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Joseph Gomes, Martin Head-Gordon, Alexis T. Bell

Institutions: University of California, Berkeley

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Gomes, Joseph
Head-Gordon, Martin
Bell, Alexis T

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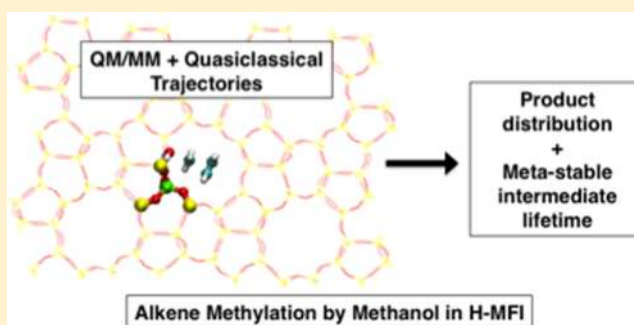
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Reaction Dynamics of Zeolite-Catalyzed Alkene Methylation by Methanol

Joseph Gomes,[†] Martin Head-Gordon,^{*,‡} and Alexis T. Bell^{*,†}[†]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720-1462, United States[‡]Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1461, United States

S Supporting Information

ABSTRACT: A hybrid quantum mechanics/molecular mechanics (QM/MM) model and the quasiclassical trajectory (QCT) method have been combined to study the reaction of alkene methylation by methanol catalyzed by the zeolite H-MFI. The rate-limiting step of this reaction is the methylation of the alkene, and the apparent activation energy calculated at the ω B97X-D/6-31G(d,p)// ω B97X-D/6-311++G(3df,3pd) level of theory for this step agrees well with experiment and previous full QM studies. Following the ethene methylation transition state toward the products along the intrinsic reaction coordinate reveals the existence of a protonated cyclopropane (PCP⁺) carbocation intermediate. A similar protonated methylcyclopropane (mPCP⁺) carbocation intermediate is found for propene methylation. The intermediates produced during the alkene methylation reaction are metastable with a lifetime of $O(1\text{ ps})$ obtained from QCTs. Because of the short lifetime of these intermediates, the available energy in the carbocation is not in thermal equilibrium distribution with the zeolite lattice before subsequent reaction occurs. The qualitative difference between product distributions obtained by static and dynamic reaction pathways suggests the pathways of zeolite-catalyzed reactions proceed through high-temperature pathways that differ from the 0 K potential energy surface. The transformation of the m-PCP⁺ intermediate to the longer-lived secondary 2-butyl carbocation observed during QCTs suggests that more stable carbocations can properly thermalize and exist as reaction intermediates for longer than 1 ps.



INTRODUCTION

Proton-exchange zeolites are solid acid catalysts that are used in a large number of processes, such as hydrocarbon cracking, isomerization, and alkylation.^{1–3} The conversion of hydrocarbons by zeolites is of great industrial relevance, yet the detailed mechanisms by which these transformations occur are not all fully understood. An important example is the conversion of methanol to hydrocarbons (MTH) catalyzed by H-MFI, which was first discovered and commercially implemented by Mobil Oil in 1986.⁴ Subsequently developed processes include the Topsøe integrated gasoline synthesis (TIGAS) process,⁵ the Lurgi methanol to propene (MTP) process,⁶ and the Norsk Hydro/UOP methanol to olefins (MTO) process.⁷

Much of the initial research on the MTH process focused on how the first C–C bond formed, given two or more methanol molecules reacting to form initial alkenes and water.⁸ One scheme proposed by Dahl and Kolboe,^{9,10} the hydrocarbon pool mechanism, assumes that light olefins are formed via repeated methylation and subsequent dealkylation reactions of aromatic reaction centers acting as organic cocatalysts within the pores of the zeolite. More recent studies have shown that methanol carbons atoms are readily incorporated into the C₃₊

olefin products in a scheme parallel to the hydrocarbon pool mechanism through the repeated methylation/cracking of olefin intermediates.^{11,12} Thus, alkene methylation is a key reaction in the conversion of methanol to hydrocarbons over the H-MFI catalyst.

Two mechanisms have been proposed for alkene methylation. The first is the concerted mechanism. In this case, methanol adsorbs molecularly at a Brønsted acid site and then reacts with adsorbed alkene to produce the next higher alkene and water. The alternative is the stepwise mechanism. The first step in this scheme is the same as that for the concerted mechanism; however, in this case, the adsorbed methanol next undergoes reaction to form methoxy species and water. Methylation occurs by reaction of the methoxy species with adsorbed alkene to form the next highest alkene. Distinguishing between these mechanisms experimentally is difficult because the observed kinetics—zero order in methanol and first order in alkene—can be rationalized using either mechanism. A recent review on the mechanistic aspects of alkene methylation

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concluded that the concerted mechanism should be the dominant mechanism; however, there is a higher temperature at which the stepwise mechanism should dominate due to the entropy gain associated with the release of water to the gas phase prior to methylation.¹³ An attempt to identify the relative importance of the concerted and stepwise mechanisms for methanol alkylation of ethene, propene, and isobutene over H-ZSM-22 (TON) has been reported in a study that combined DFT analysis of the two reaction pathways with a microkinetic simulation of the reaction kinetics.¹⁴ The authors conclude that below 350 K the concerted pathway prevails, but at temperatures above 600 K and pressures below 1 bar, the stepwise mechanism becomes dominant, and at pressures approaching 20 bar, both pathways become competitive.

A notable point is that all previous theoretical analyses of alkene methylation have focused on determining the transition states (TSs) for C–C bond formation by methanol–olefin coupling and the associated activation energy.^{15–19} The implicit assumption in these studies is that each TS leads to a unique reactant/product pair, i.e., those to which the TS leads to via the intrinsic reaction coordinate. What this approach neglects is the possibility that multiple product channels might form from a given transition state, that identical products might be formed from multiple unique transition states as well as the possibility of any metastable intermediates between the reactants and products. A recent exception is the work of Zimmerman et al. demonstrating the use of quasi-classical trajectories to investigate the unimolecular cracking of *n*-pentane in H-MFI.²⁰ The determination of the final product distribution by quasi-classical trajectories initiated at the rate-determining transition state improved the estimate of alkane cracking product selectivity compared with experimental observations by an order of magnitude relative to the estimate made by calculating rates of reaction leading from the metastable intermediate using conventional static reaction pathways. Svelle and co-workers,¹³ as well as Waroquier and co-workers,¹⁵ have reported the existence of a carbocation intermediate directly following the rate-limiting step of alkene methylation but give no information on the reaction pathways leading from these intermediates to the final product of alkene and water. Motivated by these reports, we have investigated the applicability of trajectory simulations to provide information on the reaction pathways of higher alkene formation and the lifetimes of various intermediates that can be formed in alkene methylation.

Quasi-classical trajectories (QCT) are a useful and computationally tractable tool for studying complex reaction pathways through molecular dynamics simulations. Quasiclassical sampling puts vibrational energy into each normal mode when setting up the initial nuclear velocities. The initial conditions are chosen such that the occupation numbers of the vibrational state for each mode follow a Boltzmann distribution for quantum harmonic oscillators at the simulation temperature. The rest of the trajectory is then governed by classical mechanics. QCT simulations initiated at a TS will sample realistic pathways toward the products and can therefore give the product distribution leading from a particular TS. The effectiveness of QCT's is well-known from applications in reactive scattering^{21–24} and from several successful applications to molecular dynamics simulations.^{25–27} Here, advantages over purely classical simulation techniques stem from the fact that QCT initial conditions match real chemical systems more closely by including some effects of quantum mechanical

nuclear motion. This is particularly important for systems where zero point energies are large, such as when C–H bonds are vital to the reactivity.

