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REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL & NON-STATISTICAL STUDY

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REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL & NON-STATISTICAL STUDY

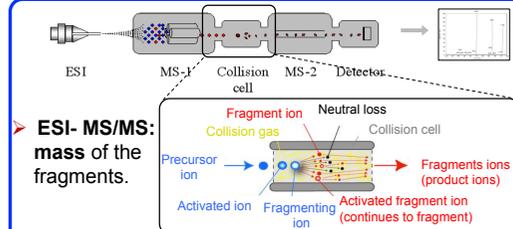
OVERVIEW

- The study of the reactivity of biomolecules in the gas phase allows to get rid of the effects of the environment: **intrinsic properties** of molecules.
- Using Collision Induced Dissociation experiments and Chemical Dynamics simulations we obtained reaction mechanisms for protonated Uracil.

INTRODUCTION

- Explain non-statistical and statistical reactivity of protonated Uracil in the gas phase and obtain predictive MS-MS spectra.

METHODS

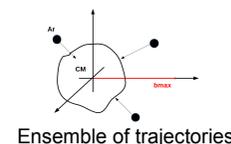
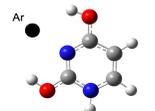


QM-MM CHEMICAL DYNAMICS SIMULATIONS [1]: non-statistical mechanisms

Potential energy function

$$V = V_{\text{ion}} + V_{\text{Ar-ion}}$$

QM MM
AM1, PM3 and DFT

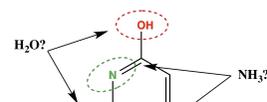
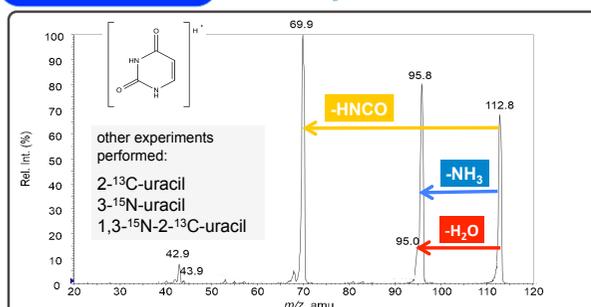


RRKM and KINETIC MONTE CARLO (KMC) SIMULATIONS: statistical reactivity.

- For trajectories that did not react before IVR (intramolecular vibrational relaxation) takes place but have enough energy to react later on.
- Following automatic protocol^[3] to find all fragmentation pathways, **TSs** and **minima**. Then this is used as input for RRKM and KMC simulations.

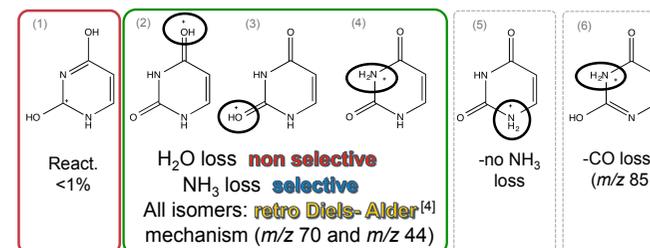
RESULTS

Experiments



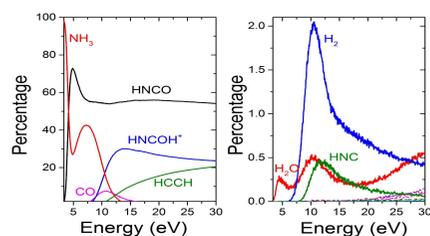
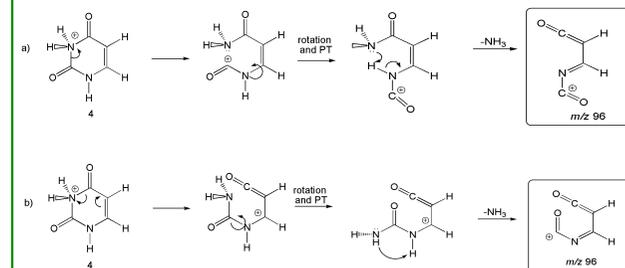
from RRKM analysis:
H⁺ transfer
ns
(out of simulation time)

Chemical Dynamics Simulations^[2]

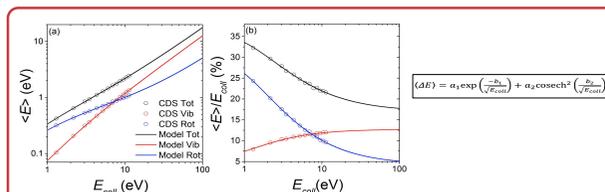


RRKM and KMC

Example of NH₃ loss mechanism for isomer 4.



Product yields of the different fragmentation channels of the C₄H₅N₂O₂⁺ system obtained in the KMC simulation as a function of the excitation energy.



CONCLUSIONS

- As suggested by experiments, m/z 70 is obtained by a retro Diels-Alder (rDA) mechanism.
- rDA reaction does not follow the minimum energy path along the reaction coordinate, while stepwise mechanisms do. In experiments, both mechanisms can co-exist.
- Initial protonation state of the ion plays a crucial role in determining the fragmentation pathway.
- NH₃ loss is a selective reaction, while H₂O loss it is not.

Refs.:

- [1] Hase et al. JPCA (1999)
- [2] Rossich Molina et al. J. Mass Spectrom. (2015)
- [3] Martínez Nuñez. Phys. Chem. Chem. Phys. (2015)
- [4] Diels and Alder. Chemische Berichte. (1929)
- [5] Rossich Molina et al. PCCP (2016)

