# Natural Bond Orbital Analysis of the Acid-Catalyzed Dehydration of Ethanol

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Introduction

One of the reaction mechanisms that students learn early on in sophomore-level organic chemistry is that of alcohol dehydration. In the presence of acid and heat, an alcohol, like ethanol, dehydrates to give an alkene.
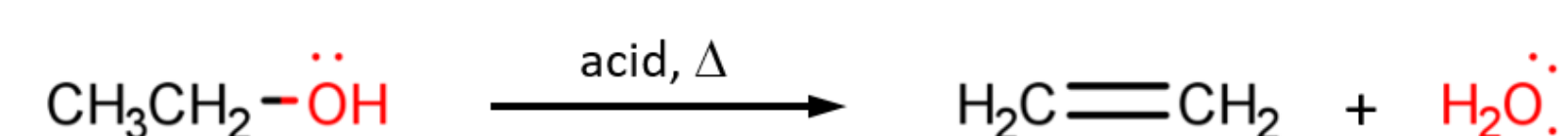
Ethanol is a primary alcohol that, following protonation, undergoes dehydration via an E2 mechanism, which is usually represented as follows:
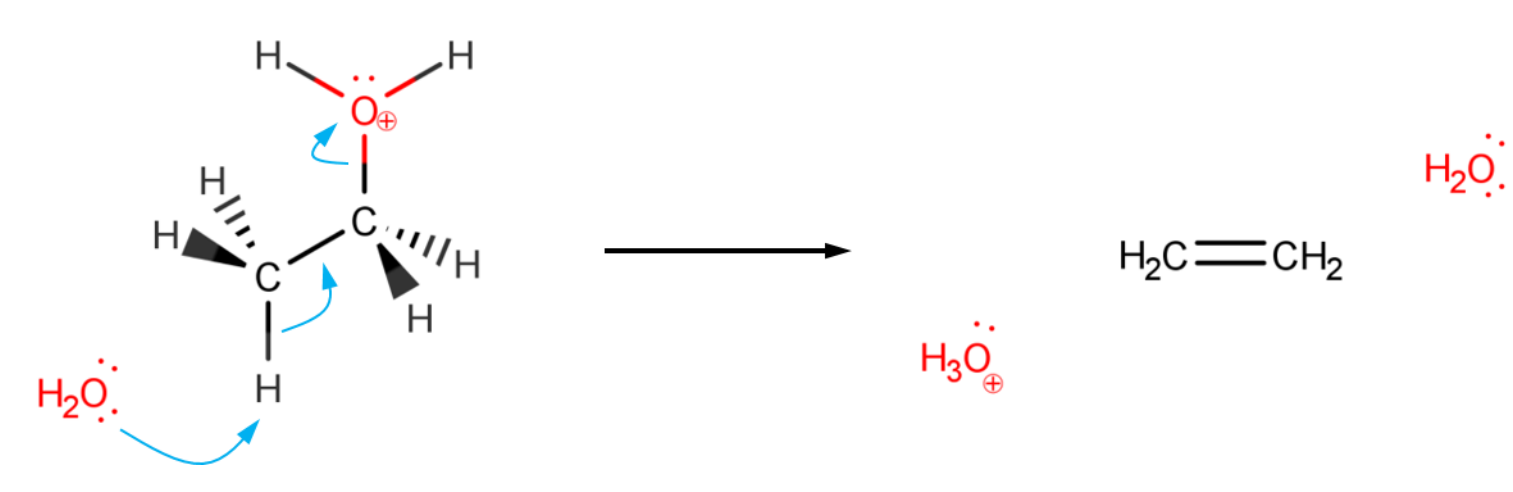
In this work we demonstrate how students can use density functional theory calculations and natural bond orbital analysis to explore an organic reaction mechanism, like ethanol dehydration, to gain insight into the bond breaking and making processes.

Methods

Gaussian-16 calculations were performed at the B3LYP/cc-pVDZ level using an implicit solvent model (scrf=pcm,smd) to approximate the aqueous environment of the reaction. All geometries were optimized using "tight" convergence thresholds. Vibrational frequency calculations were performed to characterize the nature of each stationary geometry (equilibrium or transition state). Intrinsic reaction coordinate (IRC) calculations mapped the minimum energy surface from reactants to products, and thermodynamic corrections were applied to calculate free energies (ΔG) at 298 K. Natural bond orbital (NBO) and natural resonance theory (NRT) analysis was performed using the NBO7 program.