In this study, we utilize the combination of QCT and QM/MM to sample the reaction pathways leading away from the rate-limiting transition states of ethene and propene methylation. The reaction intermediates and transition states observed from QCT were also located on the potential energy surface to develop a complete description of the reaction pathways of alkene methylation by methanol that includes carbocation intermediates. The QCTs are used to determine the lifetime of the metastable carbocation intermediate formed post-rate-limiting step and to calculate a product distribution associated with each transition state. The qualitative difference between product distributions obtained from static (Gibbs free energy 623 K) and dynamic (QCT 623 K) reaction pathways suggests that zeolite-catalyzed reactions proceed via high-temperature pathways that differ from those predicted from 0 K potential energy surface. The transformation of these intermediates to the longer-lived secondary carbocations suggests that more stable carbocations can properly thermalize and exist as the selectivity-determining intermediates of the alkene methylation reaction.

THEORETICAL METHODS

Quantum Mechanics/Molecular Mechanics. The zeolite H-MFI was represented by a cluster model containing 464 tetrahedral (T-) centers (Figure 1). The crystallographic

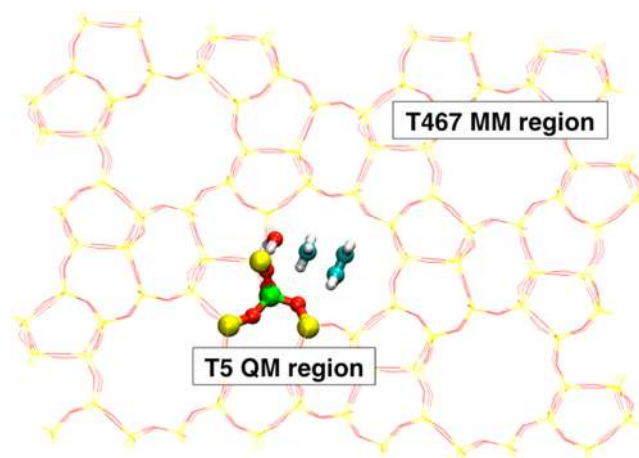


Figure 1. Model of H-MFI containing 467 tetrahedral (T-) atoms used in this work.

structure of MFI was used to determine the positions of all atoms in the zeolite cluster model. The charges on the atoms located at the cluster surface were scaled such that the cluster had net zero charge.²⁸ The lattice atoms away from the active region were frozen at their crystallographic positions. To produce an acidic site, a Si atom in the cluster was isomorphically substituted by an Al atom, and the resulting charge imbalance was compensated by a proton. The Brønsted acid site was modeled using a QM region of five tetrahedral atoms and the balance of the cluster modeled by molecular mechanics. The MFI unit cell has 12 unique T atom positions that can be substituted to produce an acid site. While the distribution of Al in MFI is unknown and depends on the conditions of zeolite synthesis, there is some evidence that the T12 position is favored.^{29,30} For this reason, we consider the Al

to be in the T12 site and found the proton to be most stable in the Al12–O20(H)–Si3 position.

Dynamics simulations were carried out using the B97-D density functional³¹ paired with the 6-31G* basis set. For the position of the zeolite represented by MM, the charges and Lennard-Jones parameters for Si and O chosen were taken from our previous work²⁵ in which these parameters had been selected to achieve close agreement with all-QM and experimental values of heats of molecular adsorption and activation energies. The MM charge parameters were $0.7e$ and $-0.35e$ for Si and O framework atoms, respectively. The Lennard-Jones parameters were $\epsilon_{\text{Si}} = 0.2$ kcal/mol, $\epsilon_{\text{O}} = 0.075$ kcal/mol, $R_{\text{Si}} = 2.2$ Å, and $R_{\text{O}} = 1.77$ Å for the framework atoms. Lennard-Jones parameters for hydrocarbons were taken from CHARMM.³² Although optimized geometries from the B97-D/6-31G* level of theory were used to minimize computational effort in the dynamics simulations, additional optimizations were performed using ω B97X-D functional³³ and the 6-31G** basis with single point calculations done by dual-basis extrapolation³⁴ to the ω B97X-D/6-311++G(3df,3pd) level of theory to obtain the final energy describing the reaction pathways.³⁵ All transition state geometries were determined by optimization of the highest lying point along the freezing string pathway connecting reactant and product.³⁶ Frequency computations were performed on all intermediates to ensure that geometries corresponded to local minima (i.e., zero negative eigenvalues) or transition states (one negative eigenvalue). Reported energies for the methylation TS's were zero-point corrected and further converted to enthalpies and free energies at 623 K using the Grimme's modified rigid rotor-harmonic oscillator approximation.³⁷

Reaction Path Simulations. Three types of reaction path simulations are compared: the minimum energy pathway (MEP) obtained from IRC steepest descent simulations, a dynamic reaction coordinate (DRC) (corresponding to a single trajectory launched along the IRC), and QCT. The minimum energy pathway (MEP) leading from the methylation transition states was determined by following steepest-descent path in mass-weighted Cartesian coordinates using a predictor-corrector algorithm by Schmidt, Gordon, and Dupuis.³⁸ In all MEP calculations, the reaction pathway was terminated once the norm of the gradient at the reaction path end point reached a threshold of 10^{-3} Ha bohr⁻¹. The pathway was terminated because the search direction became ill defined as the gradient converged, leading to divergence from the true reaction pathway. The resulting geometries at the end points of the MEP were geometry optimized. To produce the final reaction pathway, a growing string³⁹ calculation was initiated between the optimized minimum and the true saddle point. This reaction pathway was optimized until the sum of the magnitude of perpendicular forces on all nodes is less than 0.1 Ha Å⁻¹. All simulations were performed utilizing a development version of the Q-Chem 3.2 software package.⁴⁰

Molecular Dynamics. Direct dynamic simulations, in which the energy and force are computed via *ab initio* theory at each time step, were carried out in order to sample reaction pathways followed after the rate-determining step. QCT trajectories were initiated by sampling the excitation levels of each vibrational mode at the TS geometry. The energy from these vibrations was placed into the kinetic energy of each normal mode, and these vibrations were converted to Cartesian velocities to start the trajectory. To this end, we employed a modification of the QCT implementation of Lambrecht et al.²⁴

in a development version of the Q-Chem program package.³⁴ We modified the code so that the transition state mode was populated in a specified direction (i.e., forward or reverse) along with the remaining vibrational modes. The QCT approach assures that the initial nuclear velocities are selected so as to represent the quantum effects of nuclear motion and, most importantly, that each mode contains at least zero-point energy. Each trajectory is integrated for a total of 1.3 ps with a time step of 0.5 fs.

The DRC is a dynamic reaction path corresponding to a trajectory which is initiated in the forward direction while all orthogonal modes are initiated at zero velocity.⁴¹ DRC provides the minimum description of system dynamics starting at the TS while excluding the influence of nuclear motion in the vibrational modes orthogonal to the TS. The DRC is a trajectory that can be considered as an intermediate situation between IRC and QCT, where some but not all effects of dynamics are taken into account.

