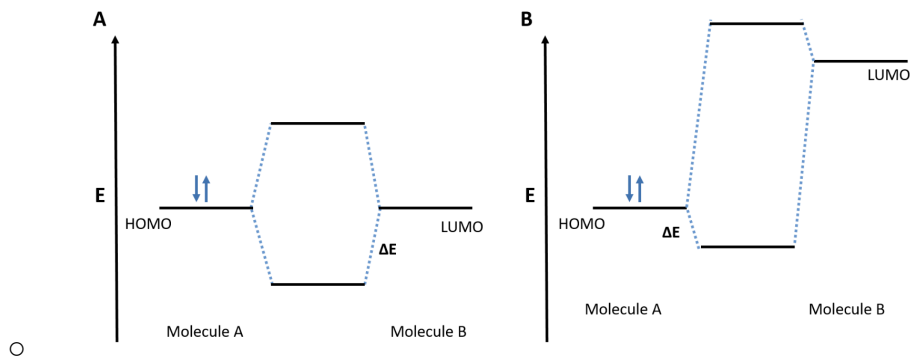


5.0 introduction

- Frontier Molecular Orbital theory (FMO) describes reactivity of reactions

5.1 Frontier Molecular Orbital theory (FMO) theory

- The **closer the energy (smaller ΔE)** of the HOMO (highest occupied molecular orbital) is to the LUMO (lowest unoccupied molecular orbital), **the more stable the reaction (better mixing)**

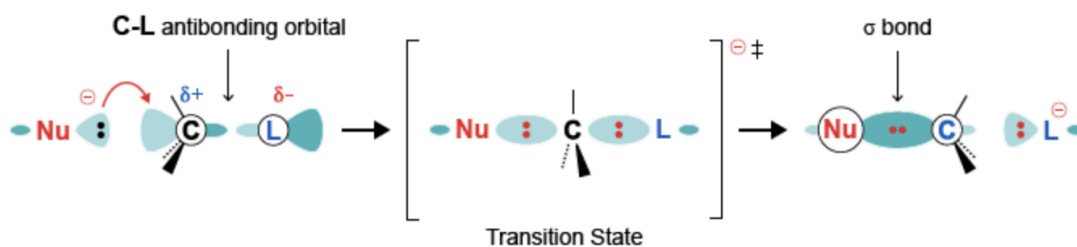


- The **HOMO** behaves as an electron pair **donor** to the **LUMO** which acts as an **acceptor**

5.3A Application of FMO Theory



- **Substitution** reactions are those in which a nucleophile replaces a leaving group
 - The lowest ΔE is the more favorable reaction, determining which HOMO and LUMO will be used
- **Nucleophiles:** molecules/atoms with “electron-rich centers” (lone pairs)
- **Electrophiles:** molecules/atoms with “electron-poor centers”



Substitution reaction pattern

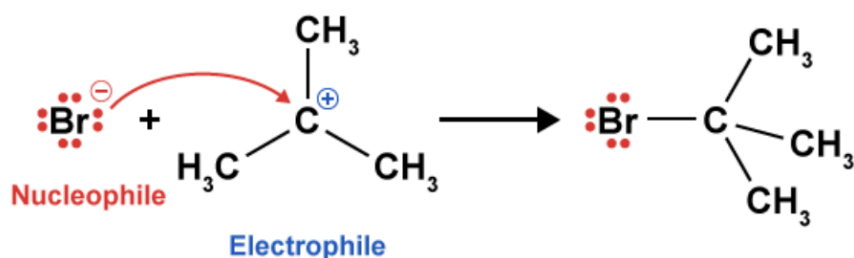
5.3B Properties that impact reactivity for substitution reactions

Rate of substitution reaction

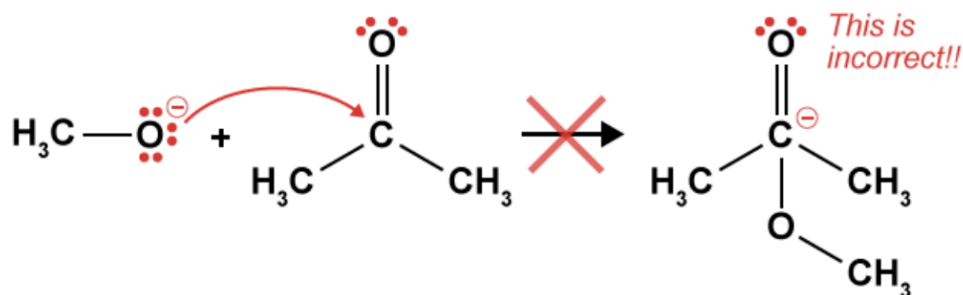
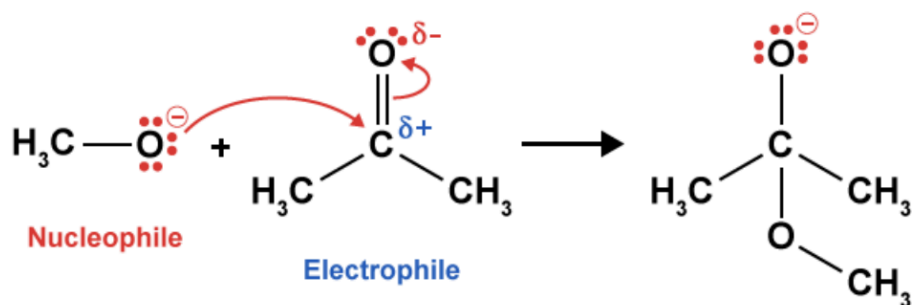
- **Nucleophilicity:** measure of a nucleophile's strength; the more reactive the Nu, the quicker the reaction.
- **Electrophile structure:** the more accessible the electrophile site, the faster the reaction. Hydrocarbons (the line structures coming from atoms in a molecule) are nonreactive structures that physically block interactions between Nu and E.
- **Leaving Groups:** leaving group efficiency is reliant on the ability for the LG to stabilize a negative charge. This ability is based on:
 - **Size:** larger atoms are better LGs
 - **Electronegativity:** more electronegative atoms are better LGs

5.4 Another representation of reaction mechanisms

1A. Single step nucleophilic attack



1B. Two step nucleophilic attack

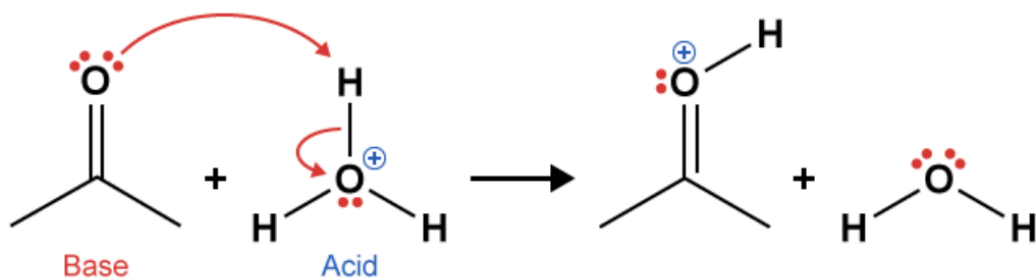


2. Loss of a leaving group



3. Proton transfers

Protonation of a carbonyl oxygen



Deprotonation of an oxonium ion