Results

The following energies, free energies, and minimum frequencies were calculated for the uncatalyzed and H_3O^+-catalyzed reactions. Geometries include reactants (**R**), reactant complexes (**RC**), transition states (**TS**), product complexes (**PC**), and products (**P**). Labels for the geometries of the uncatalyzed reaction include an asterisk.

| geometry	E (a.u.)	ΔE (kcal/mol)	ΔG (kcal/mol)	ν_{min} (cm^{-1})
Uncatalyzed Reaction				
CH_3CH_2OH (**R***)	−155.049696	0.0	0.0	272
TS*	−154.941589	67.8	62.5	2014i
$CH_2=CH_2\cdots H_2O$ (**PC***)	−155.026152	14.8	9.1	103
$CH_2=CH_2+H_2O$ (**P***)	−155.020204	18.5	5.4	
Catalyzed Reaction				
$CH_3CH_2OH+H_3O^+$ (**R**)	−231.908372	0.0	0.0	
$H_2O\cdots CH_3CH_2OH_2^+$ (**RC**)	−231.913944	−3.5	4.9	55
TS	−231.872410	22.6	25.6	847i
$H_3O^+\cdots CH_2=CH_2\cdots H_2O$ (**PC**)	−231.892737	9.8	13.7	39.1
$H_3O^++CH_2=CH_2+H_2O$ (**P**)	−231.878879	18.5	5.4	

Reaction Profile

Reaction profiles for the uncatalyzed and catalyzed reactions are shown below. Uncatalyzed dehydration proceeds via *intramolecular* proton transfer from C_β to the hydroxyl O, followed by H_2O elimination. The reaction has an exceptionally high activation energy of 67.8 kcal/mol.
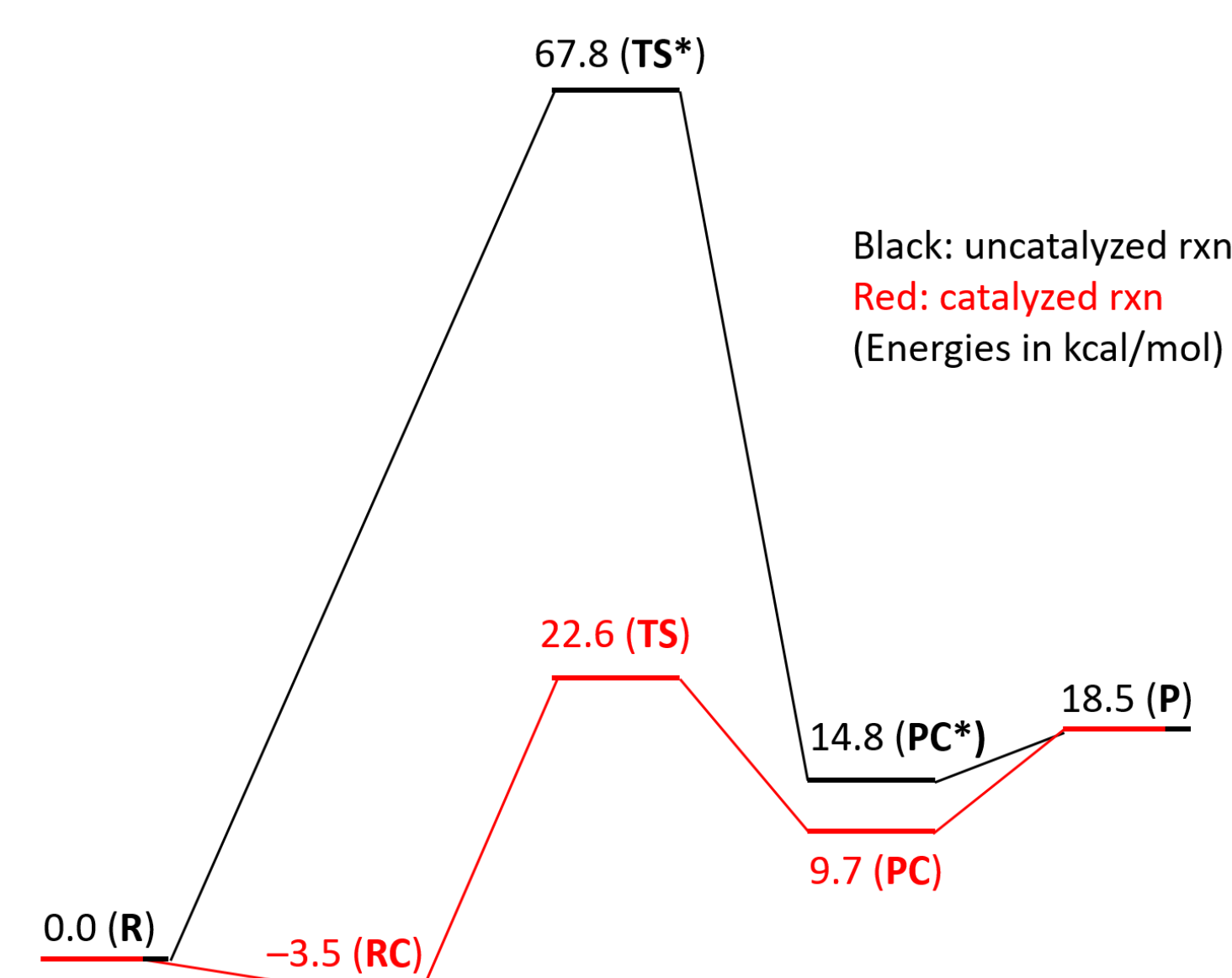