At termination after 1.3 ps, the QCT trajectories were further analyzed to give information about the product distribution of each reaction and on the lifetime of metastable intermediates formed after the rate-limiting transition state of methylation. The products of the methylation reaction were sorted into five categories: carbocation and water, alkene and water, alkoxide and water, oxonium ions (protonated alcohol), and cyclic alkane and water. Trajectories which remained as carbocation intermediates were considered unreactive. The time at which a trajectory becomes reactive was determined by following the formation of chemically relevant C–O and O–H bonds while noting the time step where the bond length is at or below a certain threshold ($r_{\text{CO}} = 1.6$ Å and $r_{\text{OH}} = 1.1$ Å). The ratio of unreactive trajectories to total trajectories was calculated at each time step and used to determine the survival probability of the metastable intermediate formed after the rate-limiting transition state. To obtain the lifetime of the intermediate, the rate constant was obtained by modeling the survival probability as a first-order decay process. The fit was done over all times where the decomposition rate was greater than 0.01 fs⁻¹.

RESULTS AND DISCUSSION

Choice of Reaction Mechanism. As noted in the Introduction, methanol alkylation of alkenes can occur via two mechanisms: concerted and stepwise. Analysis of the Gibbs free energies for these two pathways (see Supporting Information) reveals that at 1 bar and 623 K the apparent Gibbs free energies of activation for the two pathways are virtually the same, but the apparent Gibbs free energy for the concerted pathway becomes lower with increasing pressure. Thus, for conditions typical of those used in industry for the MTH process (623 K and 20 bar), reaction via the concerted pathway is 25-fold higher than via the stepwise pathway.¹³ For this reason, we have limited our subsequent discussion to an analysis of the enthalpy and Gibbs free energy changes occurring along the pathway for the concerted mechanism.

Ethene Methylation Minimum Energy Pathway. The minimum energy structure for methanol at the T12 site in H-MFI is adsorption end-on over the acid site located in the 10-membered ring of the sinusoidal channel leading into the intersection of H-MFI, forming a strong hydrogen bond interaction between the acidic proton and the methanol oxygen. Further stabilization of the adsorption complex is provided by an additional hydrogen bond between the hydroxyl proton and a zeolitic oxygen atom. The heat of adsorption of

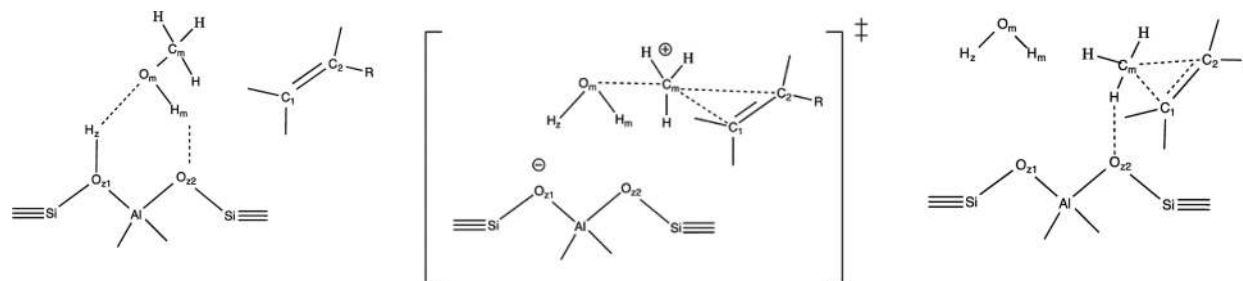


Figure 2. Depiction of alkene methylation by methanol in H-MFI (R = H ethene and R = CH₃ propene): (1) coadsorption of methanol and alkene, (2) alkene methylation transition state, and (3) metastable intermediate formed after methylation.

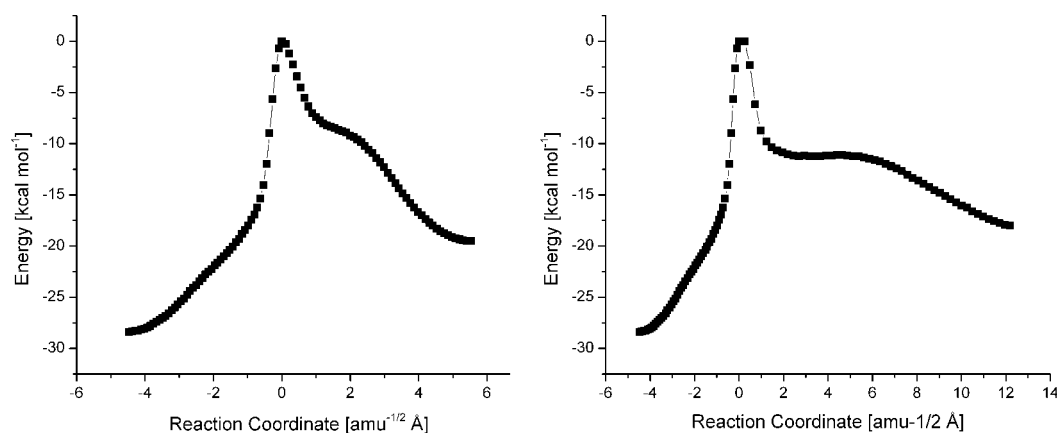


Figure 3. Intrinsic reaction coordinate diagrams for ethene methylation (A) and propene methylation (B).

methanol over H-MFI at 623 K is calculated to be 28.1 kcal mol⁻¹, in good agreement with the experimental heat of adsorption determined by microcalorimetry (-27.5 ± 1 kcal mol⁻¹ at 400 K).⁴² The free energy of methanol adsorption is favorable compared with the gas phase (-4.1 kcal mol⁻¹, Supporting Information, Table IVa). This state is predicted to be the lowest lying point on the free energy surface, making it the resting state of the catalyst under methylation operating conditions. The minimum energy structure for coadsorption of methanol and ethene in H-MFI is depicted in Figure 2. The heat of coadsorption relative to the gas phase is -33.6 kcal mol⁻¹. Methanol remains in the 10-membered ring end-on over the acid site, while ethene is physisorbed in the intersection of the straight and sinusoidal channels. The strong preferential adsorption of methanol over the active site prevents ethene from interacting with the acidic proton, resulting in the weak physisorption of ethene to the wall of the zeolite surrounding the channel intersection.

The structure of the transition state for the methylation of ethene by methanol is shown in the middle panel of Figure 2. The acidic proton of the zeolite attacks methanol to produce a molecule of water. The transition state is S_n2 in nature, with the methyl cation that is produced upon methanol protonation undergoing an umbrella-like inversion. The methyl cation is located between the water and the double bond of ethene to produce a carbocation complex in the zeolite intersection. The formation of this complex is the rate-limiting step in ethene methylation and has an intrinsic activation enthalpy of $+31.2$ kcal mol⁻¹. The apparent heat of activation can be compared with published experimental studies of methylation of alkenes in H-MFI at 623 K. Experimental studies of the methylation of ethene by methanol show that, under reaction conditions with a high methanol/ethene molar ratio, the reaction is first order in

ethene and zero order in methanol.⁴³ This suggests the adsorbed methanol complex is the resting state of the catalyst under operating conditions, in agreement with the calculated free energy surface at 623 K. The apparent heat of activation measured experimentally is the difference in enthalpy between the methylation TS and the methanol–zeolite complex, as depicted in Figure 1. The calculated apparent heat of activation is $+25.7$ kcal mol⁻¹ (Figure 4A), in good agreement with the experimental value of 24.9 kcal mol⁻¹ (104 kJ mol⁻¹) measured by Svelle et al.⁴⁰ and slightly higher than the experimental value of 22.5 kcal mol⁻¹ (94 kJ mol⁻¹) measured by Hill et al. for the methylation of ethene by dimethyl ether under similar operating conditions.⁴⁴ Previous theoretical studies of the methylation of ethene by methanol in H-MFI have identified a nearly identical transition state as the rate-determining step. Our calculated apparent activation energy is in good agreement with calculations done with a periodic boundary condition PBE:MP2 method (24.9 kcal mol⁻¹)¹⁶ and slightly higher compared with calculations done with a mechanical embedding QM/MM method at the ω B97X-D/6-31+G(d,p) level of theory (21.7 kcal mol⁻¹).¹⁹

