

STUDYING THE REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL vs. NON-STATISTICAL APPROACH

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STUDYING THE REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL vs. NON-STATISTICAL APPROACH

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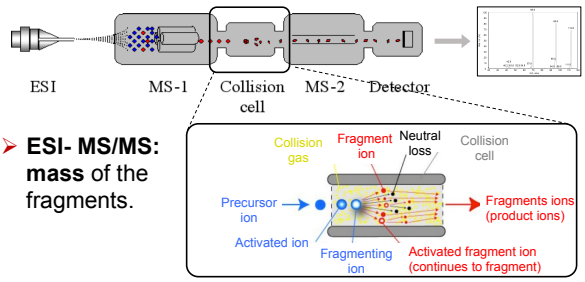
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c- University of Santiago de Compostela, Physical Chemistry, Santiago de Compostela, Spain

INTRODUCTION

- Studying the reactivity of biomolecules in the gas phase allows to get rid of the effects of the environment: **intrinsic properties of the molecule**.
- System: **Uracil in DNA has cytotoxic and mutagenic potential**.

Our AIM

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

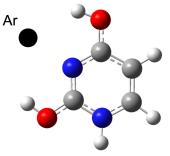


ESI- MS/MS:

mass of the fragments.

QM-MM CHEMICAL DYNAMICS SIMULATIONS [1]:

non-statistical **mechanisms**



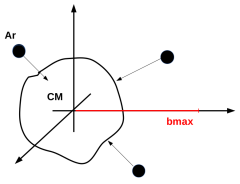
Collision system

Potential energy function

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

QM: AM1, PM3 and DFT

MM



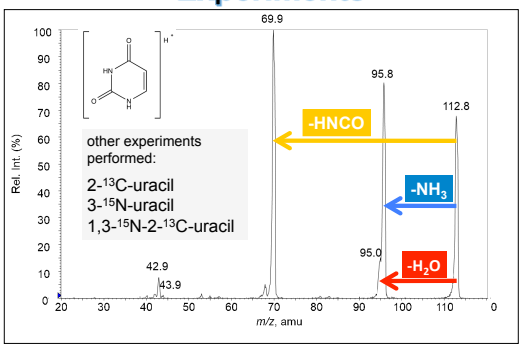
Ensemble of trajectories

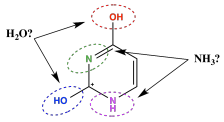
RRKM and KINETIC MONTE CARLO (KMC) SIMULATIONS : statistical reactivity.

- 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 fot RRKM and KMC simulations.

RESULTS

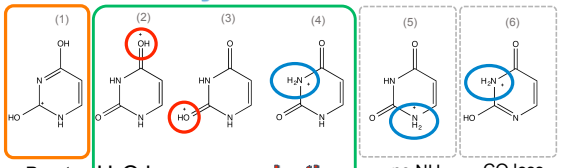
Experiments





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

Chemical Dynamics Simulations[2]



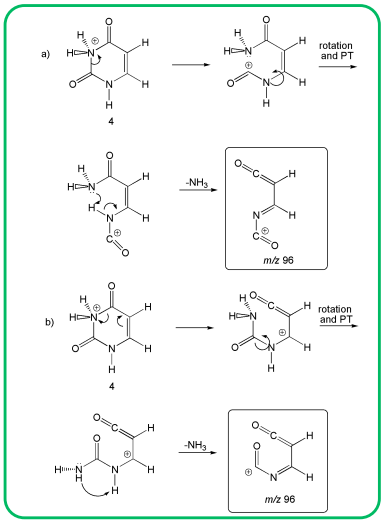
React. <1%

H_2O loss **non selective**
NH_3 loss **selective**
All isomers: **retro Diels-Alder** [5] mechanism
(*m/z* 70 and *m/z* 44)

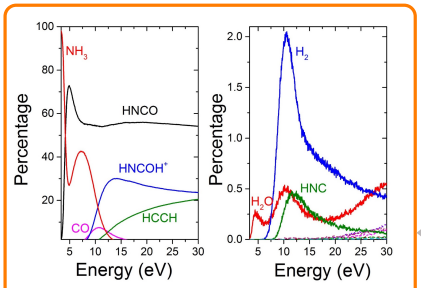
-no NH_3 loss

-CO loss (*m/z* 85)

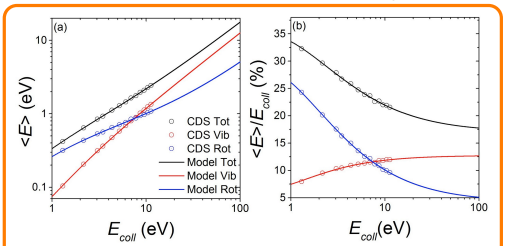
Example of NH_3 loss mechanism for isomer 4.



RRKM and KMC



Product yields of the different fragmentation channels of the $C_4H_5N_2O_2^+$ system obtained in the KMC simulation as a function of the excitation energy.



$$\langle \Delta E \rangle = a_1 \exp\left(\frac{-b_1}{\sqrt{E_{coll}}}\right) + a_2 \mathrm{cosech}^2\left(\frac{b_2}{\sqrt{E_{coll}}}\right)$$

a) Average final (internal) energies of [uracil]H⁺ as a function of the collision energy (in the center of mass framework) for Ar + [uracil]H⁺ collisional system. (b) Percent energy transfer values to [uracil]H⁺ internal degrees of freedom. Symbols and solid lines correspond to the chemical dynamics simulation (CDS), and energy transfer model results, respectively.

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.
- NH_3 loss is a selective reaction, while H_2O loss it is not.

Refs.

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