

Kinetic investigation of a promising synthetic route for several prebiotic molecules: the reaction between vinyl alcohol and radical cyanide



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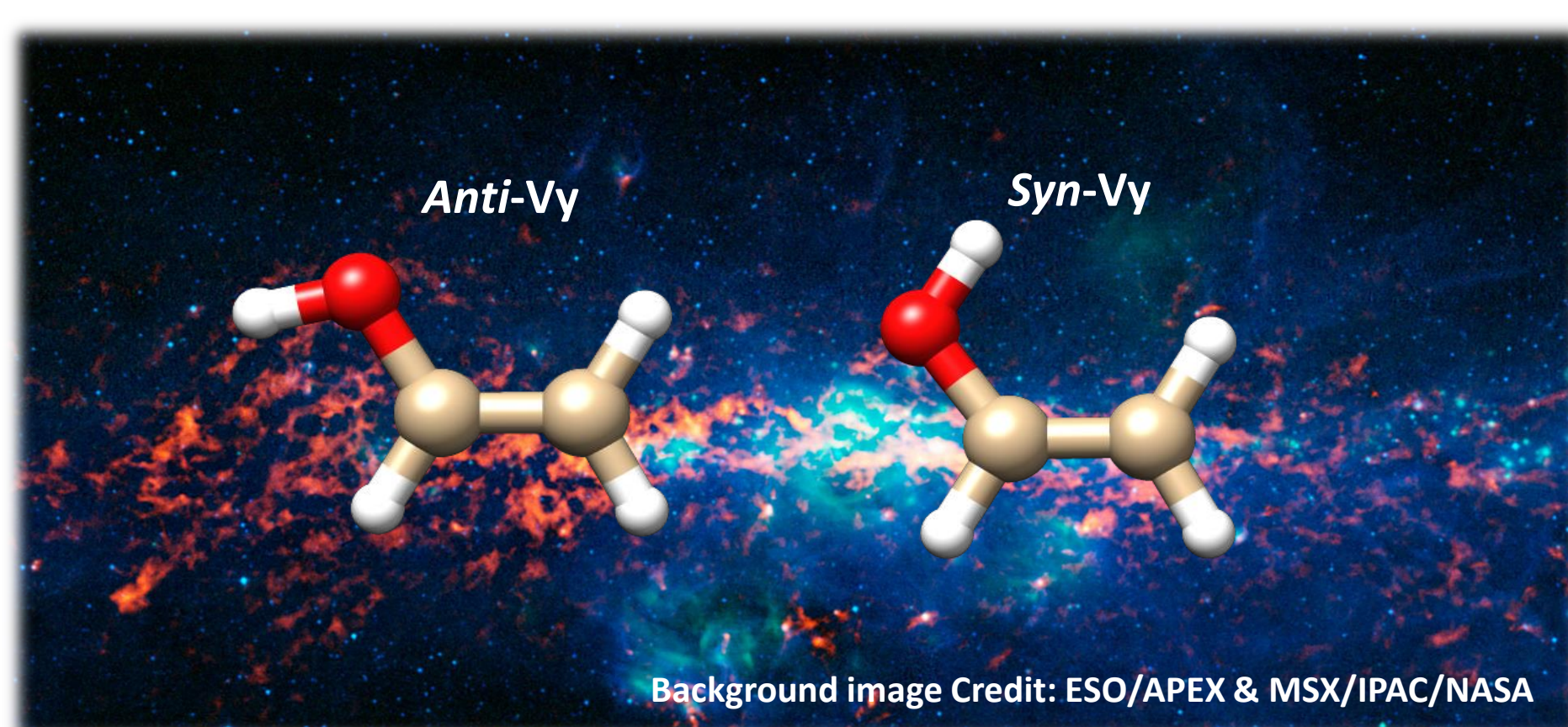
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Introduction

Over the years, the astronomical observations have allowed the identification of many molecular species of different kinds in the interstellar medium (ISM), from simple biatomic to much more complex polyatomic molecules, such as fullerenes and aromatic compounds, named interstellar complex organic molecules (iCOMs). The formation of prebiotic molecules in space has raised considerable interest in the scientific community because they are considered as precursors of more complex biological systems involved in the origin of life in the Universe. The investigation of how the synthesis of iCOMs occurs in the harsh and extremely diversified conditions of the ISM is a pivotal challenge in the astrochemistry research field. With this purpose, computational modeling of chemical reactions is playing a central role to get much more precise information about the reaction mechanisms and the kinetics of the formation and destruction pathways for such complex organic molecules. To find out possible iCOMs formation pathways, investigations are ongoing in our group on the gas-phase reactions between vinyl alcohol (Vy) conformers and radical cyanide (CN) for which, to the best of our knowledge, no kinetic data are available in the literature.



