Theoretical Study of the Validity of the Polanyi Rules for the Late-Barrier Cl + CHD₃ Reaction

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S *Supporting Information*

ABSTRACT: The Polanyi rules, which state that vibrational energy is more efficient in promoting a late-barrier reaction than translational energy, were questioned recently by an experimental unexpected finding that the CH stretch excitation is no more effective in promoting the late-barrier Cl + CHD₃ reaction than the translational energy. However, the present quantum dynamics study on the best-available potential energy surface for the title reaction reveals that the CH stretch excitation does promote the reaction significantly, except at low collision energies. Further studies should be carried out to solve the disagreements between theory and experiment on the reaction.

Cl + CHD₃ → HCl + CD₃
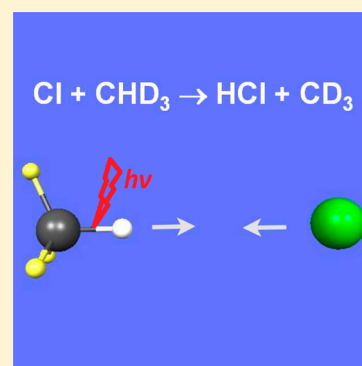
SECTION: Kinetics and Dynamics

In a typical chemical reaction with an energetic barrier, there is a saddle point that the reactants must surmount to reach the product side. Which form of energy initially deposited in reactants, translational or vibrational, is more efficacious in surmounting the barrier is one of the central topics in the field of reaction dynamics. In 1972, on the basis of theoretical studies of some model atom−diatom reactions, Polanyi proposed the well-known Polanyi rules, which state that vibrational energy is more efficient in promoting a late-barrier reaction (that is, a transition state resembling the products) than translational energy, whereas the reverse is true for an early barrier reaction.[1] Over the past decades, the rules have enjoyed great successes not only on the atom−diatom reactions[2,3] but also on the H and Cl + H₂O reactions and their isotope analogues.[4−9]

However, the generality of these rules for the Cl + CH₄ reaction was questioned recently by an unexpected experimental finding on the title reaction.[10] Following the early work, carried out in the groups of Crim,[11] Zare,[12] and Orr-Ewing,[13] Liu and co-workers performed crossed molecular beam experiments on the title reaction with the CH vibration in the ground and first stretch vibrational excited states and measured integral and differential cross sections for product CD₃ in the ground vibrational state (CD₃($\nu = 0$)). They found that at the same total energy, the integral cross section for

CD₃($\nu = 0$) for the initial CH stretch excited state, $\sigma_s(\nu = 0)$, is smaller than that at low collision energies and becomes comparable at higher collision energies to the corresponding one for the ground initial state, $\sigma_g(\nu = 0)$. On the basis of their estimation that the CD₃($\nu = 0$) product accounts for 2/3 of the total product distribution for the initial CH excited state, they concluded that the CH stretch excitation is no more effective[10] or slightly more effective[14] in promoting the late-barrier Cl + CHD₃ reaction than an equivalent amount of translational energy, in contradiction with the Polanyi rules. Equally interesting, the same group also found that the CH stretch excitation inhibits CH bond cleavage in the early-barrier F + CHD₃ reaction.[15]

To study the reaction theoretically, Czakó and Bowman recently developed a high-quality, full-dimensional global potential energy surface (CB PES) for the system based on accurate ab initio calculations.[16,17] Quasiclassical trajectory (QCT) calculations carried out on the PES achieved unprecedented agreement with experiment on the rotational distributions of the HCl product for the Cl + CH₄($\nu = 0$) → HCl($\nu'=0,j'$) + CH₃ reaction.[16−19] The calculated ratio

between $\sigma_s(\nu = 0)$ and $\sigma_g(\nu = 0)$ as a function of total energy agreed with experimental result rather well for the title reaction. However, when summing over all product states, the QCT total cross section for the CH excited initial state, σ_s, was considerably larger than σ_g at high total energies, indicating that the Polanyi rule works quite well except at low collision energies. Because the QCT method is not exact, it is highly desired to carry out a quantum dynamics study to investigate the influence of CH stretch excitation on the reaction more accurately.

