

Theoretical rate coefficients for the reaction between C₃N with H₂ and CH₄



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Introduction

Understanding how the molecules interact, collide and are able to form and break bonds in very low temperatures and densities environments motivated a large number of theoretical studies.^[1,2] Such studies are of particular interest for astrophysical applications in order to better understand the rich chemical complexity that is found in molecular clouds of the interstellar medium.^[1,2] Here, we study chemical reactions of C₃N, a precursor of longer and more complex molecules detected in space, with H₂ and CH₄, two important constituents of the universe.

We have used high-level ab initio calculations to identify the stationary points (and their intrinsic properties) on the reaction path (See R₀, R₀ and R₁ on Figure 1) in combination with transition state theory-based methods to compute the temperature variation of the reactive rate coefficients.



Stationary points

The C₃N reactions with H₂ and CH₄ have been studied using the CCSD approach with the aug-cc-pVDZ basis set of the Gaussian16 program.^[3]

The identity of stationary points was determined by a frequency analysis (zero or one imaginary frequency for a minimum or transition state, respectively).



Pre-exponential factors

Using partition functions, at room temperature of the transition states (TS) for the reactions and its respective reactants, we calculated the Arrhenius' pre-exponential factors.



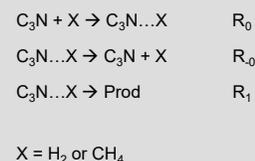
Correction of electronic energies

The electronic energies for all the stationary points for both reactions were refined. We use the CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ level of theory to compare.



Calculation of rate coefficients

The mesmer program^[4] was used to calculate the rate coefficients. The barrierless rate coefficients for the formation/dissociation of the pre-reactive complexes (R₀ and R₀) were calculated with the Inverse Laplace Transform (ILT) (the pre-exponential factor is necessary). For the processes with a TS were used the RRKM theory with the Eckart's tunneling correction.



- As shown on Figure 1, we have compared our theoretical results with those provided by the KIDA database^[5] as well as with recent experimental results obtained using the CRESU technique. As one can see, a good representation of the pre-exponential factor allowed us to be in good global agreement with the experimental results, demonstrating our capabilities to model such environment.

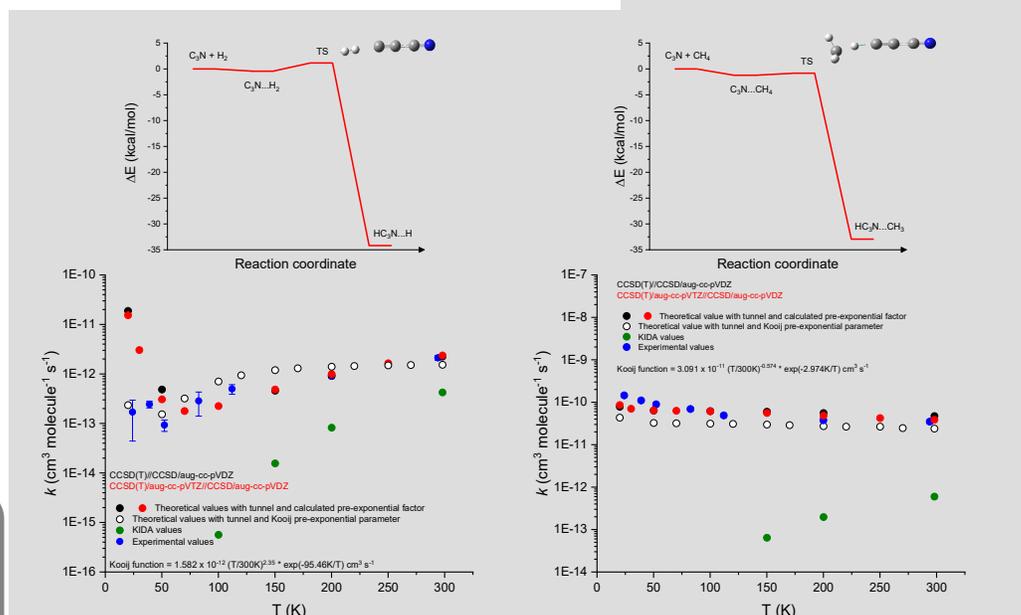


Figure 1. Relative electronic energies (in kcal/mol) for the stationary points calculated at the CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ level of theory for the C₃N + H₂ or CH₄ reactions, and the comparison between the experimental, KIDA and calculated rate coefficients at different temperatures.

Methodology and Results

Conclusions

The rate coefficients for the reaction of C₃N with H₂ and CH₄ were calculated for the first time at several temperatures. The initial hydrogen abstraction process for this reaction was theoretically investigated at the CCSD(T)/aug-cc-pVDZ (CCSD(T) and CCSD(T)/aug-cc-pVTZ) level of theory, and the reaction rate coefficient was calculated with the microcanonical transition state theory considering the calculated pre-exponential factors, leading to values in good agreement with the experimental results.

References

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