The reaction pathway based on the intrinsic reaction coordinate was determined in order to locate the minimum to which the methylation transition state connects. The reaction coordinate profile of ethene methylation is shown in Figure 3A. Following the reaction coordinate backward, we obtain the coadsorbed methanol–ethene complex described previously. Following the reaction coordinate forward, however, leads to the formation of a cyclic carbocation, protonated cyclopropane (PCP⁺) rather than the intended product, propene and water. The potential energy surface leading away from the transition state along the intrinsic reaction coordinate has a sharp drop in energy due to the formation of the partial

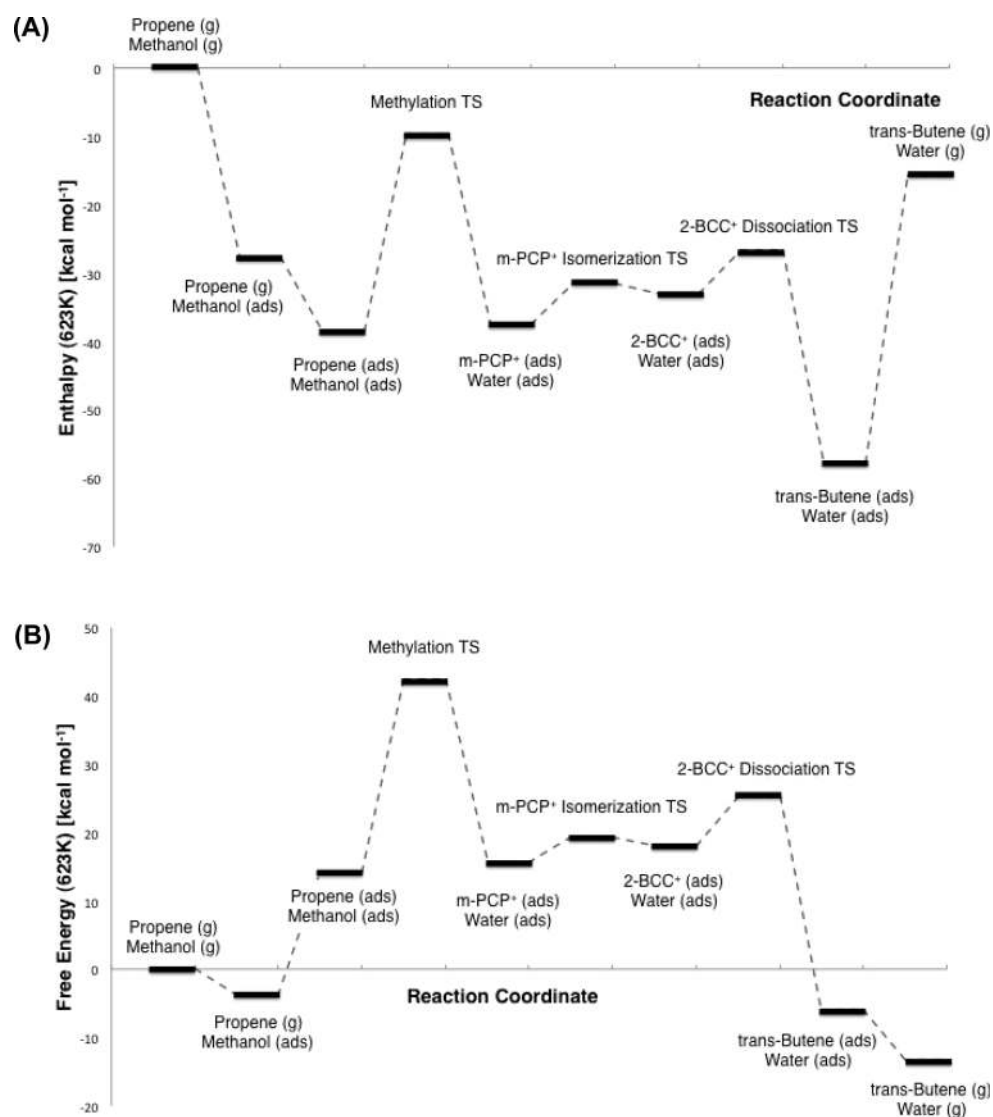


Figure 4. Enthalpy (623 K) (A) and Gibbs free energy (623 K) (B) diagram for ethene methylation to form propene calculated at the ω B97X-D/6-31G(d,p)// ω B97X-D/6-311++G(3df,3pd) level of theory.

C–C bonds that stabilize the methyl cation. As the initial formation of the carbocation complex occurs (around $s = 2$ amu^{-1/2} Å of Figure 3A), the molecule reaches a flat shoulder in the potential energy surface, corresponding to the translation and rotation of this carbocation. Significant additional stability of the carbocation is gained through hydrogen bonding interactions with the zeolite lattice as the molecule relaxes to the most stable configuration at $s = 5$. The molecule of water formed during reaction acts to prevent the chemisorption of the carbocation to the deprotonated acid site by stabilizing the deprotonated site and lowering its proton affinity as well as physically blocking the site.

The relatively flat potential energy surface in the vicinity of the PCP⁺ intermediate allows the intermediate to rotate, translate, and react to form various reaction intermediates with relatively little energetic cost. The rotation of the PCP⁺ intermediate to a less favorably oriented PCP_{rot}⁺ structure has a free energy barrier of 10 kcal mol⁻¹. In the PCP_{rot}⁺ structure, the methyl group of the PCP⁺ complex rotates 60° away from water molecule (Figure 2) toward the entrance to the sinusoidal channel. During this transformation, the PCP⁺ complex transforms from corner-protonated to bond-proto-

nated. Rotation of the PCP⁺ structure to PCP_{rot}⁺ allows reaction to occur between basic oxygen atoms in the water molecule and deprotonated acid site and the unsaturated carbon atoms in the PCP⁺ complex to form other intermediates. The abstraction of a proton by water from a methylene carbon of PCP_{rot}⁺ leads directly to the expected products, propene and water. The ring-opening of PCP⁺ occurs before the transition state is reached, and the free energy of activation is small: $\Delta G^\ddagger < 2$ kcal mol⁻¹ (Figure 4B). The isomerization of PCP⁺ to the more stable 2-propyl carbocation proceeds thru a concerted ring-opening hydride shift, with a higher intrinsic free energy of activation of $\Delta G^\ddagger = 13$ kcal mol⁻¹. The abstraction of a proton from the 2-propyl carbocation by water to form propene proceeds through a higher barrier ($\Delta G^\ddagger = 18$ kcal mol⁻¹) due to the stability of the 2-propyl cation.

