COMPUTATIONAL KINETIC STUDY FOR THE UNIMOLECULAR DECOMPOSITION PATHWAYS OF CYCLOPENTANONE

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1. INTRODUCTION

- The search for new fuel is important given the growing concern about environment and sustainability.
- Cyclopentanone is a promising candidate that can be produced by the pyrolysis of biomass or the hydrogenation of furfural[1].
- Cyclopentanone can be used as a starting point for the production of high energy density fuels[2].

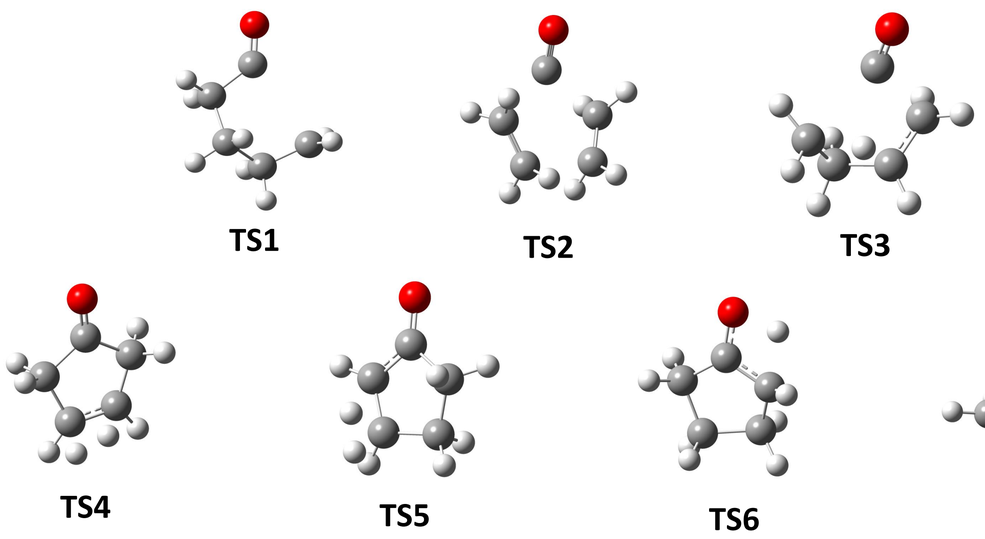
→ **This study reports the first computational kinetic investigation on the unimolecular decomposition pathways of cyclopentanone [3].**

2. METHODOLOGY AND CONSIDERED PATHWAYS

Method

- Structures computed with the G3B3 compound method implemented in Gaussian 09[4].
- Rate constants calculated by means of RRKM theory implemented in MESMER[5].
- Single imaginary frequency for each TS and verification by means of Intrinsic Reaction Coordinate (IRC) calculations.

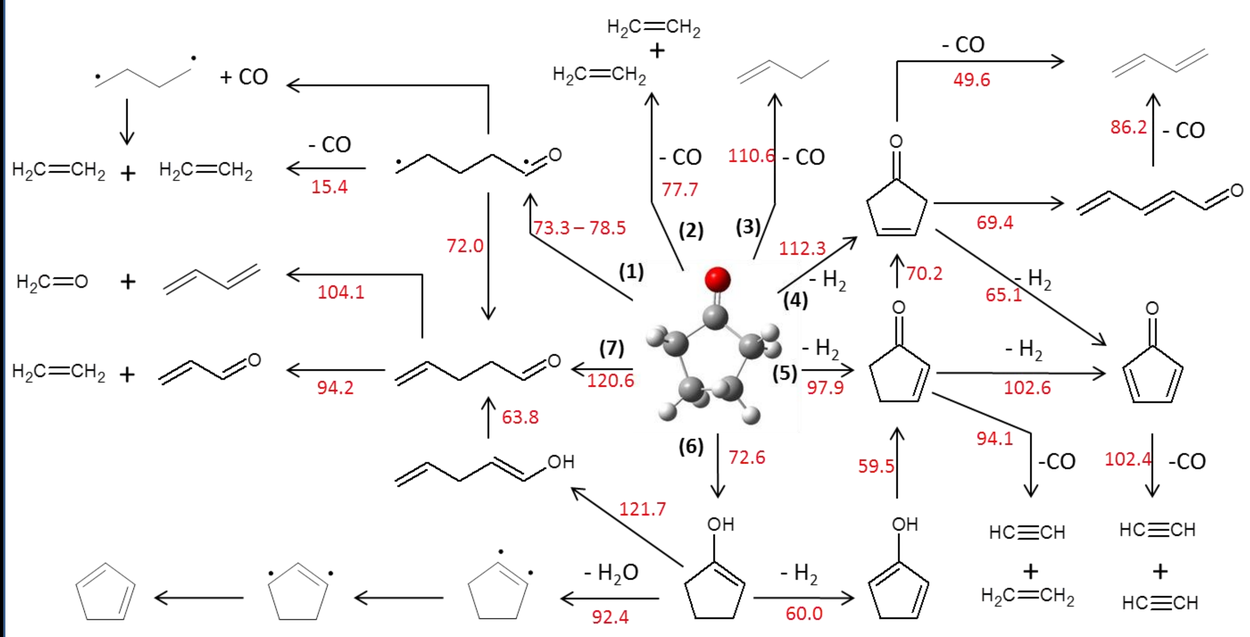
The G3B3 method
- 6 steps compound method.
- Opt+freq: B3LYP/6-31G(d).
- 4 single point calculations.



Transition states located for the main steps of cyclopentanone decomposition.

