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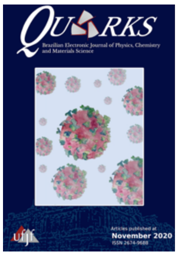

On apparent barrier-free reactions

Maikel Y. Ballester

Universidade Federal de Juiz de Fora, Departamento de Física, CP 36036-330, Juiz de Fora- MG, Brazil

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Abstract

Rate coefficients of bi-molecular chemical reactions are fundamental for kinetic models. The rate coefficient dependence on temperature is commonly extracted from the analyses of the reaction minimum energy path. However, a full dimension study of the same reaction may suggest a different asymptotic low-temperature limit in the rate constant than the obtained from the energetic profile.

Keywords: Potential Energy Surface, Molecular Dynamics

1. Introduction

In the study of a molecular system, the full Schrödinger equation is commonly circumvented using the Born-Oppenheimer approximation (BOA) [1]. Within the BOA, the nuclear and electronic coordinates are separated due to the large mass difference between the atomic nuclei and the electron. In that view, the solution of the electronic problem leads to a potential energy surface (PES) on which the atomic nuclei move.

From the topological analysis of the PES, one can extract the minimum energy path (MEP) connecting reactants and products or the intermediary complex. Properties from reactive molecular collisions in the gas phase are usually predicted in terms of MEP profiles [2, 3, 4]. The absence of a saddle point in the MEP for the approximation of the colliding partners is commonly identified with a barrier-less process [5, 6, 7]. The absence of a saddle point in the MEP for the approximation of the colliding partners is commonly identified with a barrier-less process [5, 6, 7]. In the classical trajectories view, the MEP is mistakenly confused with the more-likely pathway for reactive or complex-forming trajectories. This rationalization may produce erroneous rate constant dependence upon temperature, particularly for the low-temperature regime. Remarkably the low-temperature limit for reaction rate constants used in astrophysics kinetic models can be affected following this issue [8]. The aim of this work is to discuss some details of the type of reaction not presenting an entrance barrier, yet, with excitation function typical for a barrier-like process. For such a task, two radical-radical bimolecular reactions will be analyzed.

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*Corresponding author. E-mail: ✉ maikel.ballester@ufjf.edu.br

2. Theory

Barrier-free bi-molecular reaction are often described in the frame of the classical capture theory [9]. Within this approach the collision is represented by a central force in a one-dimensional problem. The effective potential is then of the type:

$$V_{eff} = \frac{Eb^2}{r^2} - \frac{C_n}{r^n} \quad (1)$$

where r is the distance between the center of mass of the collision partners, C_n and n characterize the interaction, E is the initial translational energy, and b is the impact parameter. For such a potential the capture cross section is given:

$$\sigma(E) = \pi b_m^2 = \pi \left[\frac{n}{n-2}\right]^{(1-\frac{2}{n})} \left[\frac{nC_n}{2E}\right]^{(\frac{2}{n})} \quad (2)$$

b_m is the maximum impact parameter. In several cases the reactive excitation functions are accurately described by equation 2. (see Refs. [10, 11]). Then, assuming a Maxwell-Boltzmann distribution over the translational energy E, the obtained reaction rate constant is:

$$k(T) = \pi g_e(T) \left(\frac{8}{\pi\mu}\right)^{1/2} \Gamma\left(2-\frac{2}{n}\right) \left(\frac{n}{n-2}\right)^{\frac{n-2}{n}} \left(\frac{nC_n}{2}\right)^{\frac{2}{n}} (k_B T)^{\frac{1}{2}-\frac{2}{n}} \quad (3)$$

where $g_e(T)$ is the electronic degeneracy function and Γ is the gamma function. Assuming a constant value of g_e, n essentially dictates the dependence of the rate constant upon the temperature as $k(T) \sim T^{(n-4)/2n}$. Thus, for $2 < n < 4$ the rate constant increase as temperature goes to zero. In turn, for $n \geq 4$, k(T) is either constant (the Langevin rate) or goes to zero in the low temperatures regime.

In this view, in the absence of a saddle point in the minimum energy path for a bi-molecular reaction, the excitation function can presumably be represented using a capture-like model. On top of that, the rate constant is expected depends upon temperature as discussed in the previous paragraph.