The various reaction pathways for PCP⁺ decomposition to form other C₃ products are listed in the Supporting Information, Table IVA. Proton abstraction from the methyl group of the PCP⁺ intermediate ($\Delta G^\ddagger = 7.5$ kcal mol⁻¹) leads to the formation of cyclopropane and water. The ring-opening reaction of the PCP⁺ intermediate directly over a basic oxygen

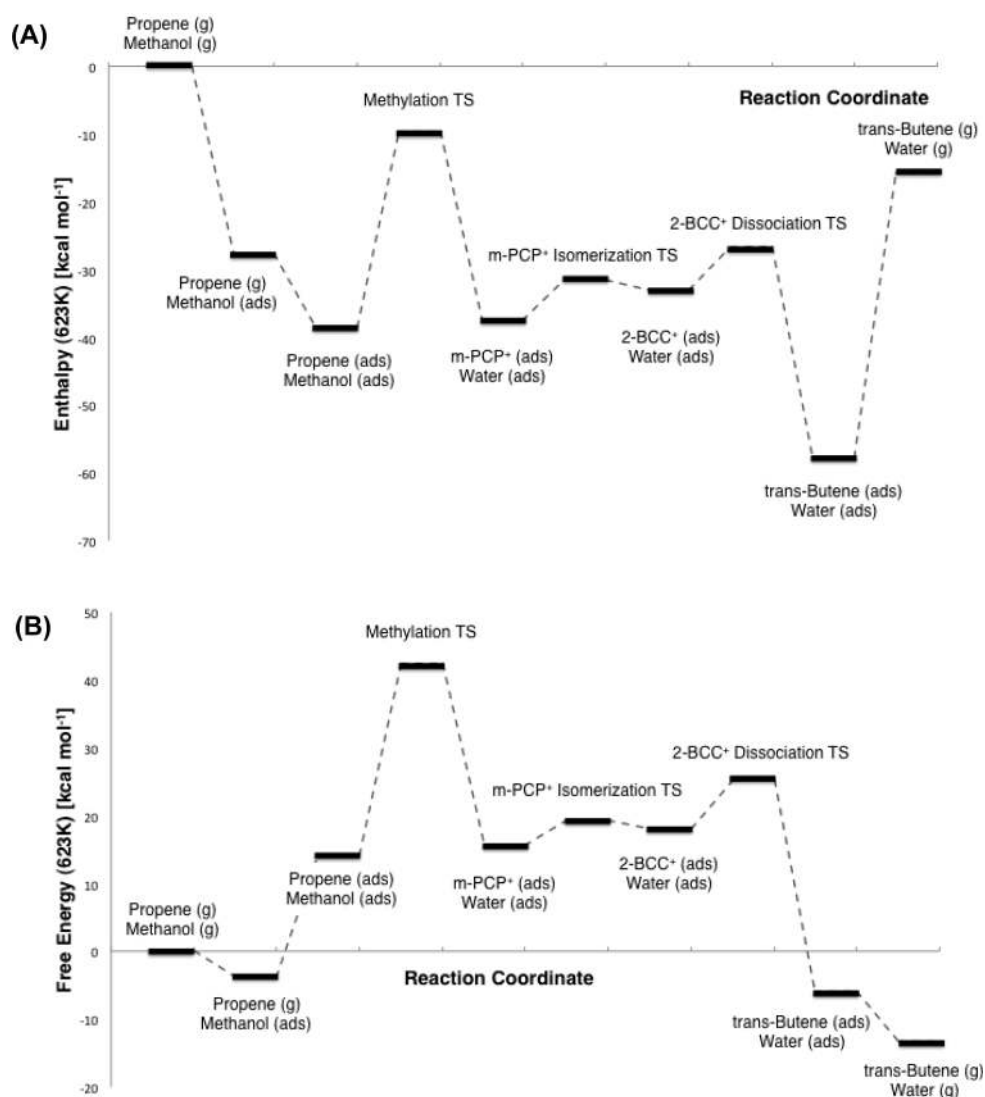


Figure 5. Enthalpy (623 K) (A) and Gibbs free energy (B) (623 K) diagram for propene methylation to form *trans*-2-butene calculated at the ω B97X-D/6-31G(d,p)// ω B97X-D/6-311++G(3df,3pd) level of theory.

of the deprotonated zeolite site ($\Delta G^\ddagger = 10.6 \text{ kcal mol}^{-1}$) forms a primary propoxide. This transformation is slightly exothermic; however, the formation of a σ -bond between C_3^+ and the zeolite results in the loss of entropy relative to the carbocation and destabilizes the alkoxide intermediate relative to the other products. The formation of an oxonium $H_2O-C_3^+$ (protonated alcohol) complex is highly exothermic and proceeds by the attack of the basic oxygen of water on a methylene carbon of PCP^+ . The PCP_{rot}^+ intermediate must rotate another 60° during the oxonium reaction, and the configuration of the PCP^+ intermediate at the transition state is unfavorable compared with transition state for alkoxide formation. This leads to a higher free energy of activation ($\Delta G^\ddagger = +13.8 \text{ kcal mol}^{-1}$). These products are not observed in the gas phase due to the rapid isomerization that occurs through the PCP^+ intermediate. The product distribution predicted in the gas phase via this static reaction pathway is propene:cyclopropane:propanol = 10^4 :10:1.

Propene Methylation Minimum Energy Pathway. The structure of the transition state for the methylation of propene by methanol is shown in Figure 2, where $R = CH_3$. The transition state is also S_n2 in nature, but the transition state

geometry is asymmetric with the methyl cation favoring the least-substituted methylene carbon. The methyl cation is located between the water and the double bond of propene to produce a carbocation complex in the zeolite intersection. The formation of this complex is the rate-limiting step of propene methylation and has an intrinsic activation enthalpy of $28.9 \text{ kcal mol}^{-1}$ (Figure 5A). Following the reaction coordinate forward from the propene methylation transition state leads to the formation of an initial configuration of the cyclic carbocation, protonated methylcyclopropane ($m-PCP^+$) (Figure 3B, $s = 2 \text{ amu}^{-1/2} \text{ \AA}$). The potential energy surface leading away from the transition state along the IRC again has a sharp drop in energy due to the formation of the partial C–C bonds that stabilize the methyl cation. A large portion of the intrinsic reaction coordinate ($s = 1.5\text{--}6.5 \text{ amu}^{-1/2} \text{ \AA}$) is flat and corresponds to the rotation of the $m-PCP^+$ complex about an axis perpendicular to the plane formed by the three-membered ring. After rotation, the methyl group shifts from edge to bond protonated and hydrogen bonds with the newly formed molecule of water to reach the most stable configuration.

The potential energy surface in the vicinity of the $m-PCP^+$ intermediate is flat with respect to translational and rotational

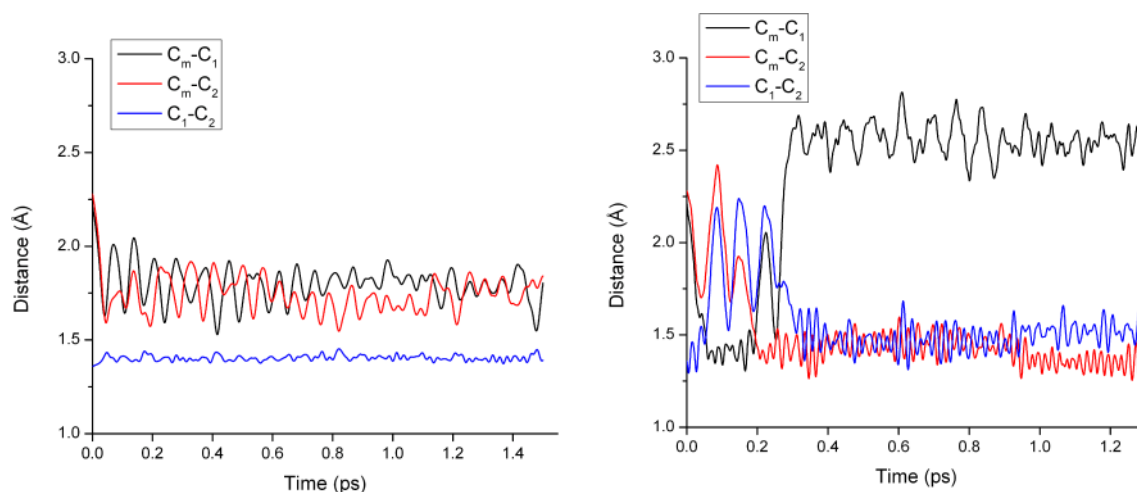


Figure 6. C–C bond distances obtained from the dynamic reaction coordinate trajectory (A) and a quasi-classical trajectory (B) launched at the ethene methylation transition state. Atomic labels in key refer to those in Figure 2.

degrees of freedom, similar to that of the PCP^+ intermediate in ethene methylation. The isomerization to the more stable 2-butyl carbocation can occur without a hydride shift, and the free energy of activation is similar to other rotation barriers: ~ 4 kcal mol $^{-1}$. A variety of C_4^+ intermediates exist, similar to those described for the PCP^+ intermediate. The primary product observed experimentally, *trans*-2-butene and water, is formed by the abstraction of a proton ($\Delta G^\ddagger = 9.7$ kcal mol $^{-1}$) from the 2-butyl carbocation by water (Figure 5B).

