# Quantum Mechanics

- Molecular properties are governed by interactions between electrons and nuclei.
- Electrons and nuclei are governed by quantum mechanics.
- Quantum mechanics gives an accurate description of molecular systems.

# Quantum effects

- Energy quantization.
- Uncertainty principle.
- Zero-point energy.
- Particle-wave duality.
- Tunneling.
- Interference.

# Quantum Chemistry

- Application of quantum mechanics to chemical problems.
- The exact limit of quantum chemistry gives accurate description of molecular properties and reaction pathways.

# Capabilities of Quantum Chemistry

- With the advances in computer power, we can now study
  - systems with up to few (2-5) atoms with extremely high accuracy (~1 kcal/mol).
  - systems with up to 10-20 atoms at moderate accuracy (~5 kcal/mol).
  - systems with up to 100 atoms with reasonable accuracy (~10 kcal/mol).

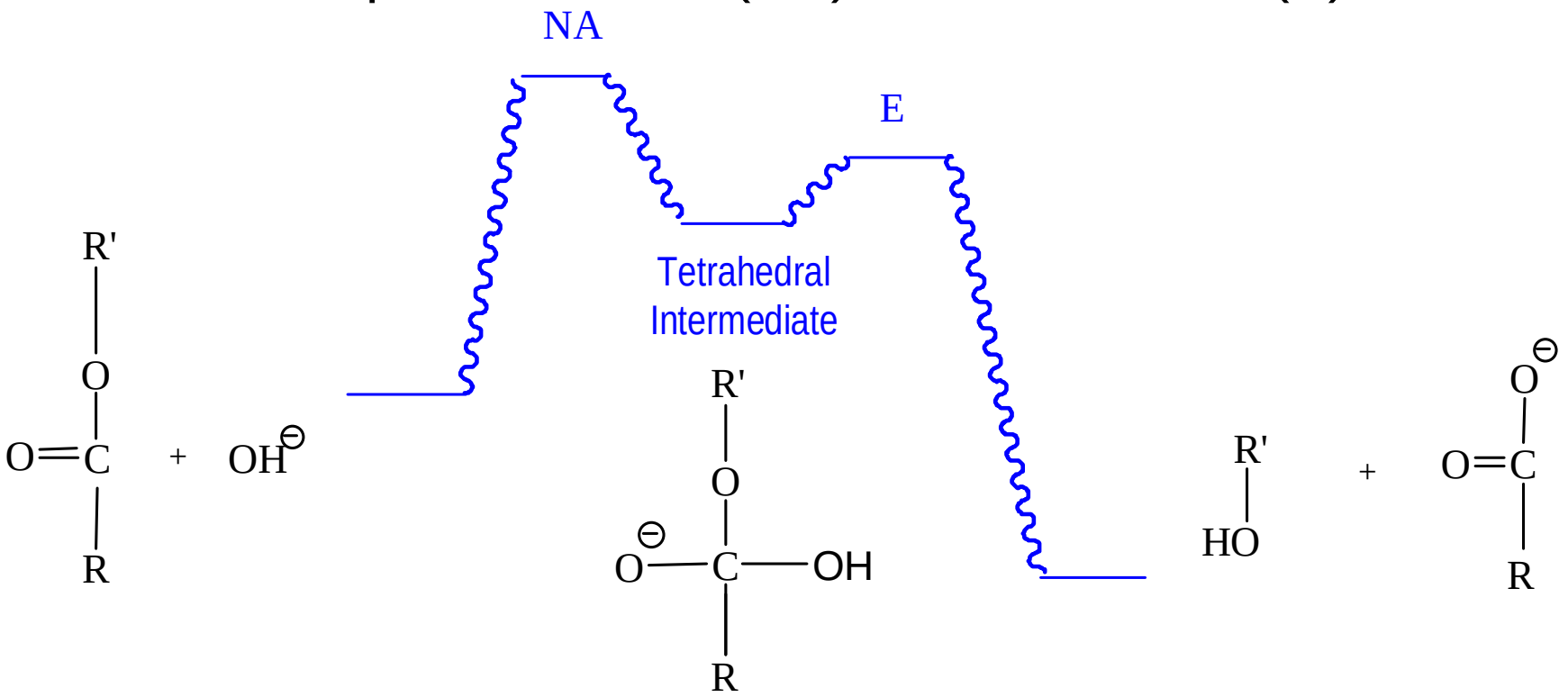
# Applications

- Organic chemistry: transition state, solvent effects, stereoselectivity, hydrogen bond, hydrophobic interactions, etc.
- Inorganic chemistry: metal ligand interactions, photochemistry, etc.
- Biological chemistry: reaction mechanism, electrostatic interaction.
- Materials science: adsorption, nano-materials, etc.

# Hydrolysis of alkyl-esters

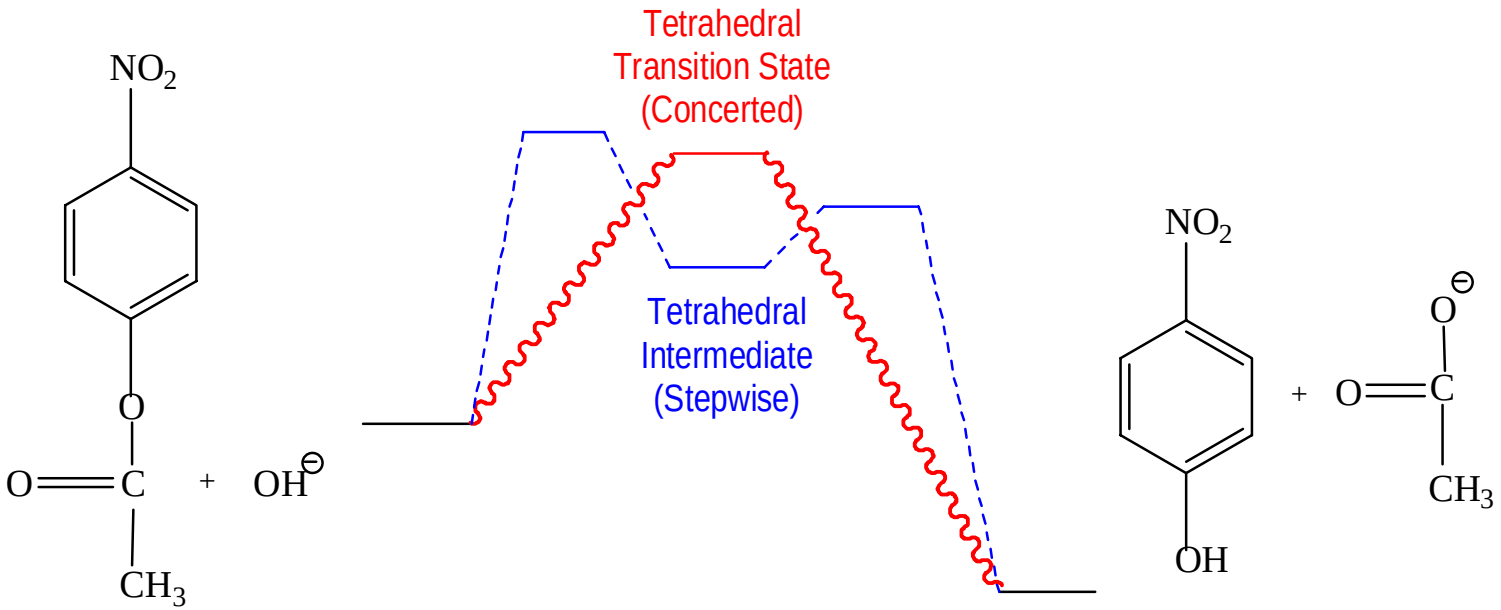
- Classical mechanism of hydrolysis:
  - Stepwise:

    nucleophilic addition (NA) and elimination (E)