The H_3O^+ catalyst decreases the activation energy to 22.6 kcal/mol. The catalyzed reaction begins with proton transfer from H_3O^+ to ethanol. Protonated ethanol then eliminates H_2O as a proton on C_β transfers to an adjacent solvent molecule.

An IRC calculation of the catalyzed reaction reveals a minimum energy pathway that connects the reactant complex to the product complex via the transition state. The IRC includes 122 geometries along the pathway, from IRC=−7.26 to IRC=+6.68. The transition state is at IRC=0.00.
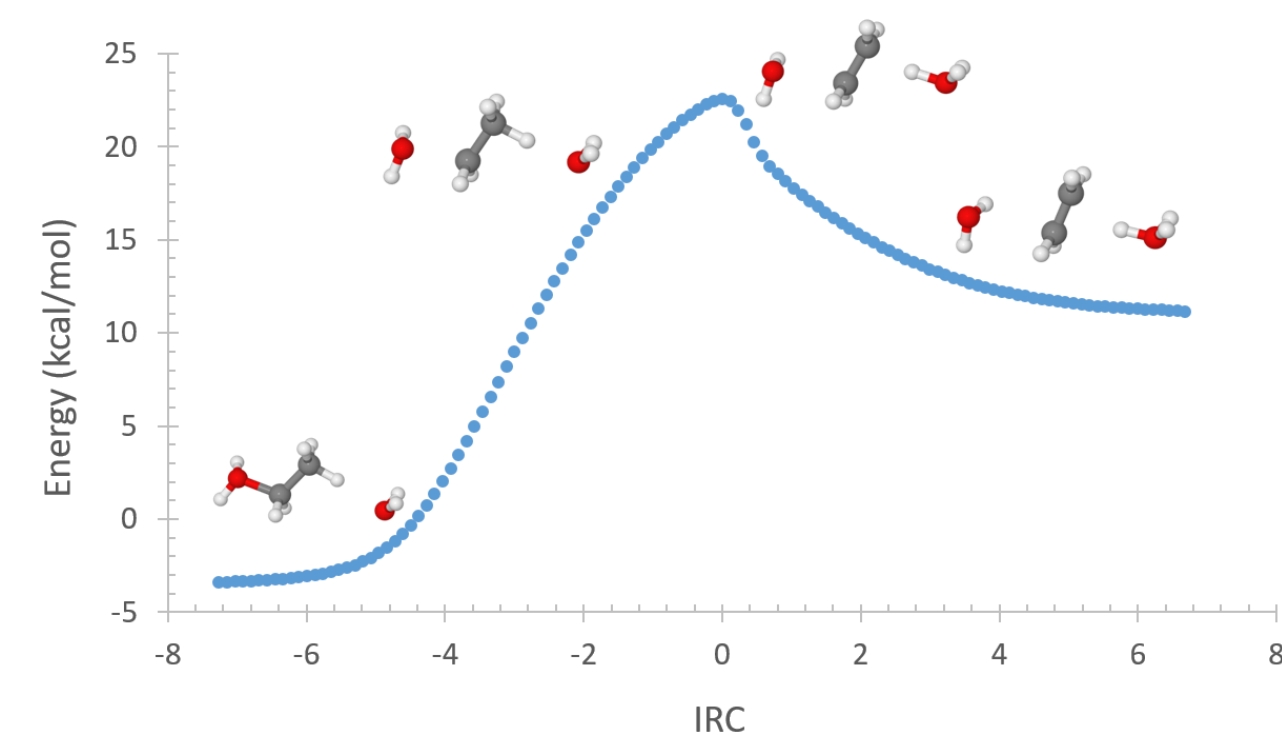
## Natural Resonance Theory Analysis