Ethene Methylation Quasiclassical Trajectories. Molecular dynamics simulations of the system as it evolves from the transition state toward the products were performed using DRC initial conditions. The DRC trajectory initiated at the ethene methylation transition state leads to the protonated cyclopropane intermediate. The DRC trajectory is integrated for a total of 2 ps, during which the PCP^+ intermediate persists through the entire trajectory. Figure 6A shows the evolution of the three C–C bonds formed in the PCP^+ complex. The PCP^+ intermediate is formed in approximately 50 fs, equivalent to one-half the period of reaction coordinate mode ($-435i$ cm $^{-1}$, 61 fs). During the entire trajectory, the carbon atom with which the methyl cation is most closely associated changes several times. No rotation or translation of the PCP^+ intermediate is observed. The large amplitude vibrational modes of the PCP^+ complex correspond to symmetric and asymmetric rocking of the methyl cation relative to ethene. This can be observed in the DRC trajectory shown in Figure 6A, which shows that the change in the bond lengths C_m-C_1 and C_m-C_2 (Figure 2) appear in and out of phase, respectively. The end of the DRC trajectory cannot determine the final product leading from the transition state. The absence of any reaction during the DRC leads to the inference that the population of vibrational modes orthogonal to the methylation reaction coordinate are important in the conversion of this metastable intermediate into the final products.

In contrast to the DRC trajectory, QCTs typically show formation of final products within 1 ps. One such trajectory, which ultimately leads to propene and water, is shown in Figure 6B. The intermediate dissipates energy through translation and rotation as well as vibration. The PCP^+ intermediate isomerizes to the more stable 2-propyl cation within 250 fs. Activation of the C_1-C_2 bond promotes the hydride shift necessary to complete this transformation. The 2-propyl carbocation persists

for an additional 650 fs, until a proton is abstracted from a methyl carbon by the water molecule to re-form the active site and produce propene and water.

The product distribution from 166 QCT trajectories initiated at the ethene methylation transition state is shown in Figure 7.

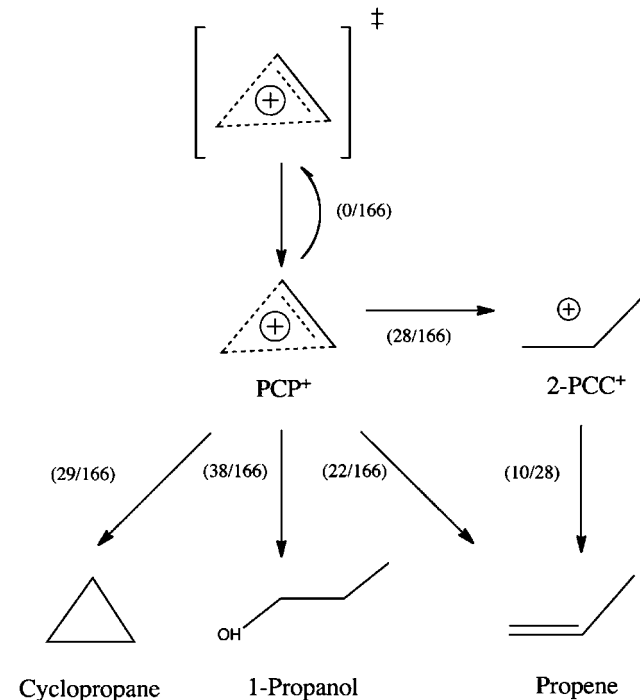


Figure 7. Reaction pathway network of PCP^+ decomposition to form C_3 products. Numbers given in parentheses are the total fluxes through each reaction pathway calculated by QCT. Trajectories that form 1-propoxide are shown by the arrow leading from PCP^+ to propene. Not shown are trajectories resulting in 2-propanol from 2-PCC $^+$ (4/28).

No recrossing is observed from the transition state back to the reactants. The PCP^+ carbocation formed post-TS can then undergo elimination (cyclopropane 29/166), nucleophilic substitution (1-propanol 38/166, 1-propoxide 22/166), or isomerization (2-PCC $^+$, 28/166). After isomerization, the secondary carbocation can undergo elimination (propene, 10/

28) or nucleophilic substitution (2-propanol, 4/28), with the remaining trajectories persisting as carbocations past 1.3 ps. The product distributions predicted by the 623 K free energy surface and QCTs assuming no secondary reaction are shown in Table 1. The minimum energy pathways suggest that

Table 1. Product Distribution (in %) at 623 K Associated with PCP Intermediate Determined by the Potential Energy Surface and QCT

	$\Delta G(623\text{ K})$	QCT(623 K)
propene	44.62	9.71
1-propoxide	28.03	21.36
cyclopropane	25.06	32.04
1-propanol	2.28	36.89

elimination products (propene and cyclopropane, 70%) are favored relative to nucleophilic substitution (1-propanol and propoxide, 30%), while the product distribution observed from QCT predicts qualitatively similar ratios between nucleophilic substitution (59% of reactive trajectories) and elimination (41%). This evidence suggests that the dissociation of the PCP⁺ intermediate proceeds through higher energy pathways that differ from the minimum energy pathway.

The frequency of reaction events observed during ethene methylation QCTs is shown in Supporting Information Figure S4A. Very few reaction events occur before $t < 200$ fs, after which the frequency of reaction events rises to a maximum at 300 fs. Similar plots showing the frequency of reaction events leading to specific C₃ products are shown in Figure S4B–E. We observe a similar maximum in reaction events at 300 fs in Figure S4B, corresponding to the production of cyclopropane. The excitation of C–H stretching modes in the methyl cation during the initialization of some QCTs leads to the fast dissociation of PCP⁺ to cyclopropane. From our analysis of the underlying free energy surface, we know the mode corresponding to C–H dissociation to form cyclopropane is particularly hard (-1096 cm^{-1}). Other reactions of PCP⁺ observed during QCT proceed through a much softer imaginary mode ($\sim -200\text{ cm}^{-1}$), and the observed reaction frequencies for these products are relatively constant in time. The formation of these products occurs when vibrational modes of the PCP⁺ complex and water/zeolite lattice become coupled, and the kinetic energy gained when leaving the transition state is converted into potential energy to overcome these shallow and loose barriers.