3. Study Cases

The reactive collisions between two NH radicals were recently studied [12]. There, the quasi-classical trajectory methodology was used combined with a previously developed potential energy surface (PES) for the ground electronic state of N_2H_2 [13]. The energetic profile of such PES is depicted in Figure 1.

From such a profile, the reactions:

$$NH + NH \rightarrow N_2H + H \quad (4)$$

$$\rightarrow N_2 + H_2 \quad (5)$$

$$\rightarrow N_2 + H + H \quad (6)$$

proceed through the formation of a four-body complex and then dissociate to the corresponding product channel. As intermediate structures and products are well below the reactants channel reactions 4-6 are expected to show barrier less behavior.

A similar profile was also observed for the reaction [14, 15]:

$$OH + SO \rightarrow H + SO_2 \quad (7)$$

The Figure 2 displays the energetic profile for such a reaction, according to the global PES reported in Ref. [16] The blue and black lines in the Figure 2 represent different reaction pathways. From molecular dynamics studies, the path represented with a black line is the more likely to be followed [11].

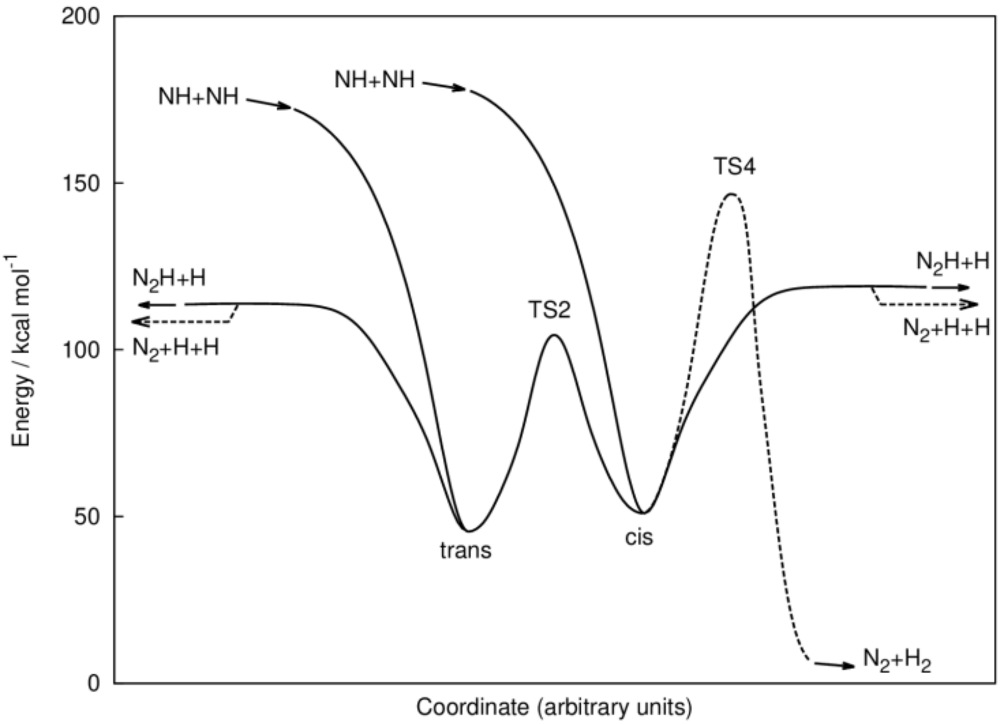

Figure 1: Energetic profile of the N_2 H_2 potential energy surface.

The radical-radical bi-molecular reactions 4-7 are similar considering the profiles presented in Figures 1 and 2. Thus, excitation functions are expected to be also similar. However, from full dimension molecular dynamic studies presented in Refs [12, 11] very different situations are reported. In the case of reaction 7 a typical capture-like behavior dominates the low energy region. This is illustrated in Figure 3. Results from quasi-classical calculations and zero-point energy corrected calculations (VEQMT C) are reported. A salient feature from this Figure is the lower energy limit, with the reactive cross-section reaching the highest values as the energy goes to zero. Consequently, the thermal reaction rate constant increases as the temperature decrease [8, 11].

In turn, for reactions 4 to 6, the excitation function assumes the form displayed in Figure 4. Corrected calculation and, pure quasi-classical results, reported in Ref. [12] are there displayed. Noticeably, more than 85% contribution in the cross section represented in the Figure 4 is from reaction 4. A salient feature is that the reactive cross-section tends to zero as the translational energy goes to the lower values.