Decomposition pathways for cyclopentanone

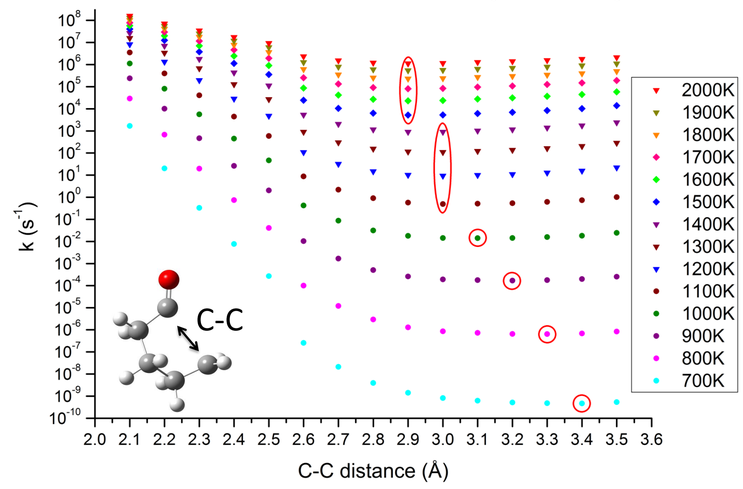
- 7 main pathways + 20 secondary decomposition reactions identified.
- Reactions considered by Delles et al.[6] + 2 new pathways
- Enol formation analogous to cyclohexanone [7].
- Main products: CO, C_2H_4, 2- cyclopenten-1-one.



Identified decomposition pathways for cyclopentanone, values of barrier heights in kcal/mol.

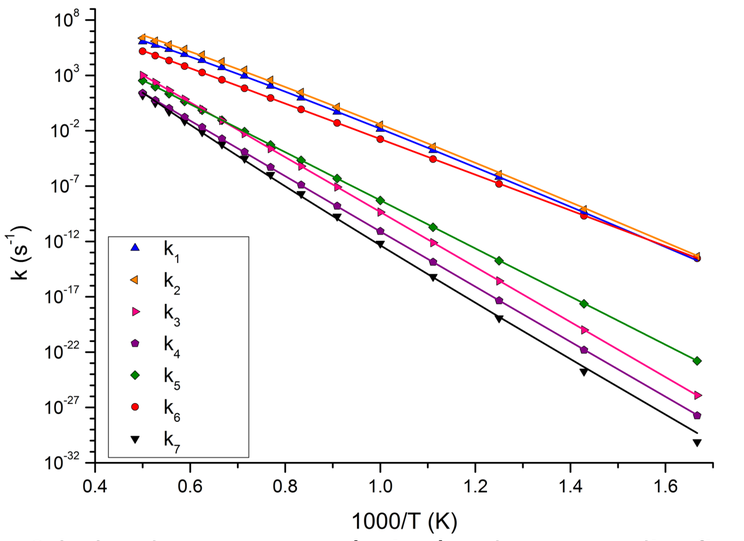
3. RESULTS

Rate constants of main pathways



Variational treatment for k_1

- 15 C-C distances considered.
- Rate constant calculated for each structure.
- Slowest rate selected at each temperature.



Calculated rate constants (points) and corresponding fits (lines) for the main pathways.

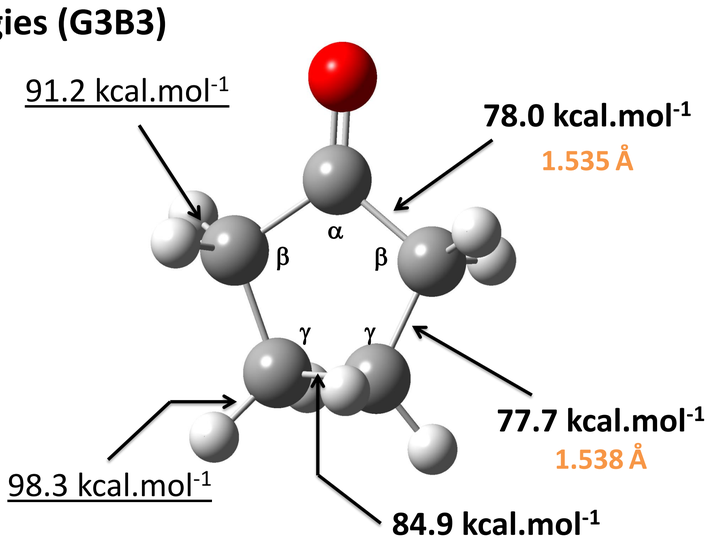
- Pathways 1, 2 and 6 are the fastest.
- The observed trend in k is consistent with the barriers trend.
- k_1 and k_2 are almost equivalent.
- Pathways 1 & 2 entropically more favorable than pathway 6.

k	$\Delta E^{\neq}$ (kcal/mol)	A	n	E (cal/mol)
k_1	73.3 – 78.5	2.01 x 10^{40}	-7.28	92779
k_2	77.7	2.42 x 10^{37}	-6.3	91046
k_3	110.6	2.90 x 10^{17}	-0.58	114662
k_4	112.3	3.26 x 10^{11}	0.68	112793
k_5	97.9	9.14 x 10^{13}	-0.15	99724
k_6	72.6	3.06 x 10^{15}	-0.63	74782
k_7	120.6	3.10 x 10^{13}	0.25	119851

Modified Arrhenius parameters for main pathways considered.

Bond dissociation energies (G3B3)

- Ketone functional group weakens C_β-H bond.
- C_α-C_β bond: slightly shorter and stronger than C_β-C_γ bond.
- C_γ-C_γ bond: strongest C-C bond (no influence from the ketone functional group).



BDEs for cyclopentanone (kcal/mol). Underlined values: C-H bond; bold values: C-C bonds.

4. CONCLUSION AND PERSPECTIVES

- 7 decomposition pathways identified for cyclopentanone.
- Rate constants calculated for these pathways between 700 and 2000K.
- Additional work in progress regarding secondary pathways.

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