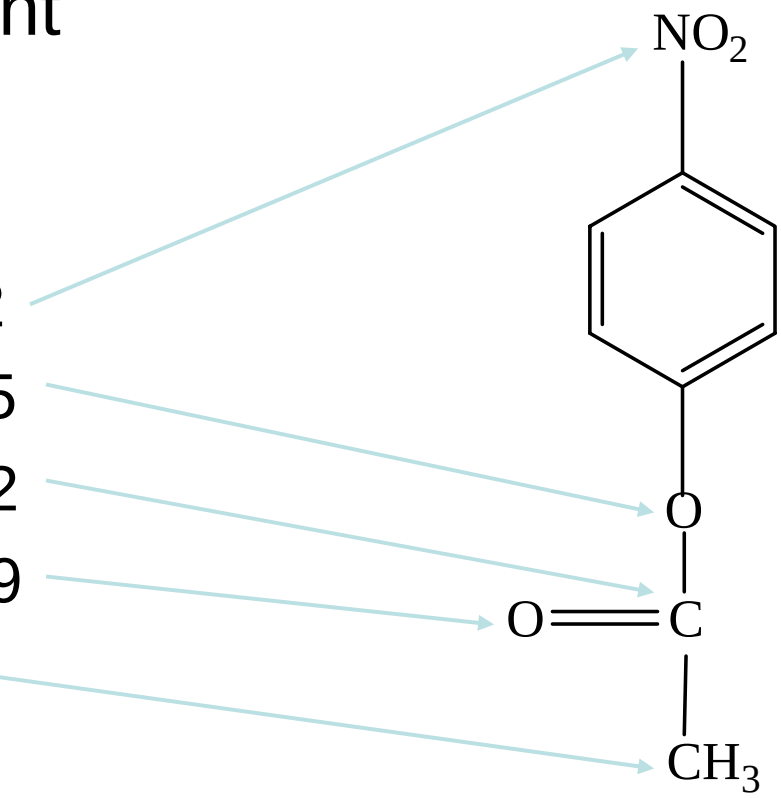
# Hydrolysis of aryl-esters

- Experiments indicated a concerted mechanism
  - Kinetic isotope effects
  - Bronsted correlation
- But have no transition state structure.



# Kinetic isotope effects

- Rate ratio for different isotopes:
  - $^{14/15}N(NO_2)$ = 1.0002
  - $^{16/18}O(PhO)$ = 1.0135
  - $^{12/13}C(C=O)$ = 1.0342
  - $^{16/18}O(C=O)$ = 1.0039
  - $^{1/2}H(CH_3)$ = 0.9562




p-nitrophenyl acetate (pNPA)