Both collision NH+NH and SO+OH are dipole-dipole dominated processes [11, 12]. For them, orientation effects are essential in the formation of the four bodies' moiety. Yet, despite similarities, the reactive cross-sections in the lower translational energy limit behave rather oppositely. Correspondingly, one gets a positive dependence for OH+SO [8, 11].

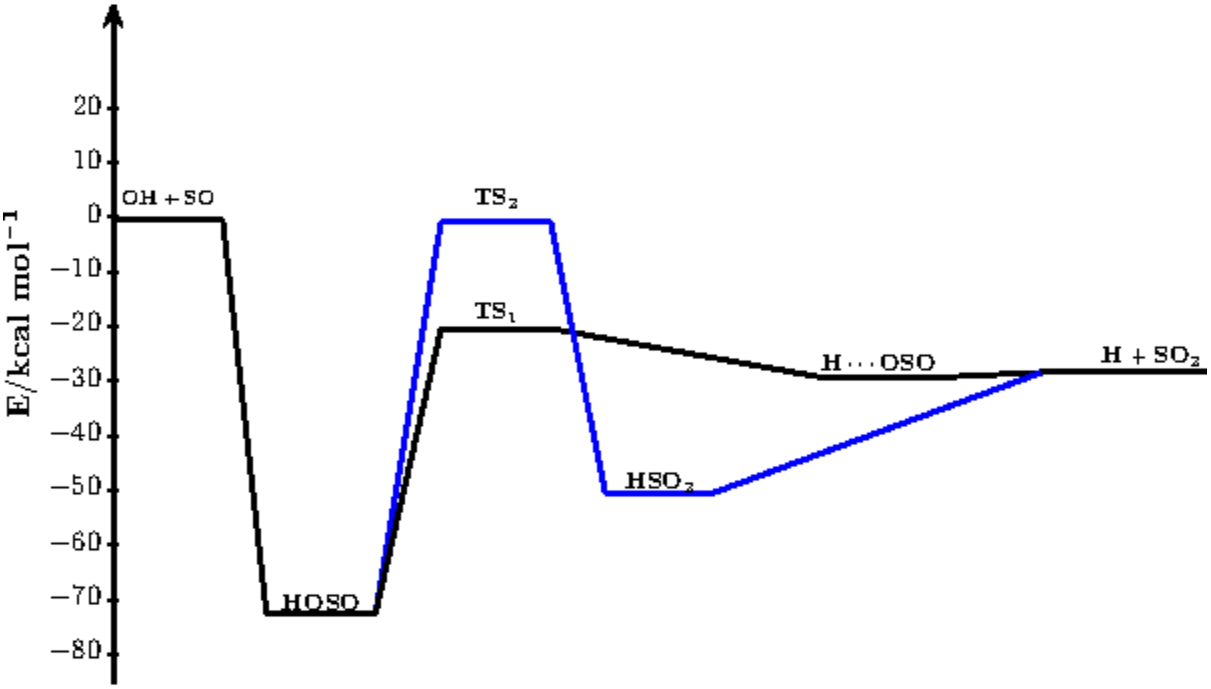

Figure 2: Energetic profile for the reaction 7 according to Ref. [16].