Vy and CN are two relatively abundant molecules present in the ISM. In particular, Vy's microwave transitions have been detected in emission toward the dense molecular cloud SagittariusB2 (N) which is one of the most studied by astronomers because it is rich in prebiotic iCOMs. It can exist in two rotameric forms, *syn* and *anti*, depending on the value assumed by the dihedral angle ϕ (C=C-O-H), which defines the position of the hydroxyl hydrogen with respect to the double bond [1].

Computational details

ELECTRONIC STRUCTURE CALCULATIONS

Geometry optimizations and zero-point corrected electronic energies of reactants, transition states, intermediates, and products along the reaction pathways were obtained by the rev-DSD-PBEP86-GD3BJ double-hybrid functional in conjunction with the jun-cc-pVTZ basis set. After that, for all stationary points, improved electronic energies were obtained by means of the junChS-F12[2] composite method, which includes core-valence correlation energy and complete basis set extrapolation at the MP2-F12 level on top of CCSD(T)-F12 energies computed with a triple-zeta basis set. An anharmonic zero-point vibrational energy correction based on rev-DSD-PBEP86 calculations was applied to jun-ChS-F12 electronic energies, and DFT vibrational frequencies obtained with the same functional were used for kinetics calculations. All rev-DSD-PBEP86 calculations were performed using Gaussian16, while junChS-F12 calculations were performed using MOLPRO.

KINETICS

Kinetic analysis has been performed through StarRate[3], a program specifically designed for astrochemical reactions, based on a master equation approach coupled to capture theory for the bimolecular association steps and to the Rice-Ramsperger-Kassel-Marcus for the unimolecular evolution of the intermediates. Also tunneling effect has been taken into account through the Eckart model. The initial bimolecular rate constant for the barrierless reaction has been calculated using the microcanonical Gorin's formula:

$$k(E) = \frac{3\pi}{\sqrt{\mu}} \sqrt{C_6} \sqrt{\frac{E}{2}}$$

where E is the translational energy, μ the reduced mass and C_6 a parameter obtained by fitting the minimum energy paths of the barrierless association reaction to the expression of a long-range interaction potential $V(R)=V_0-(C_6/R^6)$.

Results

Anti-Vy + CN

By our calculation, for the reaction between *anti*-Vy conformer with CN, the barrierless hydrogen abstraction which leads to the formation of P8 is strongly favored with respect to the association of CN to the double bond.