The unimolecular decomposition rate of the PCP⁺ intermediate is calculated from the QCT trajectories and shown in Table 2. The survival probability and least-squares fit

Table 2. Unimolecular Decomposition Rate Constants and Half-Life for PCP and m-PCP Intermediates

	k [ps^{-1}]	$t_{1/2}$ [ps]	t_{onset} [ps]
PCP	0.8853 ± 0.001	0.783	0.162
m-PCP	0.8375 ± 0.001	0.827	0.232

are shown on a semilog plot in Figure 9. There remain 65 unreacted carbocations out of 166 total trajectories after 1.3 ps, corresponding to a $\ln[N_u/N_{\text{tot}}] = -0.94$, where N_u is the number of unreacted trajectories and N_{tot} is the total number of trajectories. The first-order rate constant associated with the unimolecular decay of PCP⁺ is $0.8853 \pm 0.001\text{ ps}^{-1}$, which gives a half-life of 0.783 ps. T_{offset} the time at which the rate becomes

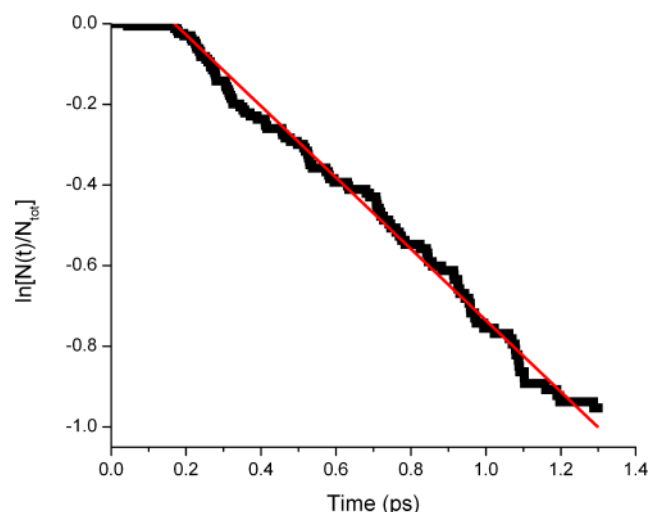


Figure 9. Decomposition rate of PCP⁺ intermediate. Semilog plot of survival probabilities of ethene methylation reactive trajectories. Points are original PCP⁺ lifetime distribution, while solid line is the least-squares fit ($R^2 = 0.998$).

greater than 0.01 fs^{-1} , observed for dissociation of PCP⁺ intermediate is 162 fs, or on the order of 1.5 C–C oscillations before dissociation occurs. More than half of all trajectories reach final products after 8 C–C oscillations.

Propene Methylation Quasiclassical Trajectories. The DRC trajectory initiated at the propene methylation transition state leads to the protonated methylcyclopropane intermediate. The DRC trajectory is integrated for a total of 2 ps, during which the m-PCP⁺ intermediate persists through the entire trajectory. Figure 10A shows the evolution of the three C–C bonds formed in the m-PCP⁺ complex. The m-PCP⁺ intermediate is formed in approximately 50 fs, equivalent to one-half the period of reaction coordinate mode ($-483i, 55\text{ fs}$). As in the transition state, the methyl cation favors the least-substituted carbon (C₁) during the DRC trajectory. No rotation or translation of the m-PCP⁺ intermediate is observed. The large amplitude vibrational modes of the m-PCP⁺ complex correspond to symmetric and asymmetric rocking of the methyl cation relative to the double bond of propene can again be observed in Figure 10A. The final product leading from the transition state cannot be determined by the end of the DRC trajectory. The isomerization to the more stable 2-butyl carbocation does not occur within 2 ps. The absence of any reaction during the DRC leads to the inference again that the population of vibrational modes orthogonal to the methylation reaction coordinate are important in the conversion of this metastable intermediate into the final products.

An illustrative propene methylation QCT trajectory, which ultimately leads to *trans*-2-butene and water, is shown in Figure 10B. The intermediate dissipates energy through translation and rotation as well as vibration. The m-PCP⁺ intermediate isomerizes to the more stable 2-butyl cation within 500 fs. This isomerization can occur without activation of the C₁–C₂ bond. The 2-butyl carbocation persists for an additional 300 fs, until a proton is abstracted from a methylene carbon by the water molecule to re-form the active site and produce *trans*-2-butene and water.

The product distribution from 131 QCT trajectories initiated at the propene methylation transition state is shown in Figure 11. No recrossing from the transition state back to the reactants

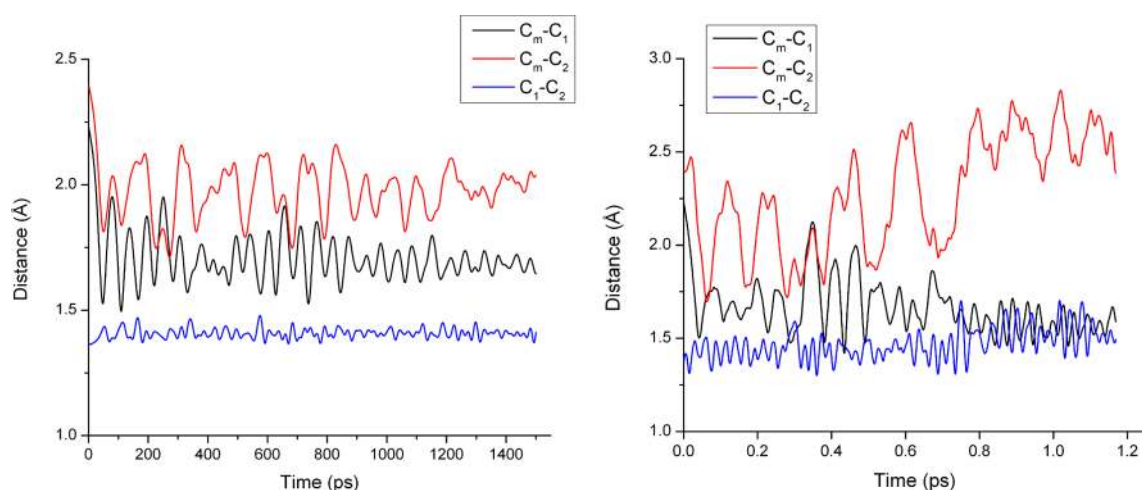


Figure 10. C–C bond distances obtained from the dynamic reaction coordinate trajectory (A) and a quasi-classical trajectory (B) launched at the propene methylation transition state. Atomic labels in key refer to those in Figure 2.

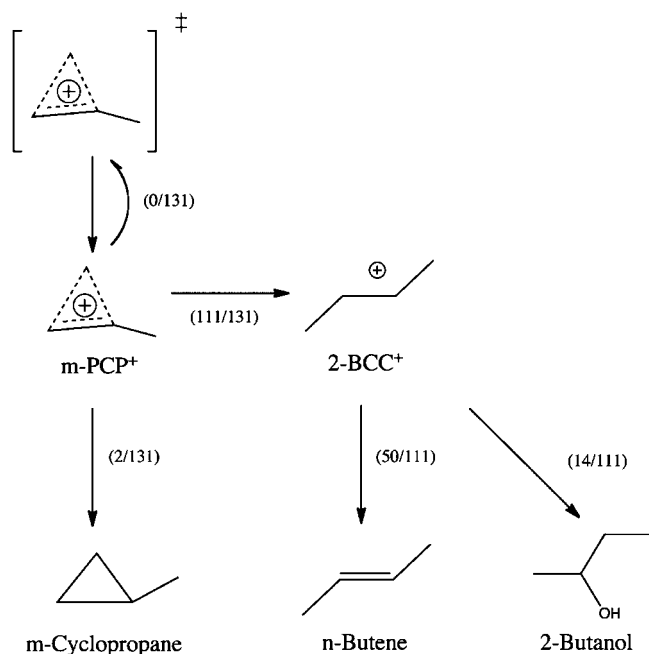


Figure 11. Reaction pathway network of $m\text{-PCP}^+$ decomposition to form C_4 products. Not shown are trajectories ending in 1-butoxide (2/131) and 1-butanol (1/131) proceeding from $m\text{-PCP}^+$.

was observed. The $m\text{-PCP}^+$ carbocation formed post-TS can then undergo elimination ($m\text{-cyclopropane}$ 2/131), nucleophilic substitution (1-butanol 1/131, 1-butoxide 1/131), or isomerization (2-butyl carbocation 2-BCC⁺, 111/131). After isomerization, the secondary carbocation can then undergo elimination ($n\text{-butene}$, 50/111) or nucleophilic substitution (2-butanol, 14/111), with the remaining trajectories persisting at carbocations past 1.3 ps. In contrast to the product distribution from PCP^+ , mostly products derived from the isomerization route are observed from QCTs due to the much fast rate of isomerization relative to substitution or elimination. The isomerization of $m\text{-PCP}^+$ to 2-BCC⁺ involves no intramolecular proton transfer, only the conversion of vibrational kinetic energy to potential energy to overcome the extremely shallow and loose (-71 cm^{-1}) reaction barrier.

