H-Atom-Abstraction and H-Atom-Addition Reactions of Fulminic Acid (HCNO) and Formaldoxime (H_2CNOH) in Solid *para*-H_2

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1. Introduction

One of the central questions of astrochemistry is how the most abundant molecule of the interstellar medium (ISM), H_2, is formed in dense molecular clouds. According to recent theoretical studies, it is possible that H_2 is generated on the surface of interstellar grains by catalytic cycles. H atoms can react with particles in H-addition and H-abstraction processes. In the case of several successive H atom reactions, catalytic cycles can occur [1].

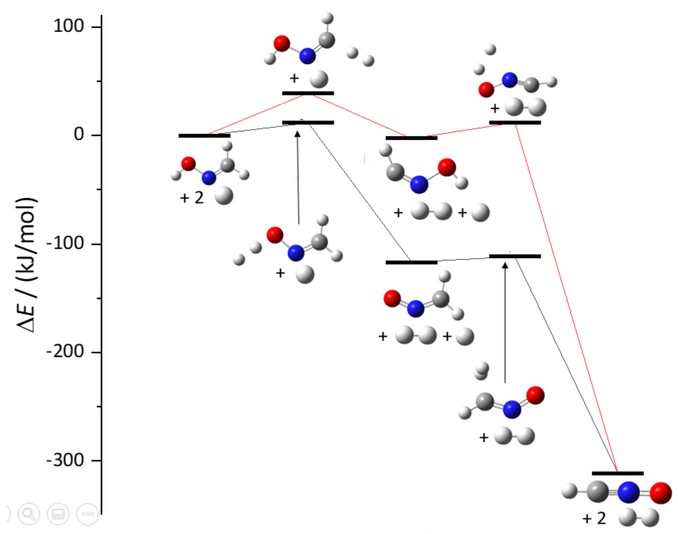
The aim of our research work was to investigate the reactions between H atom and astrochemically interesting molecules, fulminic acid (HCNO) and formaldoxime (H_2CNOH).

2. Methods

- Experiments were carried out in solid *para*-H_2 by the VIZSLA setup [2].
- HCNO was prepared from 1,2,5-oxadiazole by *in-situ* λ = 220 nm UV photolysis [3]; *trans*-H_2CNOH was prepared from its trimer complex with HCl by heating at T = 39.5 °C.
- The sample (i.e. 1,2,5-oxadiazole or *trans*-H_2CNOH) with Cl_2 were deposited in *para*-H_2 matrix at T = 3.1 K (precursor : Cl_2 : *para*-H_2 ≈ 1:3:2300) onto a gold-coated silver substrate.
- H atoms were generated by successive λ = 365 nm UV and λ = 2217 nm NIR irradiation [4].
- Secondary photolysis were carried out at λ = 390, 330, 300, 270, 240 and 216 nm.
- Irradiations were carried out by a Nd-YAG:OPO system.
- Chemical processes were followed by IR spectroscopy, using a Bruker Invenio FT-IR spectrometer in reflection-absorption mode.
- Assignments were based on comparison with computed vibrational frequencies and intensities (anharmonic B3LYP/cc-pVTZ), and were confirmed by temporal changes of relative peak intensities.

3. Barrier heights

H-Abstraction

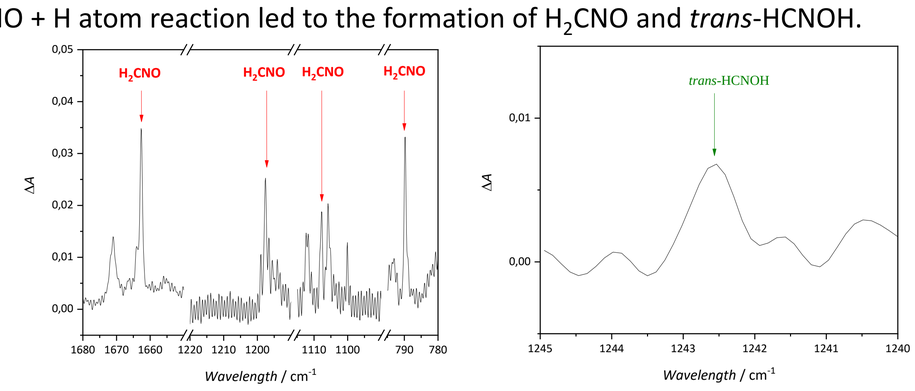


The barrier heights, determinated by theoretical computations (B3LYP/cc-pVTZ with zero-point vibrational energy correction).

The PES corresponding to the H atom addition is still under computation.

4.a The observed chemical changes – Experiment 1: HCNO + H

- HCNO + H atom reaction led to the formation of H_2CNO and *trans*-HCNOH.

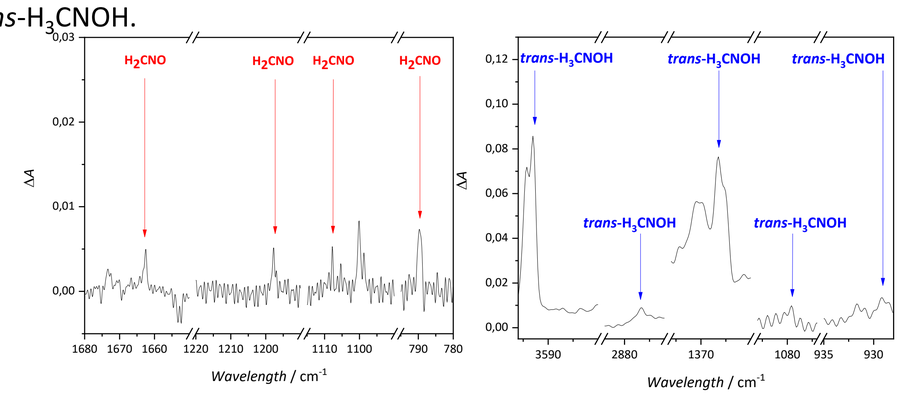


The differental spectra of the formed particles in the case of H_2CNOH.

