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Water complexes in the keto-enol tautomeric equilibrium

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Introduction

The tautomeric equilibrium is among the most important reactions in chemistry because it is involved in many processes. For example, the conformation of peptides is strongly affected by the presence of a specific tautomer. Most of the chemical and biological processes are carried out in solution and the solvent substantially alters the chemical behavior and the molecular structure.[1]

For the keto-enol tautomerism we compare the reaction path both in gas phase and in solution. In the gas phase it is found that the activation barriers are very high.[2] In this work we study the effect of the solvent using different models within the DFT framework.

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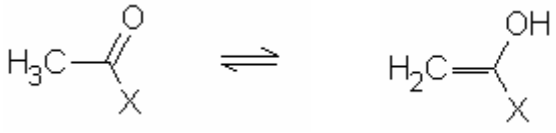
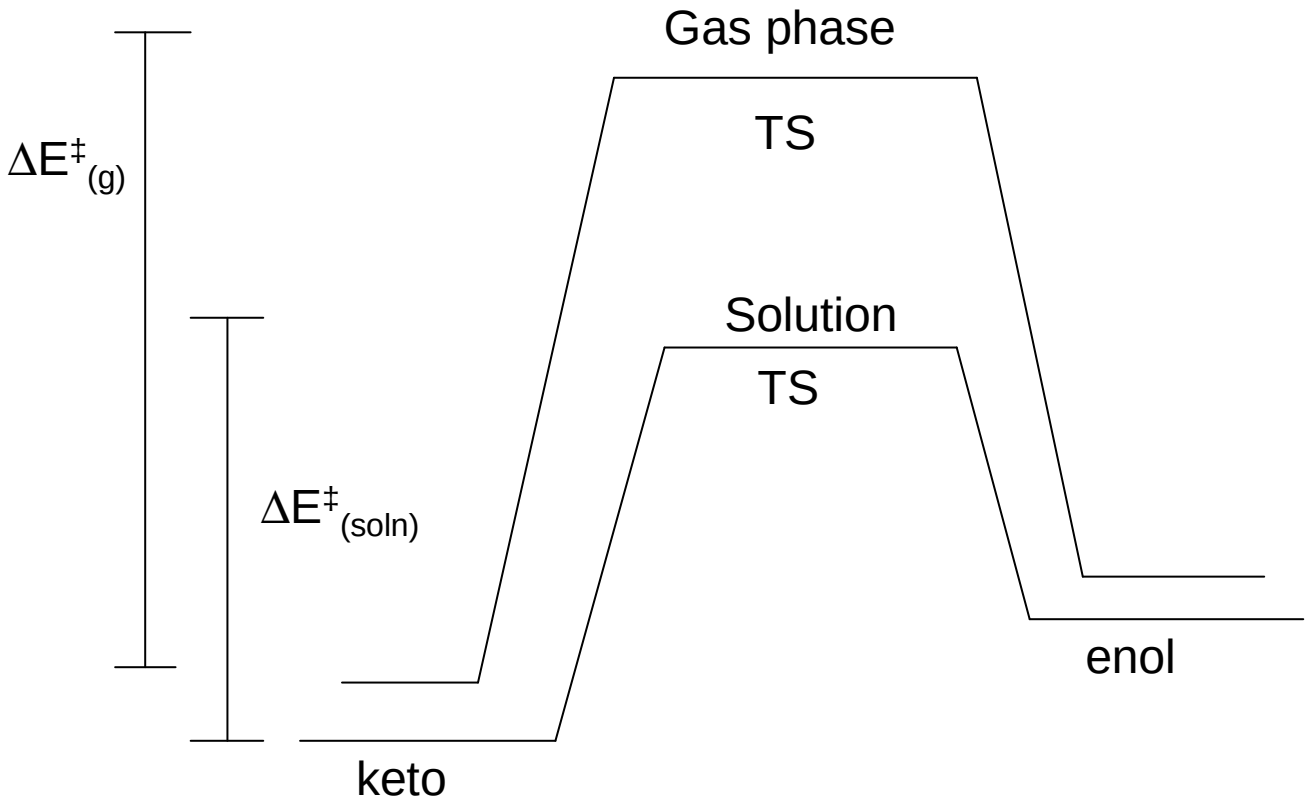
Reaction path