The *natural bond orders* of NRT analysis reveal the making and breaking of bonds across the IRC. The following shows that C-O and C-H single bonds break as a O-H single bond and C=C double bond form. These bond rearrangements are consistent with the E2 mechanism for dehydration of ethanol.
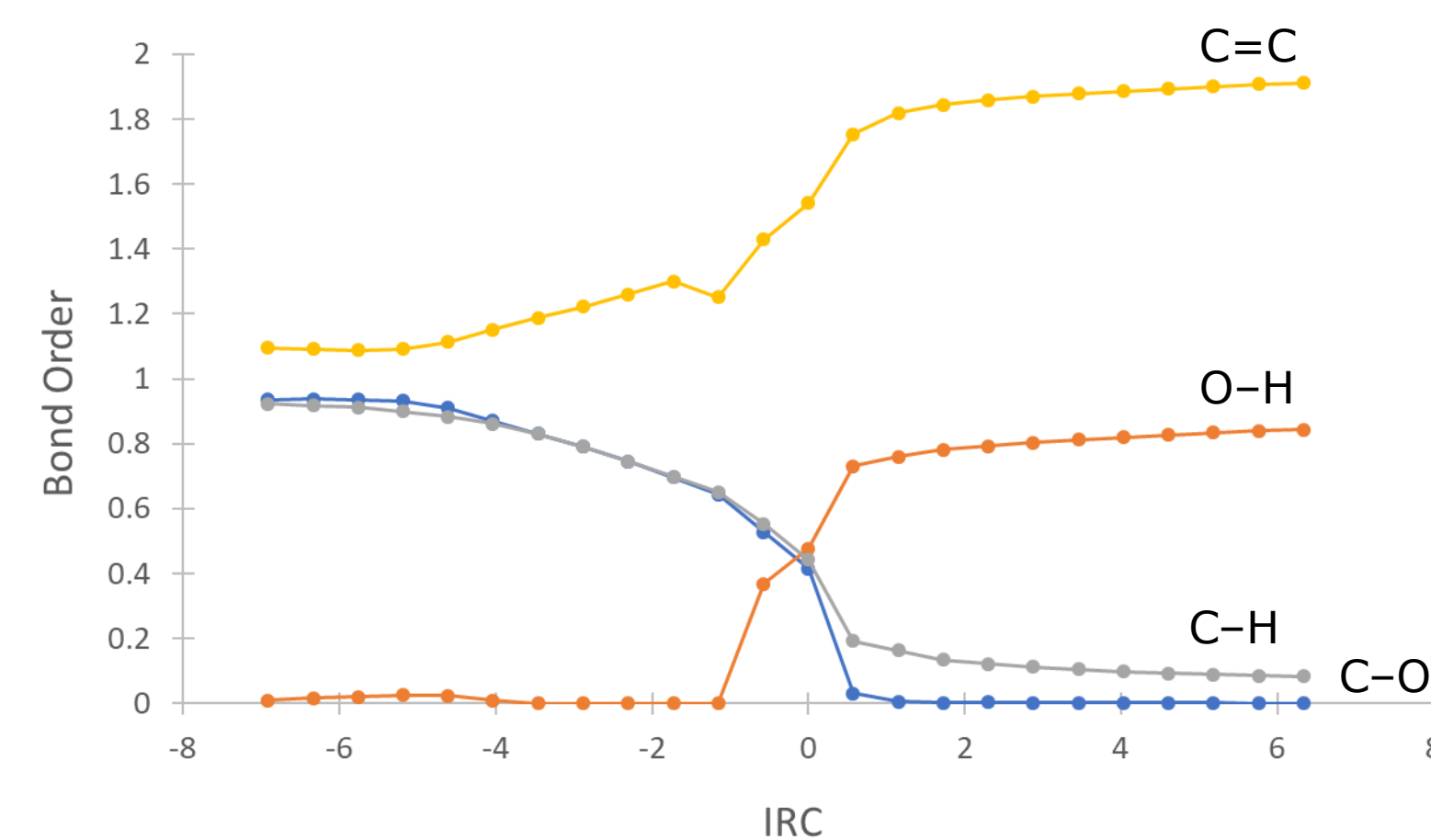
Electronic Rearrangement