In this work, we report a quantum dynamics study of the title reaction on the CB PES. Despite the fact that it is possible now to compute state-to-state differential cross sections for some simple four-atom reactions without any dynamical approximation,[20] it is still extremely difficult at present to exactly treat a six-atom reaction such as the title reaction in full dimensions, although some significant progress has been made in the direction.[21,22] Consequently, various reduced-dimensionality models[23−25] have been developed to study the reactions involving CH_4 and its isotopic variants. The model employed in this study was originally proposed by Palma and Clary[26,27] by restricting the nonreacting CD_3 group to maintain $C_{3\nu}$ symmetry. With the bond length of CD fixed at its equilibrium value because it does not change during the reaction, the number of the degrees of freedom included in the reactive scattering study was reduced to seven. This reduction was verified to have a quantitative level of accuracy[22] when the $C_{3\nu}$ assumption holds well for reactions such as the title reaction in the ground initial state or in the CH stretch excited initial states. Recently, using the model, we obtained the integral cross sections for the $H + CD_4 \rightarrow HD + CD_3$ reaction in excellent agreement with experiment.[28] The time-dependent wave packet method was employed to solve the seven-dimensional Schrödinger equation for the model.[29] In order to obtain the product CD_3 umbrella vibrational state-resolved reaction probability, we used a total number of ∼6.5 billion basis functions with a dividing surface for reactive flux measurement at a quite large C−H distance of 5 bohrs. The centrifugal-sudden approximation was employed to calculate the reaction probabilities for the total angular momentum $J > 0$ to yield the integral cross sections for the title reaction. More detailed descriptions of the quantum scattering calculations can be found in the Supporting Information (SI).

Figure 1A shows the quantum integral cross sections for the ground initial state as a function of collision energy, together with the QCT counterparts. The quantum ICS for the ground initial state, σ_g, increases more or less linearly with the collision energy with a threshold of ∼2.8 kcal/mol. Overall, it is very small, only reaching a value of about 0.09 Å^2 at E_c = 15 kcal/mol. The published QCT σ_g is larger than the current quantum ICS by more than a factor of 2 at most collision energies. However, the QCT ICS does depend significantly on how the issue of product zero-point energy (ZPE) is treated. Following our previous work,[17] we discard trajectories in which the polyatomic product, that is, CD_3, does not have a vibrational energy larger than its ZPE. This ZPE-constrained ICS agrees with the QM result rather well. For that initial state, the product CD_3 is found mainly in its ground umbrella $\nu = 0$ state, as also shown in the figure. Although the $\nu = 0$ population decreases with the collision energy, it still has a value of 67% at E_c = 15 kcal/mol, in comparison with the QCT result of 66% at E_c = 15.6 kcal/mol.
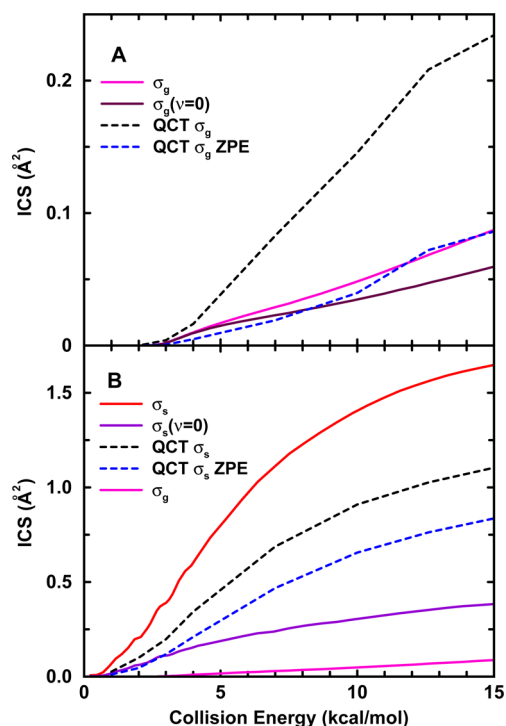
Figure 1. (A) The QM total and the product $CD_3(\nu = 0)$ cross sections for the ground initial state, in comparison with the standard QCT and ZPE-constrained ICS. (B) Same as (A), except for the initial CH excited state. The ICS for the ground initial state is also shown for direct comparison.

The ICSs for the CH stretch excited initial state are depicted in Figure 1B. The quantum σ_s has a very low threshold energy with an overall magnitude much larger than σ_g. At E_c = 15 kcal/mol, σ_s reaches 1.6 Å^2, almost a factor of 18 larger than σ_g. At lower collision energies, the ICS ratios between these two initial states are even larger. Clearly, the CH stretching excitation enhances the reactivity dramatically in the entire collision energy region. The initial CH stretch excitation also leads to a significant increase of the populations in product CD_3 umbrella excited states. The population of the product $CD_3(\nu = 0)$ only comprises ∼1/4 of the total ICS, as shown in the figure, in good agreement with the QCT result of 19% at E_c = 12.6 kcal/mol but much smaller than the experimental estimation of 2/3.[10] Overall, the behavior of $\sigma_g(\nu = 0)$ and $\sigma_s(\nu = 0)$ shown in Figure 1 are rather different from the experimental results given in Figure 2A of ref 10. In contrast to the ground initial state, the published QCT σ_s is considerably smaller than its quantum counterpart. The imposition of product ZPE constraint reduces the QCT ICS for that initial state further to about half of the corresponding QM values.