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Main goals

Describe the effect of the solvent in the keto-enol equilibrium

- Analyze the energetics in the keto-enol reaction using a continuous model

- Construct complexes with both the keto and the enol tautomers and some molecules of water

- Simulate the reaction path of keto-enol tautomeric equilibrium in the presence of the solvent

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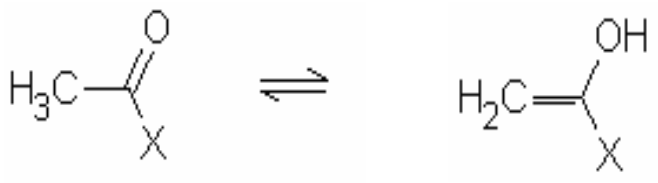
Methodology

B3LYP/6-31++g**
B3LYP/6-311++g(3df, 3dp)

NWChem 5.0

COSMO

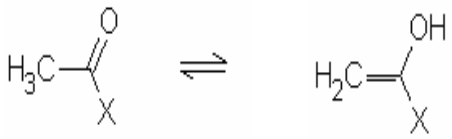
Studied systems



X= H, CH_3, NH_2, OH, OCH_3, F

Continuous solvent model

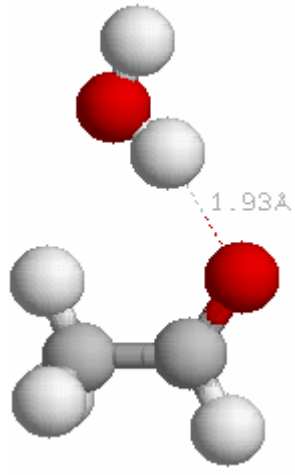
Reaction and activation energy in kcal/mol. B3LYP/6-311++g(3df, 3dp)



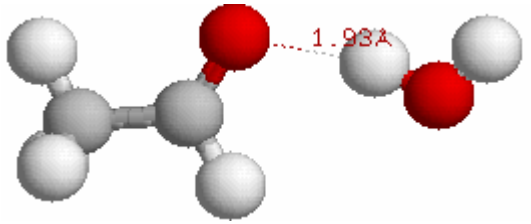
	ΔE_r		$\Delta E^{\ddagger}$	
X	COSMO	gas phase	COSMO	gas phase
H	10.8	9.6	71.5	68.8
CH_3	16.4	11.6	70.4	67.3
NH_2	28.1	24.3	68.0	66.0
OH	29.7	27.0	77.0	73.4
OCH_3	29.2	29.3	73.2	72.9
F	26.6	25.4	81.5	77.8
malonaldehyde	1.9	1.0	57.8	58.6
	2.1[a]		57.7[a]	

[a]Yamabe, S.; Tsuchida, N. and Miyajima, K. *J. Phys. Chem. A* **2004**, *108*, 2750.

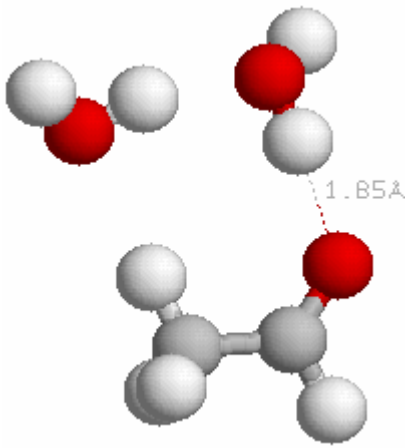
Complexes of acetaldehyde with one and two water molecules. B3LYP/6-311++g(3df, 3dp)