Plots of pNLMOs at four points across the IRC show how electron pairs rearrange during dehydration. The following "filmstrips" (columns) respectively show the three essential transformations for the reaction, including:

- an O lone pair becoming an OH bond (proton transfer)
- a CH bond becoming a CC π bond
- a CO bond becoming an O lone pair (H_2O elimination)
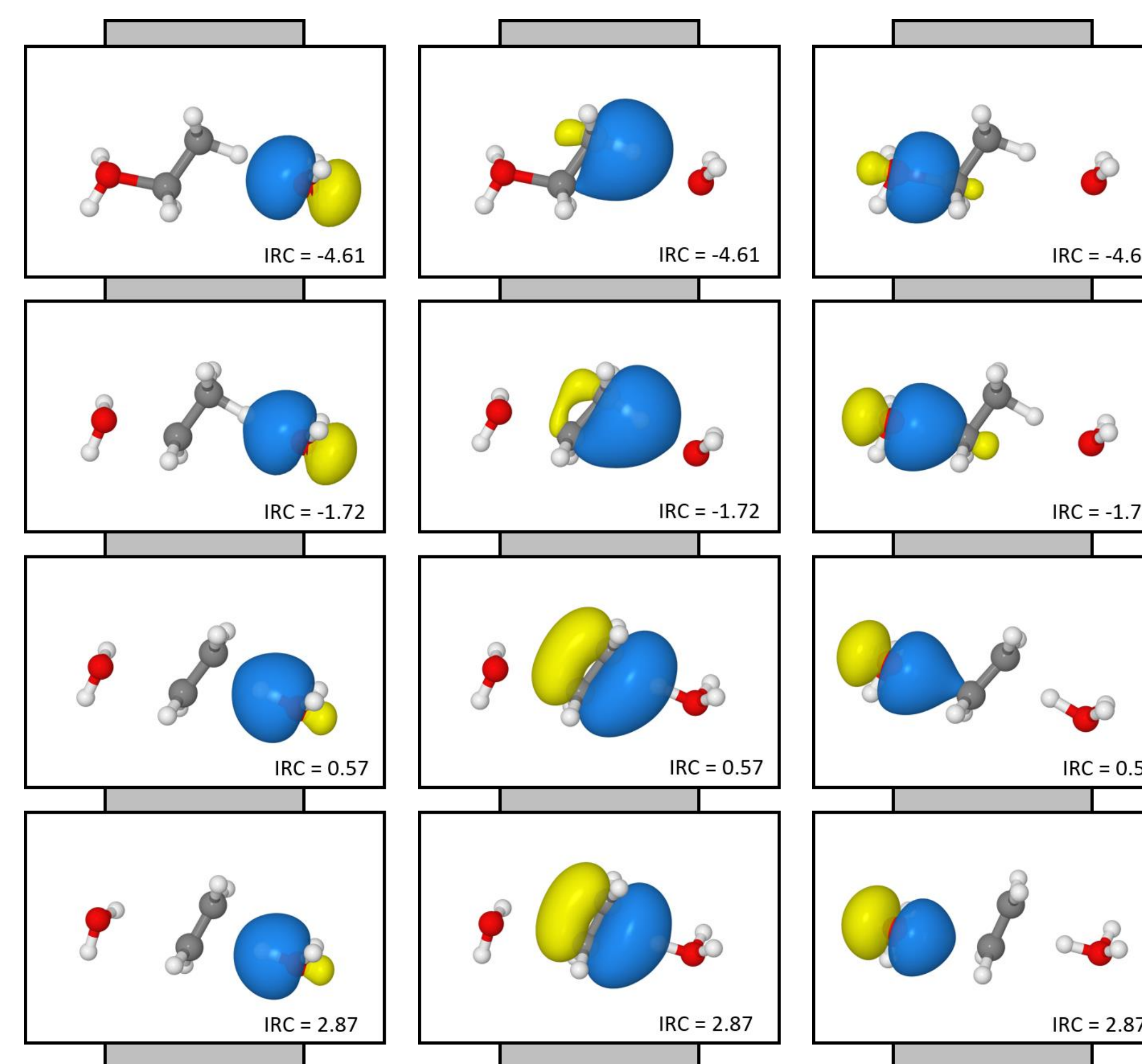
These transformations clearly show what is meant by the three curved arrows that organic chemists draw for the E2 dehydration mechanism (as shown in the Introduction).