The effect of CH stretch excitation versus an equivalent amount of translational energy in promoting the reaction can be seen from $\sigma_s(E_c)/\sigma_g(E_c + E_\nu)$, shown in Figure 2A. The QM ratio of the total cross sections increases rapidly with the collision energy, reaching 1 at E_c = 0.85 kcal/mol and the maximum value of 12.4 at $E_c \approx$ 8 kcal/mol, and it then slowly declines with the further increase of collision energy. Furthermore, although the ICS ratio for product $CD_3(\nu = 0)$ shown in Figure 2B is considerably smaller than that for the total ICS in Figure 2A, it is still substantially larger than the experimental results shown in Figure 2E in ref 10.
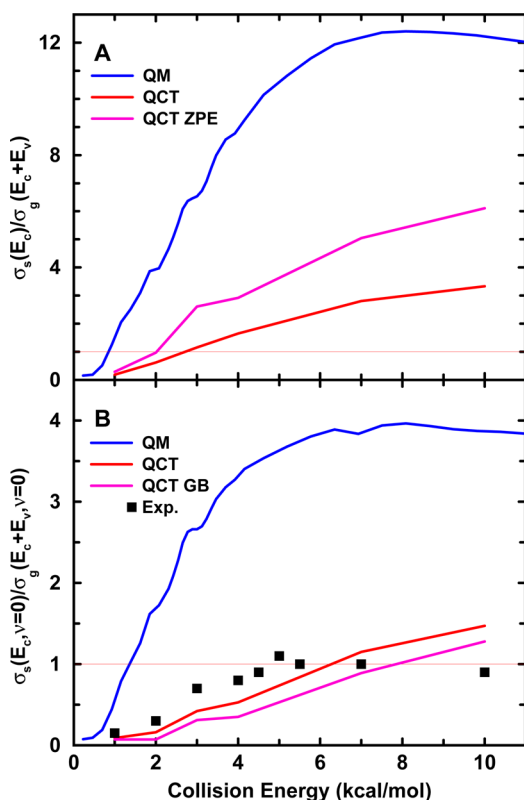
Figure 2. (A) The preferential vibrational enhancement factors of the total cross section for the CH stretch excited reactant, based on an equivalent amount of total energy, where the vibrational energy E_v is 8.5 kcal/mol on the CB PES, together with the standard QCT and ZPE-constrained counterparts. (B) The preferential vibrational enhancement factors of the product $CD_3(\nu = 0)$ cross section for the CH stretch excited reactant, in comparison with the standard QCT and GB-QCT results, as well as the experimental measurement.[10]

On the other hand, because the standard QCT $\sigma_g(E_c)$ is larger than the present QM $\sigma_g(E_c)$ by more than a factor of 2 but the standard QCT $\sigma_s(E_c)$ is smaller than the QM $\sigma_s(E_c)$ considerably, the QCT ICS ratio between these two states is substantially smaller than the corresponding QM ratio (Figure 2A). The imposition of the product ZPE constraint increases the QCT ratios considerably. The ZPE-constrained QCT ratio becomes more than 1 at $E_c = 2$ kcal/mol and reaches 6 at $E_c = 10$ kcal/mol, in reasonable agreement with the QM ratio. However, because the QCT populations for the product $CD_3(\nu = 0)$ state for both initial states are quite close to the QM counterparts, the QCT ratio for the product $CD_3(\nu = 0)$ ICS is also considerably smaller than the corresponding QM ratio (Figure 2B) but agrees with experimental results rather well, as shown in the figure. In contrast to the QCT and ZPE-constrained QCT ratios shown in Figure 2A, the imposition of the product vibrational energy constraint with the Gaussian binning (GB) procedure[30] slightly reduces the $CD_3(\nu = 0)$ ratio, as shown in Figure 2B.

Therefore, on the basis of the result of the present quantum calculation on the CB PES, the CH stretch excitation is more effective in promoting the reaction than the translational energy, except in the low collision energy region (<1 kcal/mol), implying that the Polanyi rules hold for this late-barrier polyatomic reaction, except at very low collision energies. The QCT calculations, in particular, the ZPE-constrained QCT calculation, largely support QM result. On the other hand, the

QM ICS ratio for the product $CD_3(\nu = 0)$ is considerably larger than that from the QCT calculation, which is in quite good agreement, perhaps fortuitously, with the experiment. Apparently, significant differences between experiment and QM theory exist. Differences between QM theory and QCT theory also exist. Interestingly, an ongoing experiment found that the experimental preferential vibrational enhancement factors of the product $CD_3(\nu = 0)$ cross section for the CH stretch excited reactant shown in Figure 2B were underestimated by roughly a factor of 2−3 due to neglect of the higher rotational states of $CD_3(\nu = 0)$ in probing (private communications). This may improve the agreement between experiment and the present QM calculation. Further studies, both theoretical and experimental, should be carried out to resolve the source of the differences.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
A brief description of the quantum scattering method employed in the study and the numerical parameters for the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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