

Supplemental information

Theoretical dynamics studies of the $\text{CH}_3 + \text{HBr} \rightarrow \text{CH}_4 + \text{Br}$ reaction: integral cross sections, rate constants and reaction mechanism

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S1. Interpolation of J-dependent reaction probabilities

The reaction probabilities have been evaluated with the 6DOF quantum mechanical method for every tenth partial wave. Below $J = 110$ the probabilities are nonzero in the limit of zero collision energy, while for $J > 110$ they are zero below a threshold energy. To get the reaction probabilities for every partial wave, we use different methods for the two domains. The probabilities P_J for the partial waves with $J < 110$ have been obtained by interpolation between two adjacent quantum numbers bracketing the desired J

$$P_J = P_{J_i} + (J(J+1) - J_i(J_i+1))B, \quad (1)$$

Here i is the integer part of $J/10$, $J_i = 10i$ and $J_{i+1} = J_i + 10$ and for every segment the constant B is calculated as

$$B = \frac{P_{J_{i+1}} - P_{J_i}}{J_{i+1}(J_{i+1}+1) - J_i(J_i+1)}, \quad (2)$$

For $J > 110$, where the threshold energy is positive and the successive reaction probability curves are very similar, we use the standard J -shifting method for each $(J_i, J_i + 10)$ range.¹

S2. Calculation of the full-dimensional cumulative reaction probability

The title reaction involves six atoms and so it is a twelve-degree of freedom system. However, the reduced-dimensional quantum mechanical model we use only includes six degrees of freedom. In order to obtain the full dimensional (12DOF) reaction rate constants, we use the energy- and the J and K -shifting approximations^{1,2} to account for the degrees of freedom that are not treated explicitly. First, we calculate the full-dimensional cumulative reaction probability (CRP) starting from the 6DOF CRP for $J = 0$. The latter is obtained by summing all the initial ro-vibrational-state-selected reaction probabilities

$$N_{6DOF}^{J=0}(E) = \sum_{v_1} \sum_{j_1 j_2} P_{v_1 j_1 j_2}^{J=0}(E), \quad (3)$$

where v_1 stands for the vibrational quantum number of H'Br. According to the energy-shifting approximation³

$$N_{12DOF}^{J=0} = \sum_{v_1, v_2, \dots, v_6} N_{6DOF}^{J=0}(E - E_{v_1, v_2, \dots, v_6}^\ddagger), \quad (4)$$

where v_1, v_2, \dots, v_6 are the six quantum numbers of the vibrational modes of the transition state (CH₃-H-Br) that are not included in our 6DOF model. $E_{v_1, v_2, \dots, v_6}^\ddagger$ calculated with the harmonic vibrational frequencies at the transition state,

$$E_{v_1, v_2, \dots, v_6}^\ddagger = \sum_{i=1}^6 \hbar \omega_i^\ddagger \left(v_i + \frac{1}{2} \right), \quad (5)$$

The summation in Eq. (5) includes all energetically allowed vibrational states. The full-dimensional CRP is obtained with the J and K -shifting method^{40,41} as

$$N(E) = \sum_{J=0} (2J+1) \sum_{K=-J}^J N_{12DOF}^{J=0}(E - E_{JK}^\ddagger), \quad (6)$$

Utilizing that the system at the transition state is a symmetric top molecule, we can write E_{JK}^\ddagger

as

$$E_{JK}^\ddagger = B^\ddagger J(J+1) + (A^\ddagger - B^\ddagger)K^2, \quad (7)$$

with A^\ddagger (34.39 cm⁻¹) and B^\ddagger (17.12 cm⁻¹) being the rotational constants of the transition state at the saddle point of the PES.