Delocalizing Interactions

Two orbital, donor-acceptor interactions facilitate bond rearrangement in the dehydration reaction.

$$n_O \rightarrow \sigma_{CH}^* \qquad \sigma_{CH} \rightarrow \sigma_{CO}^*$$
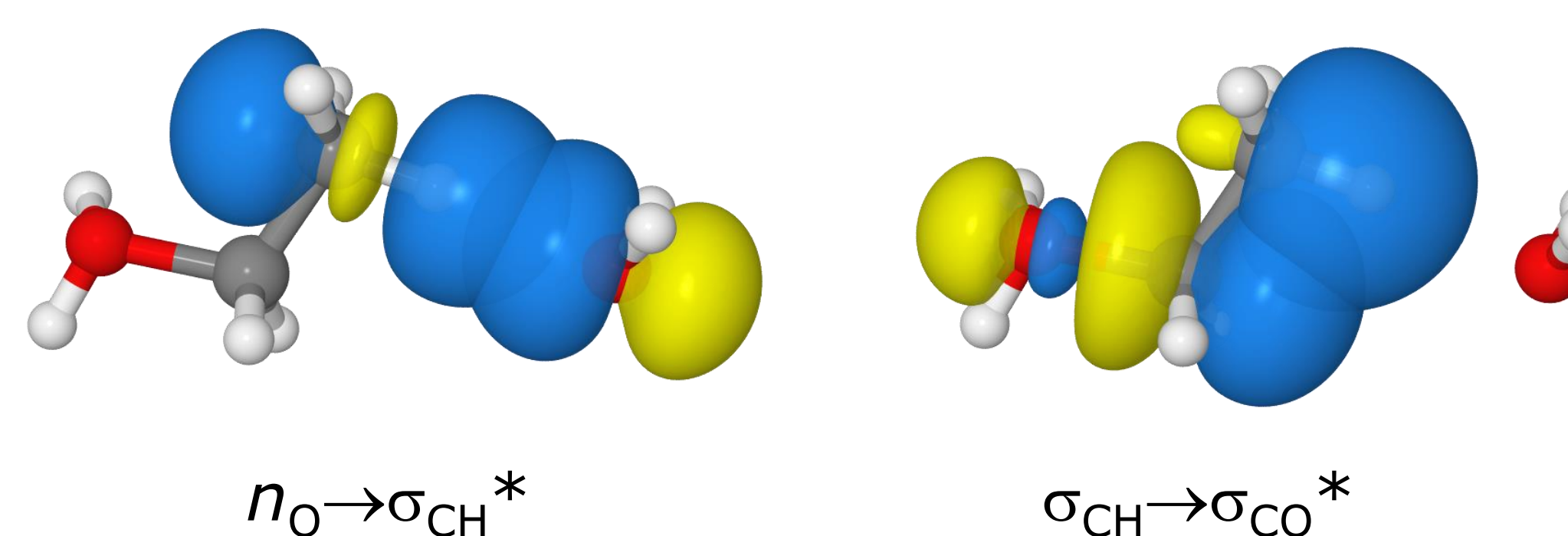
On the left, a O lone pair donates about 0.033 electrons into an unfilled CH antibond. This interaction gives rise to O-H bonding character while acting to cleave the CH bond. On the right, a CH bond donates about 0.069 electrons into an unfilled CO antibond. This yields C-C π bonding character while weakening the C-O interaction.