The frequency of reaction events observed during propene methylation QCTs is shown in Supporting Information Figure S5A. We can see that no reaction events occur before $t < 200$ fs, before reaching a maximum at 600 fs. We observe a smaller, similar peak in reaction events at 600 fs in Figure S5B, corresponding to the production of 1-butene. 1-Butene is produced by the dissociation of a C–H bond of a methyl carbon in the 2-butyl carbocation cation state. Other reaction pathways of $m\text{-PCP}^+$ dissociation observed during QCT have observed reaction frequencies relatively constant in time.

The unimolecular decomposition rate of the $m\text{-PCP}^+$ intermediate is calculated from the QCT trajectories and shown in Table 2. The survival probability and least-squares fit are shown on a semilog plot in Figure 12. At 1.3 ps, there remain 64 unreacted carbocations out of 131 total trajectories, corresponding to a $\ln[N_u/N_{\text{tot}}] = -0.72$. The first-order rate constant associated with the unimolecular decay of $m\text{-PCP}^+$ is $0.8375 \pm 0.001\text{ ps}^{-1}$, which gives a half-life of 0.827 ps. T_{offset} observed for dissociation of $m\text{-PCP}^+$ intermediate is 232 fs, or

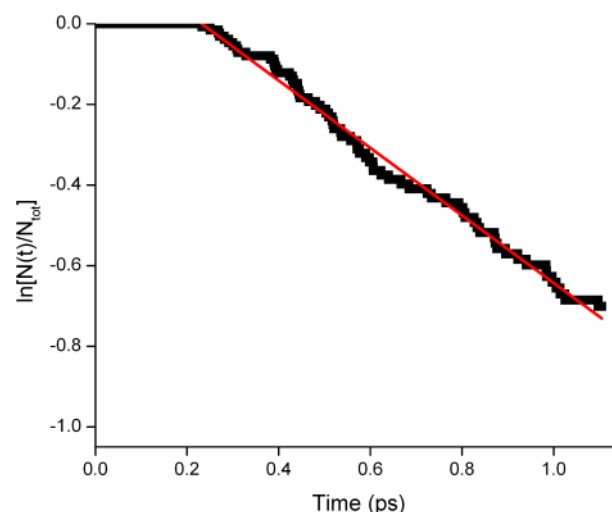


Figure 12. Decomposition rate of $m\text{-PCP}^+$ intermediate. Semilog plot of survival probabilities of propene methylation reactive trajectories. Points are original $m\text{-PCP}^+$ lifetime distribution, while solid line is the least-squares fit ($R^2 = 0.998$).

on the order of 2 C–C oscillations before dissociation occurs. At $t = 1.1$ ps, there remain 65 unreacted carbocations out of 131 total trajectories. Between $t = 1.1$ ps and $t = 1.3$ ps, there is a sharp decrease in the unimolecular decomposition rate, and only one reaction event is observed. After 1.3 ps, 49/64 unreactive trajectories remain as 2-butyl carbocations. The large fraction of population in 2-butyl carbocation state at the end of 1 ps suggests that this intermediate, a secondary linear carbocation, is longer-lived than the primary cyclic m-PCP⁺ intermediate.

CONCLUSIONS

The QM/MM method presented here reproduces experimentally measured apparent reaction barriers for the methylation of ethene and propene in the presence of H-MFI to near chemical accuracy. Following the reaction coordinate from the alkene methylation transition state toward the final products reveals the existence of a protonated three-member ring containing carbocation intermediate. The dissociation pathways of these carbocation intermediates were investigated with both static potential energy surface mapping as well as quasiclassical sampling of reaction pathways. The intermediates produced during the alkene methylation reaction are metastable with a lifetime of $O(1)$ ps obtained from QCTs. The lifetime and product distribution associated with each intermediate were calculated from a total of 166 trajectories. This procedure is adequate for obtaining a qualitative description of reaction dynamics; however, lifetimes and product distributions are not necessarily statistically converged with respect to trajectory number.

The qualitative difference between product distributions obtained by static and dynamic reaction pathways suggests the dissociation of the PCP⁺ intermediate proceed through pathways that differ from the 0 K potential energy surface. Because of the short lifetime of these intermediates, the available energy in the carbocation is not in thermal equilibrium with the zeolite lattice before subsequent dissociation occurs. The conversion of potential energy into kinetic energy that occurs between the rate-limiting transition state and the metastable intermediate produces a locally nonthermal intermediate, and the dissociation occurs before the full transfer of vibrational energy from the intermediate to the zeolite lattice can occur. This makes the application of transition state theory for determining product distribution problematic, since the products are determined by the nonequilibrium dissociation of the PCP⁺ intermediate. Some products observed during QCT (cyclopropane and 1-propanol) are not reported as major products experimentally.³⁹ These intermediates readily react via secondary reactions of ring-opening⁴⁵ and dehydration⁴⁶ to produce the primary product, propene. The reaction pathways to form propene from these intermediates are simply the reverse pathways of PCP⁺ dissociation.

The product distribution for propene methylation predicted by QCT is qualitatively different than the predicted ethene methylation product distribution. Some m-PCP⁺ carbocation produced during propene methylation react before the full transfer of vibrational energy; however, more than 80% are able to isomerize to the more stable secondary carbocation which has a lifetime longer than 2 ps. This isomerization between m-PCP⁺ and 2-butyl cation occurs in the absence of intramolecular hydride transfer, contrary to the PCP⁺ to 2-propyl cation reaction. QCTs predict *n*-butene as the primary product

of propene methylation, in good agreement with published experiments⁴⁷ and minimum energy pathway analysis.

These results as well as our previous work¹⁷ show that dynamical effects govern the selectivity of primary carbocation dissociation. Because these intermediates are common in the acid-catalyzed conversion of hydrocarbons and alcohols, their behavior and reactivity are central to understanding catalytic processes. The shape of the zeolite pore structure influences the dynamics and carbocation dissociation dynamics. The study of carbocation dynamics in different zeolite frameworks can help to understand how much of a role the carbocation–lattice interactions play in determining the selectivity of a given reaction and can be used ultimately as a tool to aid in the design of zeolite frameworks that exhibit high conversion rate and selectivity to a desired product.

ASSOCIATED CONTENT

Supporting Information

QM/MM methodology, calculation of thermodynamic quantities, and comparison between stepwise and concerted mechanism; Figures S1–S5 and Tables S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*E-mail bell@cchem.berkeley.edu (A.T.B.).

*E-mail mhg@cchem.berkeley.edu (M.H.-G.).

Notes

The authors declare no competing financial interest.

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