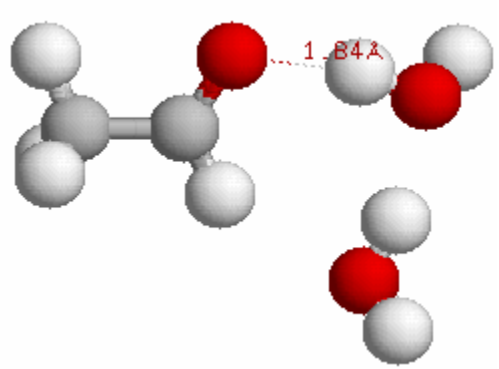
E_{int}=-5.3 kcal/mol



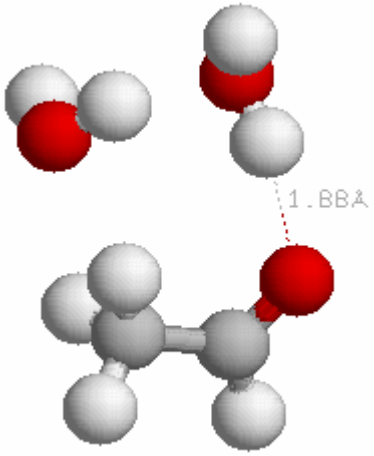
E_{int}=-5.0 kcal/mol



E_{int}=-12.8 kcal/mol



E_{int}=-13.1 kcal/mol



E_{int}=-11.9 kcal/mol

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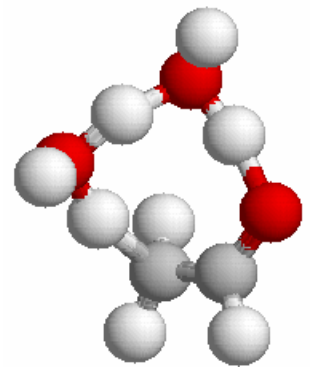
Acetaldehyde reaction path

Reaction and activation energy in kcal/mol.



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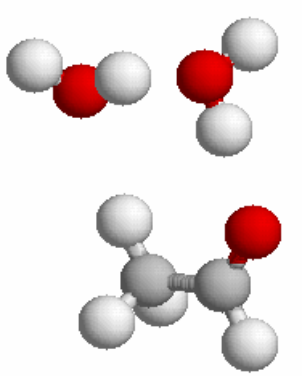
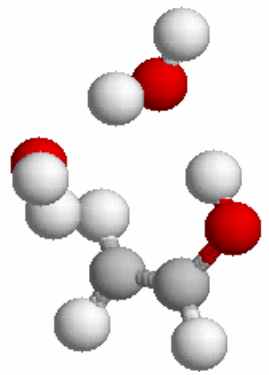


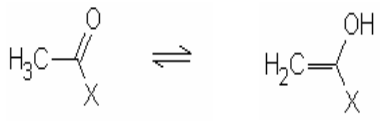
keto



enol

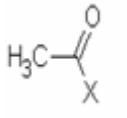
	ΔE_r	$\Delta E^{\ddagger}$
B3LYP/6-31++g**		
gas phase	11.0	69.2
with one water molecule	9.2	40.2
with two water molecules	9.0	32.6
MP2/6-31++g**		
with two water molecules	9.9	38.5
B3LYP/6-311++g(3df,3pd)		
gas phase	9.6	68.8
with two water molecules	12.7	37.7

Reaction and activation energies in the gas phase and in solution, in kcal/mol. B3LYP/6-31++g**

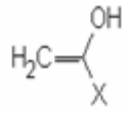


X		ΔE_r	$\Delta E^{\ddagger}$
H	gas phase	11.0	69.2
	with two water molecules	9.0	32.6
CH_3	gas phase	12.9	67.6
	with two water molecules	11.5	34.1
NH_2	gas phase	26.3	66.5
	with two water molecules	24.3	36.5
OH	gas phase	28.8	74.3
	with two water molecules	23.9	38.2
OCH_3	gas phase	30.8	73.6
	with two water molecules	26.4	39.6
F	gas phase	26.9	78.8
	with two water molecules	21.4	36.4