Influence of Explicit Solvent Molecules

We also examined H_3O^+-catalyzed dehydration of ethanol with up to eight explicit solvent molecules in the field of intrinsic solvent. Below are the reactant (left) and product (right) complexes with explicit water.
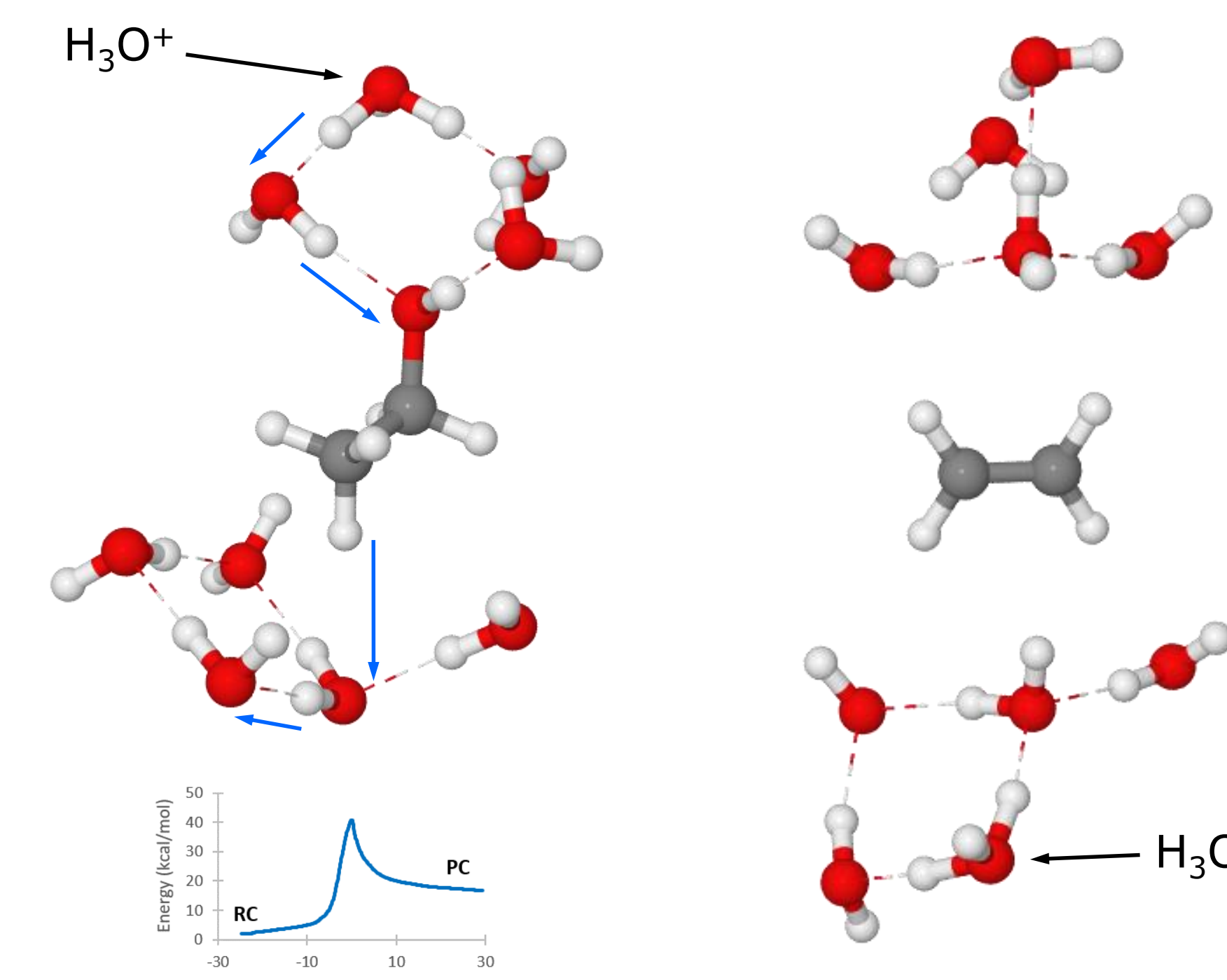
Interestingly, the reaction proceeds from reactant to product in a single step, through a single transition state, revealing a cascade of four consecutive proton transfers (depicted by the blue arrows). Hydronium starts in the upper portion of the reactant complex, becoming hydronium at the bottom of the product complex. The free energy of activation ($\Delta G^\ddagger$) for this process is 33.6 kcal/mol, which is largely consistent