the symmetric stretching, bending, asymmetric stretching, and umbrella modes, respectively. As shown in the upper panel of the figure, both QM and QCT results indicate that excitations of both the symmetric and asymmetric stretching modes, (1,0,0,0) and (0,0,1,0), clearly enhance reactivity, with the former having higher efficacy. This observation is consistent with earlier reduced-dimensional QM models17,33,34,38 and experimental studies of the X + CH4 reactions (X = F, Cl).4,5 Unfortunately, there has not been any experimental study on stretch excited CH4 with O(3P), although C–H vibrationally excited CH4 has been investigated.25 The enhancement observed here is consistent with that experiment44 and subsequent theory.15 Interestingly, excitations in these two stretching modes do not enhance the reaction more than translational energy, as shown by the lower panel of Figure 3, at least in energies less than 23 kcal/mol.

As shown in Figure 3, our QM results indicate that the excitation in the CH4 bend (0,1,0,0) promotes the reaction

Figure 1. Schematic plot of the PES along the reaction path with the geometries and energies (in kcal/mol) of the stationary points.
The Journal of Physical Chemistry Letters

Letter

strongly coupled with the reaction coordinate near the transition state, which is essentially the asymmetric stretch of the transferring H between C and O in this HLH system. It is well-known that in a vibrational adiabatic model, the frequency of the CH$_3$ symmetric stretching mode is significantly lowered when CH$_4$ is approached by a reactant such as Cl$^+$ or O$^{14,47}$ as the vibration is coupled into the reaction coordinate. Thus, the adiabatic barrier associated with the symmetric stretching excited state is lower than that of the ground vibrational state, explaining its strong capacity to enhance the reactivity. On the other hand, the enhancement of the asymmetric stretching mode is more subtle as it is associated with a spectator mode in the vibrational adiabatic model.$^{34,47}$ It has, however, been argued that this mode couples to other reactive modes nonadiabatically via Coriolis terms.$^{46}$ Our results also suggest that the influence of both the bending and umbrella modes on the reactivity is relatively small, suggesting that their couplings to the reaction coordinate are weak. This observation is in sharp contrast to an earlier reaction path analysis, which predicted strong enhancement of reactivity for umbrella excited CH$_4$ due to its strong coupling with the reaction coordinate.$^{41}$ This failure underscores the complexity in the multidimensional dynamics.

In summary, we have presented 8D QM and full-dimensional QCT studies of the title reaction on an ab initio PES. The reasonably good agreement with available experimental results confirms the accuracy of the PES. In addition, the mode selectivity of the reaction has been investigated. Our results indicate that excitations in the stretching modes of CH$_4$ significantly enhance the reaction, with the symmetric stretch having a higher efficacy. On the other hand, excitations in the bending and umbrella modes have a smaller impact. Interestingly, none of the vibrational excitations are as efficient as translational energy in promoting the reaction. These results, along with recent observations on the F/Cl + CHD$_3$ reactions,$^{8,9}$ suggest that conventional wisdom symbolized by the venerable Polanyi's rules may be in need of generalization. Theoretical studies of the reaction dynamics of these prototypical reactions will play an important role in shaping up our deeper understanding of bimolecular reactions with polyatomic molecules.

ASSOCIATED CONTENT

Supporting Information
Detailed theory and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: yangmh@wipm.ac.cn (M.Y.); czako@chem.elte.hu (G.C.); hguo@unm.edu (H.G.).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

R.L. and M.Y. were supported by National Science Foundation of China (Projects 20921004, 21073229, and 20833007), G.C. by the Scientific Research Fund of Hungary (OTKA, NK83583) and the Bolyai Research Fellowship of the Hungarian Academy of Sciences, J.M.B. by the Department of Energy (DE-FG02-97ER14782), and J.L. and H.G. by the...
Department of Energy (DE-FG02-05ER15694 to H.G.). We thank Prof. Kopin Liu for some stimulating discussions.

REFERENCES