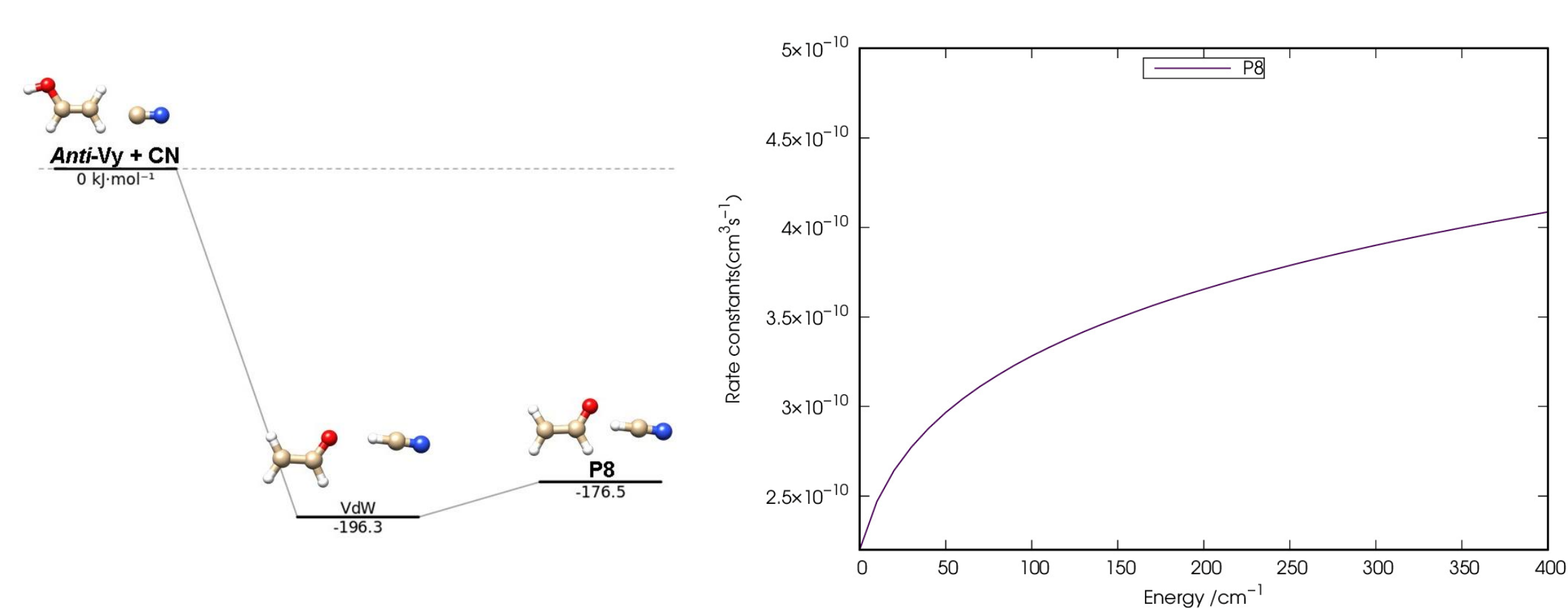


Fig 1a, 2a. On the left side the energetics of the barrierless hydrogen abstraction reaction. Energies in kJ mol^{-1} relative to the dissociation limit. On the right side a plot showing the microcanonical rate constants as a function of energy expressed in cm^{-1} .

Syn-Vy + CN

For *syn*-Vy, after a strongly favored barrierless association reaction to the double bond by radical cyanide, several isomerization and dissociation processes can occur which bring to the formation of several products not yet detected in the ISM.

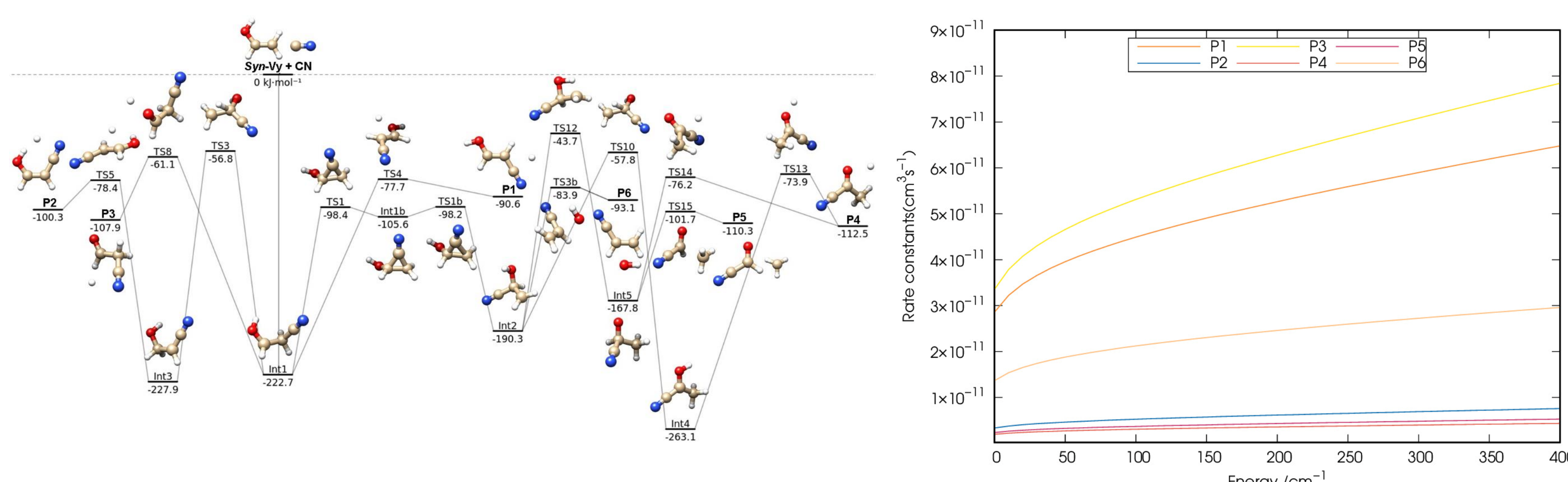


Fig 1b, 2b. On the left side the energetics of the isomerization and dissociation reactions. Energies in kJ mol^{-1} relative to the dissociation limit. On the right side a plot showing the microcanonical rate constants as a function of the products P1, P2, P3, P4, P5 and P6.

Conclusion

The modeling of the gas-phase reaction between Vy conformers and CN highlight that *syn*-Vy and *anti*-Vy show a completely different reactivity with CN.

By the kinetic analysis, P3, also known as cyanoacetaldehyde, a prebiotic molecule not yet detected in the ISM, is the favored product of the reaction between *syn*-Vy and CN.

References

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- [3] Nandi, S.; Ballotta, B.; Rampino, S.; Barone, V. A General User-Friendly Tool for Kinetic Calculations of Multi-Step Reactions within the Virtual Multifrequency Spectrometer Project. Applied Sciences. 2020, 10(5), 1872.