with estimates from experiment. The following figure shows how $\Delta G^\ddagger$ varies as explicit water molecules are added to the calculation.
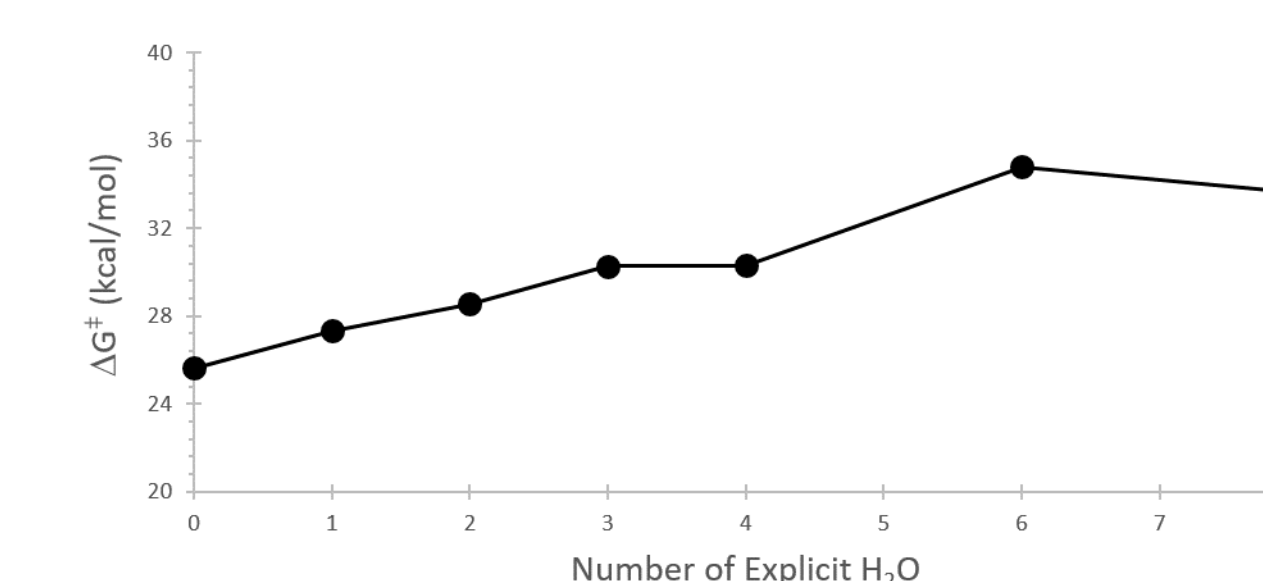
Conclusions

NBO/NRT analysis reveals bond breaking and making processes for the dehydration of ethanol that are consistent with the E2 mechanism. These processes are facilitated by donor-acceptor interactions that act to simultaneously make new bonds of the product as old bonds of the reactant break.

Including explicit solvent molecules in the vicinity of the reaction is important for calculating free energies of activation that compare favorably with experiment.

Acknowledgements

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