Chemical Physics Letters 693 (2018) 88–94

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Tunnelling and the kinetic isotope effect in $CH_3 + CH_4 \rightarrow CH_4 + CH_3$: An application of semiclassical transition state theory ☆

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ARTICLE INFO

Article history:
Received 20 October 2017
In final form 2 January 2018
Available online 3 January 2018

Keywords:
Semiclassical transition state theory
Kinetic isotope effect
Hindered rotor
Hydrogen exchange

ABSTRACT

One-dimensional semiclassical transition state theory is applied to study the rate constants of the $CH_3 + CH_4$ reaction and its hydrogen-substituted isotopic analogues. This requires calculation of vibrational frequencies at the reactant, product and transition states, and the anharmonic constants of the reaction coordinate at the transition state. The reactions studied have a hindered rotor vibration at the transition states, whose behaviour is approximated using two methods. The results show very good agreement to experimental and other theoretical results. The three reactions studied allow evaluation of both primary and secondary kinetic isotope effects in the title reaction.

1. Introduction

Calculating the rate constants of chemical reactions is a key component of modern theoretical chemistry. Whilst sophisticated quantum reactive scattering (QRS) calculations are able to provide accurate results, they are typically limited to small systems (up to 7 atoms [1,2]) due to the complexity in both constructing a full-dimensional potential energy surface (FD PES) and solving the nuclear Schrödinger equation [3]. Ring Polymer Molecular Dynamics (RPMD) has simplified the process of solving the Schrödinger equation, and is exact in the high temperature and the parabolic barrier limits, however a FD PES is still required [4–6]. Other techniques such as variational transition state theory (VTST) do not require a full PES [7]. These are based on classical transition state theory (TST), but minimise the effect of the no-recrossing assumption by optimising the position of the transition state such as to minimise the flux through the dividing surface [7]. Tunnelling corrections can be incorporated via a transmission coefficient calculated using multidimensional imaginary-action integrals [8].

Semi-classical transition state theory (SCTST), developed by Miller et al. [9–11] requires only two molecular geometries to be identified and analysed: the 'reactant' state, and the 'transition' state (TS). SCTST is also exact in the parabolic barrier limit. Using vibrational perturbation theory, the semi-classical tunnelling probability can be derived, from which the reaction rate constant can be computed. Wagner [12] suggested further modifications in order to obtain the correct behaviour in the deep tunnelling regime.

However, FD SCTST scales poorly with the system size due to both the calculation of anharmonic constants and the number of possible vibrational states. While the Wang-Landau algorithm [13] and its implementation for parallel architectures [14] have been employed to tackle the latter of these two scaling problems, the anharmonic constant calculation (which requires up to fourth order derivatives of the PES) remains a significant computational expense [15].

An alternative approach is to use SCTST within a reduced dimensionality (RD) framework, as developed and tested recently by Greene et al. [15–17] and Shan et al. [18]. In this method, only a subset of the internal degrees of freedom (DoFs) are treated anharmonically, while the remaining 'spectator' vibrational modes are treated using a simple harmonic oscillator model [17]. In doing so, this approximate method is able to tackle both scaling problems in FD SCTST. Since the anharmonic constant calculation is limited to only a small number of vibrational modes, third and fourth order derivatives of the PES only with respect to these modes are required from *ab initio* calculations. In addition, the full set of vibrational states for 1 or 2 DoFs can be enumerated with very little computational cost [13,15].

In this work, 1D-SCTST is applied to isotopic variants of the title reaction:

$$CH_3 + CH_4 \longrightarrow CH_4 + CH_3 \qquad (R1)$$

$$CH_3 + CDH_3 \longrightarrow CDH_3 + CH_3 \qquad (R2)$$

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https://doi.org/10.1016/j.cplett.2018.01.002
0009-2614/

$$CD_3 + CD_4 \longrightarrow CD_4 + CD_3 \qquad (R3)$$

Reaction R1 is known to be significant in combustion and decomposition processes [19], and so accurate rate constant values are of importance. This reaction is also used as a model for other reactions in its reaction class of a light atom transferring between two heavy molecules [20]. As such, it has been studied extensively both experimentally [21–23] and theoretically [24–30]. As it involves the transfer of a light atom, tunnelling is expected to be significant. Comparison of R1 to R2 will exhibit primary kinetic isotope effects, whilst comparison of R2 and R3 will show secondary isotope effects. These results can be compared to those calculated through reduced dimensional quantum reactive scattering calculations performed by Remmert et al. [24].

An interesting feature of these reactions is that a hindered-rotor vibrational mode is present in the TS. At low temperatures, these behave like molecular vibrations, whilst in the high temperature limit they behave like free rotors. Ellingson et al. [31] have described several practical approximation schemes for calculating the partition function of torsional modes; these range from full-dimensional path integral methods to one-dimensional approximations with analytical formulae. Since the HR vibrational mode is only found in the TS and not in either of the reactants, this reaction provides an opportunity to study the effect of different treatments to the HR partition function. In this work, we use two methods of treatment of the HR; an analytic approximation suggested by Truhlar et al. [32] to move smoothly between the harmonic and free rotor behaviours, and eigenvalue summation of the 1D rotor. These are compared to a simple harmonic approximation.