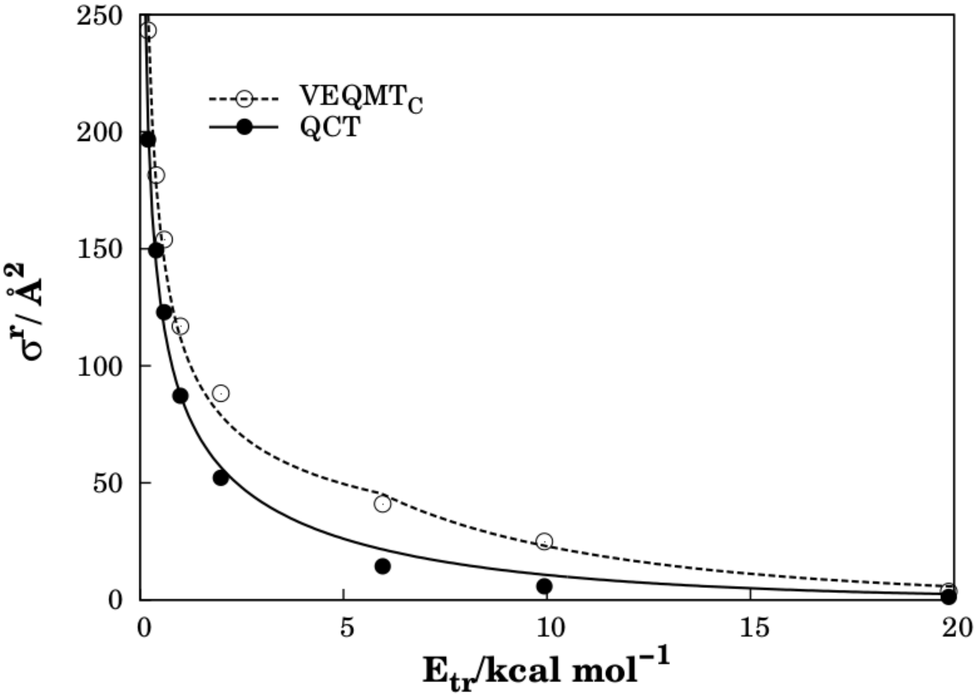

Figure 3: Excitation function for the reaction 7. Results are from a quasi-classical trajectories (QCT) study reported in Ref [11].

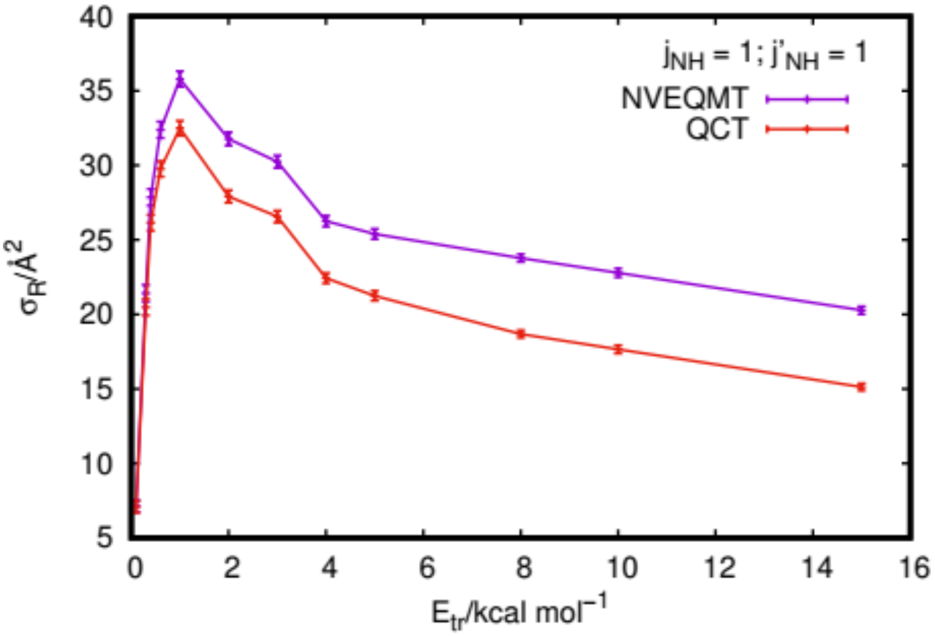

Figure 4: Excitation function for the reaction between two NH radicals as reported in ref. [12].

Other works have also reported a positive dependence of rate constant on the temperature in reaction with similar profiles than these here discussed [17, 18]. These works, and the two here discussed, considered the problem in its full dimension. Then, collision partners are free to reorient while approaching, optimizing the interaction energy while keeping constant the angular momentum. Incidentally, the latter conservation is not included in the analysis using MEPs. Thus, in the study of apparent barrier-free reactions, considering the problem in its full dimension will eventually lead to a different temperature dependence of the rate constant than the expected from the minimum energy profiles.

4.Conclusions

In this work, the temperature dependence of the rate constant for barrier-free reactions is discussed. Two radical-radical reactive collisions were analyzed. Despite having a similar minimum energy path, from full dimension molecular dynamic calculations, the excitation functions for both reactions present different low energy limit. Accordingly, the rate constant behavior in the low-temperature regime differs considerably in both cases. Thus, to consider a molecular collision in its full dimension is not only of theoretical interest but also required for obtaining accurate values of cross-sections and rate constants.

Acknowledgments

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5. References and Notes

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