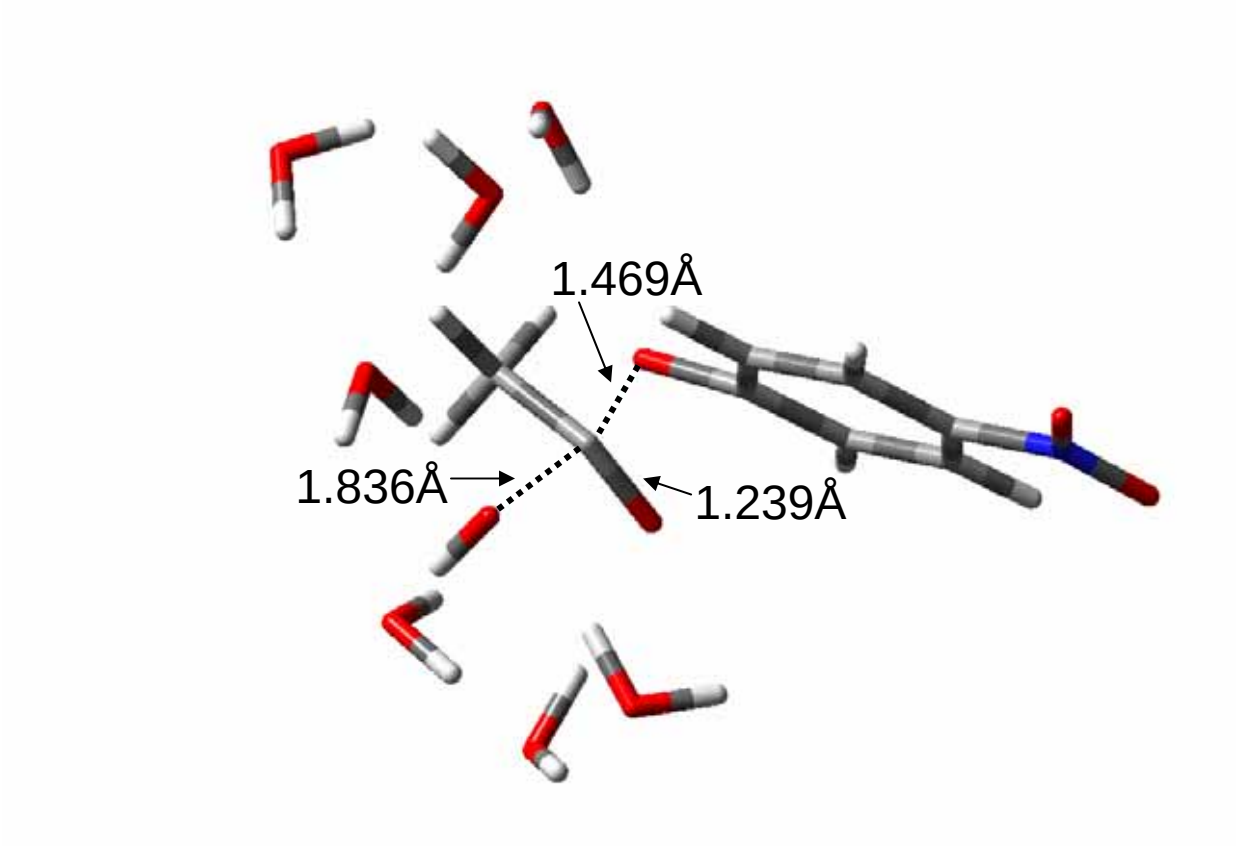
# Density Functional Theory

- Gas phase study
  - Only NA barrier is found.
  - Barrier height is 2.98 kcal/mol, significantly lower than experimental value (~15 kcal/mol).
  - KIE not in agreement with experimental data.

| KIE | $^{16/18}O(OH^-)$ | **$^{16/18}O(PhO)$** | $^{12/13}C(C=O)$ | $^{16/18}O(C=O)$ | $^{14/15}N(NO_2)$ | 3H/D(Me) |
|---|---|---|---|---|---|---|
| Calc. 1 | - | **1.0006** | - | 1.0079 | 1.0004 | 0.9505 |
| Calc. 2 | 1.0147 | **0.9982** | 1.0120 | 1.0036 | 1.0001 | 0.8597 |
| Expt. | - | **1.0135** | 1.0342 | 1.0039 | 1.0002 | 0.9562 |

# Solvent effect

- Charged species are stabilized by solvents.




Transition state with seven water solvent molecules

# Solvent effect

- Concerted transition state.
- Barrier height of 15.7 kcal/mol
- Excellent KIE agreement.

| KIE | $^{16/18}O(OH^-)$ | **$^{16/18}O(PhO)$** | $^{12/13}C(C=O)$ | $^{16/18}O(C=O)$ | $^{14/15}N(NO_2)$ | 3H/D(Me) |
|---|---|---|---|---|---|---|
| Calc. 1 | - | **1.0006** | - | 1.0079 | 1.0004 | 0.9505 |
| Calc. 2 | 1.0147 | **0.9982** | 1.0120 | 1.0036 | 1.0001 | 0.8597 |
| Calc. 3 | 1.0249 | **1.0099** | 1.0404 | 1.0056 | 1.0002 | 0.9711 |
| Expt. | - | **1.0135** | 1.0342 | 1.0039 | 1.0002 | 0.9562 |

# Summary

- Theory can be very helpful in elucidating mechanistic questions.
- Theory can help to identify the key factors that affect the reaction.
- Theory provides molecular structure of key points in reaction pathway.
- Theory may help in designing novel structures.