The remainder of this letter is organised as follows. In Section 2 we provide a theoretical overview of SCTST and treatments of the hindered rotor degree of freedom. In Section 3, we describe the computational methods used to carry out the calculations. In Section 4 the results of the calculations and the calculated kinetic isotope effects are discussed. The key conclusions of this work are then discussed in Section 5.

2. Theory

2.1. Semi-classical Transition State Theory (SCTST)

A full description of the SCTST method in full and reduced dimensions is presented by Greene et al. [33]. Here, a very brief overview is provided. SCTST calculates reaction probabilities directly from harmonic frequencies, ω_i, and anharmonic constants, x_{ij}, of the reactant and transition states. In its original formulation [9], second order vibrational perturbation theory (VPT2) [34] was used to calculate anharmonic constants (VPT2 can be extended to VPT4 [35] although this requires considerable extra computational effort). This requires up to fourth order derivatives of the potential along all degrees of freedom, and is thus computationally expensive for large systems. In 1D-SCTST, it is assumed the reaction mode is not coupled with the rest of the vibrational (spectator) modes in the TS. In such calculations, only the reaction mode is anharmonic, and its anharmonic constant, x_{FF}, can be calculated from the curvature of the PES at the TS,

$$x_{FF} = \frac{\hbar^2}{16\omega_F^2}\left(f_{FFFF} - \frac{5f_{FFF}^2}{3\omega_F^2}\right) \qquad (1)$$

where f_{FFF} and f_{FFFF} are the third and fourth order derivatives of the potential with respect to the reaction mode coordinate. These derivatives can be estimated using numerical differentiation. Richardson Extrapolation can be used to improve the results [33], whereby *ab initio* single point energies are calculated at small displacements along the reaction coordinate either side of the transition state.

Within the VPT2 treatment, a constant energy parameter, G_0, should be added to the harmonic adiabatic reaction energy barrier. Its 1D form is given by

$$G_0 = \frac{\hbar^2}{64}\left(\frac{f_{FFFF}}{\omega_F^2} - \frac{5}{9}\frac{f_{FFF}^2}{\omega_F^4}\right). \qquad (2)$$

A barrier penetration integral, $\theta(E)$, can be calculated using WKB theory,

$$\theta(E) = \pi\frac{-\omega_F + \left[\omega_F^2 + 4x_{FF}\left(\Delta V_f + G_0 - E\right)\right]^{1/2}}{2x_{FF}}. \qquad (3)$$

The canonical rate constant, $k(T)$, can then be found from a Boltzmann average of the semi-classical tunnelling probability [36], given by

$$k(T) = \frac{Q^{\ddagger}}{2\pi\hbar Q_r}\int_{E_0}^{\infty} dE\ e^{-\beta E}P_{SC}(E) \qquad (4)$$

where

$$P_{SC}(E) = \frac{1}{1 + e^{2\theta(E)}} \qquad (5)$$

and Q_r is the partition function (per unit volume) of the reactant species and E_0 is the quantum mechanical reaction threshold. $Q^{\ddagger}$ includes the electronic, rotational and translational partition functions of the TS as well as the vibrational partition function of the spectator modes.

Wagner [12] pointed out this procedure gives qualitatively incorrect results for tunnelling at low energies. The VPT2 procedure reproduces the behaviour of the barrier near the transition state, but does not incorporate the forward or reverse barrier height, thus giving the incorrect asymptotic tunnelling behaviour. This can be avoided by modeling the potential as a piecewise continuous asymmetric Eckart potential that consists of three parts. This potential function maintains the analyticity of $\theta(E)$ whilst giving the correct asymptotic behaviour. This method also requires calculation of the reverse barrier height, thus the products region must be identified and analysed as well. Within the one-dimensional framework, all products and reactant normal modes can be treated purely harmonically, as the reaction mode is not present in these states. Note that since all three reactions are symmetric, no additional computation is required to determine the properties of the product states.

To show the contribution of quantum tunnelling to the reaction, we compare the 1D-SCTST results to the standard TST rate constants, given by

$$k(T) = \frac{Q^{\ddagger}}{2\pi\hbar Q_r}\left(kT\ e^{-E^{\ddagger}/kT}\right). \qquad (6)$$

Note that in 1D-SCTST, $Q^{\ddagger}$ is the same as that of a standard TST calculation.

2.2. Treatment of the hindered rotor

Hindered rotational modes present a challenge to treat in a simplified manner. Whilst expensive treatments include the effects of torsional mode coupling and the existence of multiple, distinguishable conformers [37], here we focus on simplified treatments. An initial assumption is that the hindered rotor is separable from all other vibrational degrees of freedom. This is justified by noting that the frequency of a hindered rotor vibration is typically at least an order of magnitude less than other vibrations. Moreover, it can be verified that when projecting the hindered rotor degree of free-