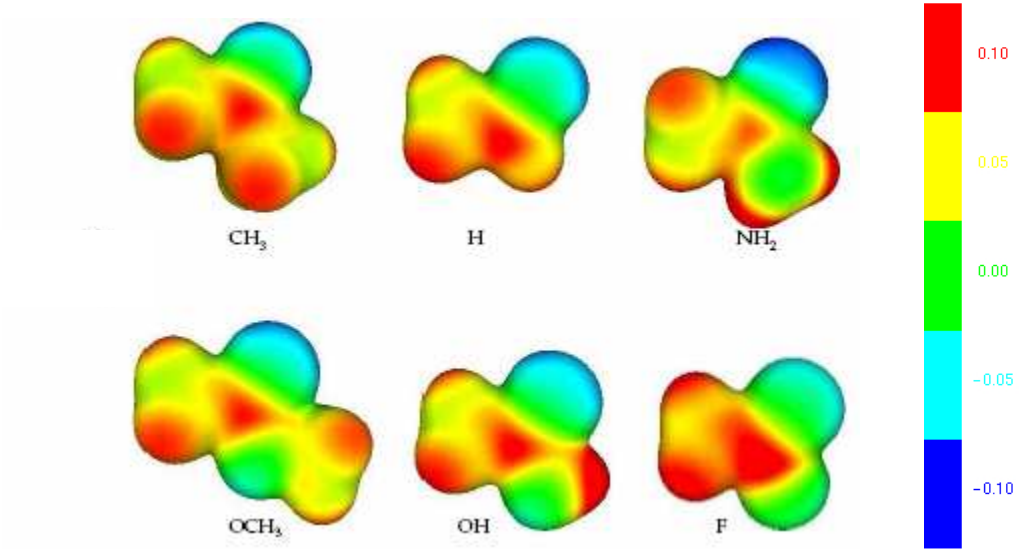
Interaction energy of complexes with two water molecules. B3LYP/6-31++g**

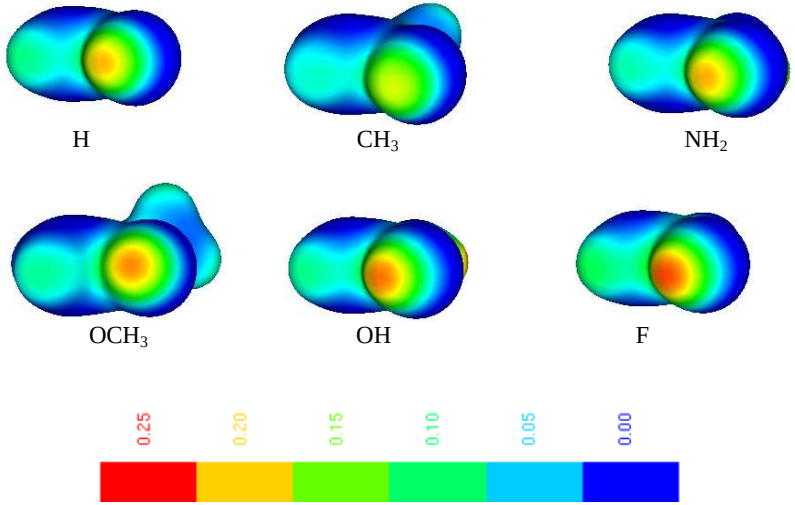


X	ΔE_{int}
H	-14.9
CH_3	-15.5
NH_2	-17.3
OH	-15.1
OCH_3	-15.4
F	-14.2



X	ΔE_{int}
H	-17.0
CH_3	-16.9
NH_2	-19.2
OH	-20.1
OCH_3	-19.8
F	-19.7





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Conclusions

The use of the continuous solvent model produces a very small effect on the reaction and activation energies (a few kcal/mol).

On the water-solute complexes, the water molecules interact with the polar faces of the solutes. There are many stable complexes, but only a few are suitable for the assisted proton shift.

A considerable reduction on the proton shift energy barriers (~30 kcal/mol) is found when the water-solute complexes are formed.

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References

1. Carey, F. A. and Sundberg, R. J. *Advanced Organic Chemistry (Part A): Structure and Mechanism*, Plenum, 4th ed, 1990.

2. González-Rivas, N. *Evolution of the reactivity and the substituent effect on systems with tautomerism by proton shift.*; Thesis, UAM: 2005.