The full-dimensional rate constants can be calculated using the full-dimensional CRP,

$$k(T) = \frac{1}{hQ_r} \int_0^\infty N(E) e^{-E/k_B T} dE, \quad (8)$$

This equation can be simplified using the J - K shifting expression of Eq. (4) to obtain the final rate constant expression,

$$k(T) = \frac{Q_{rot}^\ddagger}{hQ_r} \int_0^\infty N_{12DOF}^{J=0}(E) e^{-E/k_B T} dE, \quad (9)$$

S3. Numerical parameters of the Reduced-Dimensional Quantum Mechanics Calculations

For the translational coordinate R , 108 sine basis functions are used to propagate the wave function in the range from 3.8 to 11.5 bohr, including 59 sine basis functions in the interaction region as well as 30 vibrational basis functions for the r_1 coordinates in the range from 1.2 to 6.0 bohr. 31 spherical harmonic rotational functions are used for θ_1 , 20 and 10 spherical harmonic rotational functions for θ_2 and θ_3 , respectively. The three angular momenta are coupled to give a set of 372,504 parity adopted total angular momentum basis functions. The time-dependent wave-packet is propagated with a time step of 15 a.u. for a total time of about 12,000 a.u.. To obtain converged reaction cross sections for nonrotating reactants and vibrational ground-state CH₃, 208, 231 and 240 partial waves were needed for H'Br vibrational states $\nu_1 = 0, 1$ and 2, respectively.

Our calculations show that at the low end of the energy range covered by the wave packet calculations, below 0.04 eV, the probability did not. To ensure that that we report converged reaction probabilities, we set the low-energy boundary to a small positive value (0.04 eV). As a consequence, the lowest energy for which we report RDQM reaction cross sections is about 1 kcal/mol.

In order to get the CRP, the reaction probabilities were calculated for three vibrational states of H'Br ($\nu_{1max} = 2$) with 24 rotational states ($j_{1max} = 23$) for each, combined with 12 rotational states of HCX ($j_{23max} = 11$). The harmonic vibrational frequencies of CH₃ and H'Br are listed is

Section II.1; those of the transition state needed in Eq. (4) are 707 cm^{-1} , 709 cm^{-1} , 1446 cm^{-1} , 3105 cm^{-1} , and 3304 cm^{-1} (2).

S4. Some details of the QCT Calculations

When normal mode sampling was applied, the rotation of the radical was treated separately from the vibrations. CH_3 was approximately described as a symmetric rotor.

The angular momentum vectors of HBr and of CH_3 and the position of the center of mass of the diatom as well as the direction of the latter with respect to the center of mass of CH_3 were oriented randomly in space in each initial quasi-classical state.

The integration of Hamilton's equations of motion in Cartesian coordinates was performed by the sixth-order Adams-Moulton predictor-corrector method. The time step was 4 a.u., which ensures energy conservation within 0.01 kcal/mol.

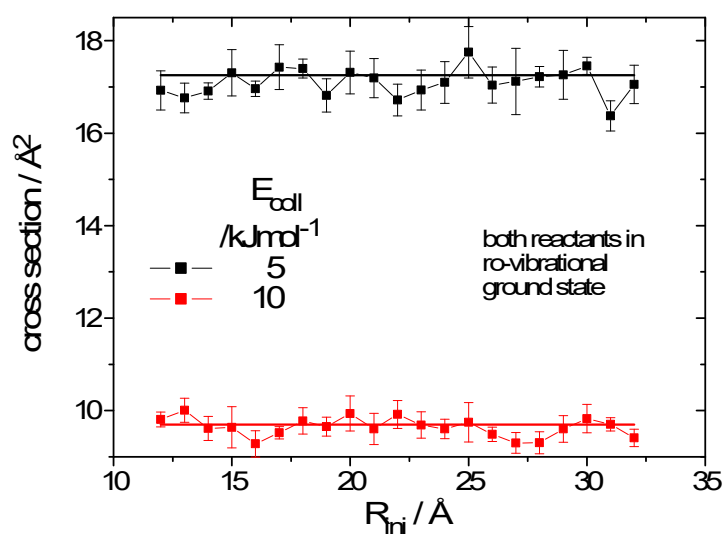


Figure S1. The dependence of the QCT reaction cross sections for reaction (R1) on the initial center-of-mass separation of the reactants at two collision energies. The straight lines represent the average values. There is no tendency or periodic changes when the flight time before the reactants enter the strong interaction region is varied. This shows that the possible internal relaxation of the CH_3 radical from initial states generated by normal mode sampling, if exists, does not influence the reaction cross sections. See Ref. 4 for details.

Reference

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