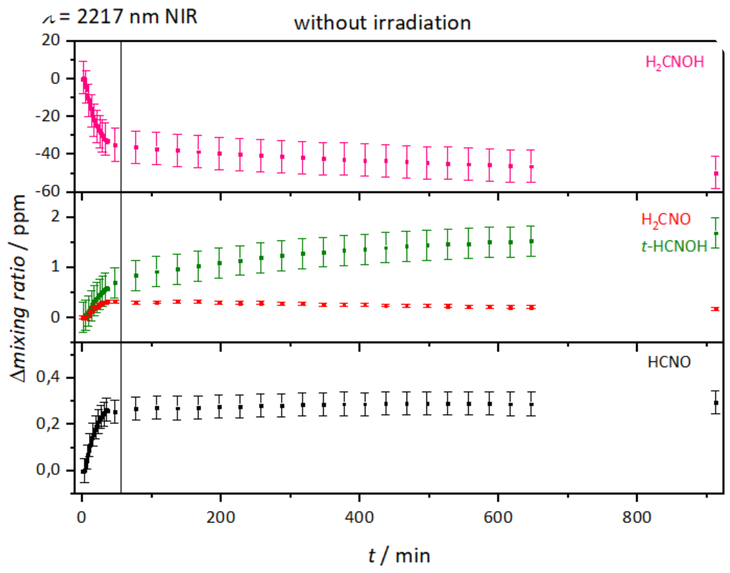
Changes of the quantity of the species in the time.

4.b The observed chemical changes – Experiment 2: H_2CNOH + H

- H_2CNOH + H atom reaction led to the formation of H_2CNO, *trans*-HCNOH, HCNO and *trans*-H_3CNOH.

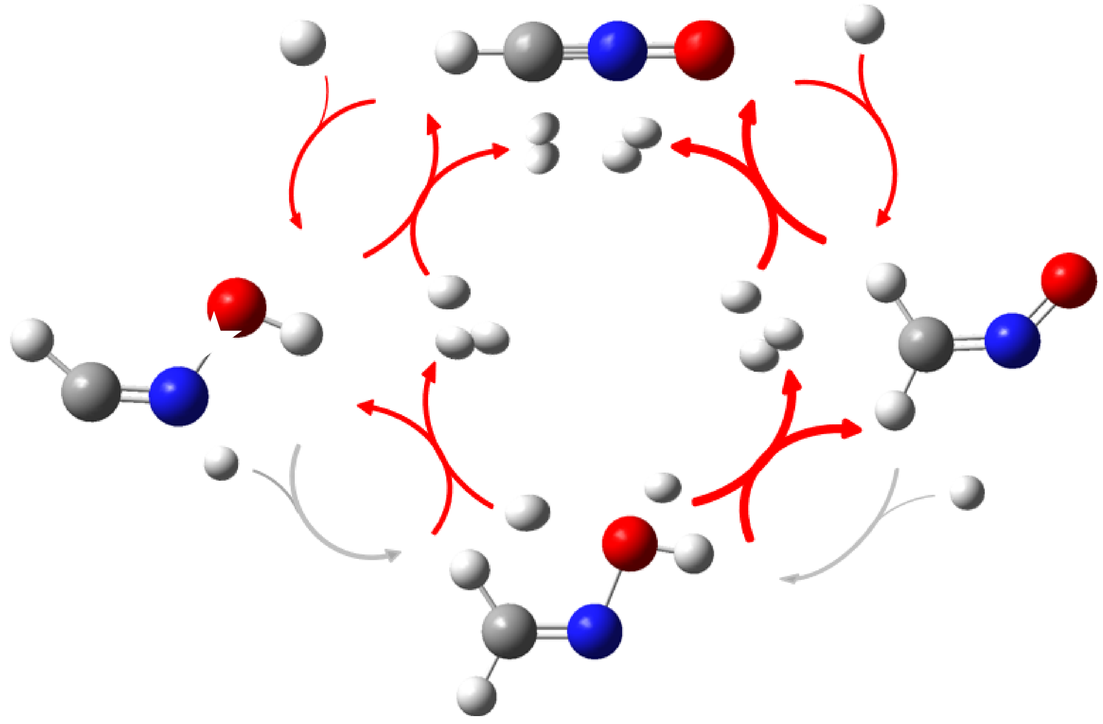


Examples for the differental spectra of the formed particles in the case of H_2CNOH.



Changes of the quantity of the species in the time.

5. Catalytic cycle



Reactions between HCNO and H_2CNOH. The red and grey arrows show the reactions observed and not observed, respectively, upon the experiments.

6. Conclusions

- HCNO and H_2CNOH can react with H atoms at 3.1 K, the same reactions might also occur in the dense molecular clouds.
- HCNO and H_2CNOH are chemically linked, the quasi-equilibrium is shifted towards HCNO. This may explain the non-detection of H_2CNOH in the ISM.
- The IR spectra of several small molecules were recorded in *para*-H_2. In the future, these laboratory spectra might help to identify these particles in the ISM.

References

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