The role of the Solvent

Most organic chemistry is **heterolytic!!** Heterolytic reactions are typically carried out in solution.

The role of the Solvent

- Extremely important
- Intimately involved
- Solute molecules & ions are solvated

Secondary Bonding

- Ion-ion bonds
- Dipole-dipole bonds
  - The most powerful is the hydrogen bond
    - hydrogen bond donor
    - hydrogen bond acceptor
  - Purely electrostatic attraction between a s $^{+}$ & s $^{-}$species
- Van der Waals forces
- Ion-dipole bonds

The solubility of non-ionic solutes is highly dependent upon polarity -- i.e. ability to form hydrogen bonds.

Water

- A major solvent
- Biological systems

- hydrophilic
- hydrophobic or lipophilic

The solubility of ionic solutes is dependent on highly polar solvents with a high dielectric constant.

Aprotic solvents

- Cannot form hydrogen bonds
- Dissolve ionic compounds through solvation of cations

The S_N1 Reaction

$$R - X \rightarrow \left[\overset{\sigma^+}{R} \cdots \overset{\sigma^-}{X} \right] \rightarrow R^+ + X^-$$

Reactant Transition State

More polar than reactant(s), therefore stabilized more by solvation

- The rate determining step is bond-breaking
- The energy absorbing process is counter-balanced by the formation of bonds (an energy releasing step) in forming solvated ions
- The solvation of the cation is relatively weak
- The solvation of the anion is very important
- The solvation of the anion is very important
  - requires hydrogen bonding - protic solvents
  - Water, alcohols, and mixtures of water & alcohols
  - S_N1 reactions do not proceed as well in aprotic solvents (DMF, DMSO, & HMPT)
  - The solvent promotes heterolysis by pulling apart the substrate molecule

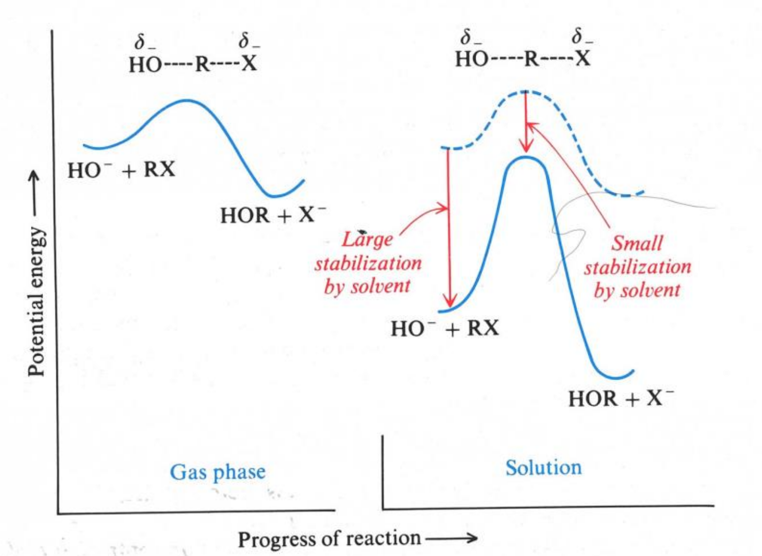

Figure 7.6 Effect of the solvent on the rate of attack by hydroxide ion on an alkyl halide. The nucleophile has a more concentrated charge than the transition state, and is more stabilized by ion–dipole bonds.

The S_N2 Reaction

$$R-X+OH^{-} \rightarrow \left[HO\overset{\sigma^-}{\cdots}R\cdots\overset{\sigma^-}{X} \right] \rightarrow HO-R+X^{-}$$

Reactant | Transition State | Product

Concentrated charge: stabilized more than the transition state by solvation

Dispersed charge

- The solvent slows down the S_N2 reaction by factors as large as 10^{20}
  - The alkyl halide has a dipole moment - thus forming weak dipole-dipole bonds with the solvent
  - The hydroxide ion carries a full negative charge - thus forming very powerful ion-dipole bonds with the solvent
  - The transition state carries a full negative charge, but the charge is divided between the attacking hydroxyl and the departing halide
  - The solvent thus stabilizes the more concentrated charge, i.e. the reactants
- The solvent deactivates the nucleophile

- The strength of solvation varies from ion to ion, and so does the strength of deactivation
- Among similar solvents, the greater the polarity, the slower the S_N2 reaction
- The change from a protic solvent to an aprotic solvent results in a spectacular increase in reaction rate -- as much as a million times faster
- Phase-transfer Catalysis -- This process allows the chemist vastly increased control over the organic reaction

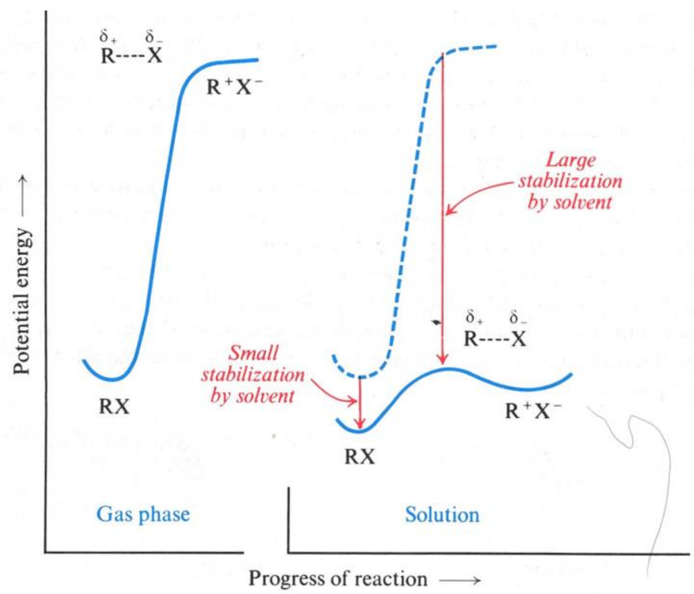

Figure 7.5 Effect of the solvent on the rate of heterolysis of an alkyl halide. The transition state is more polar than the reactant, and is more stabilized by dipole–dipole bonds.

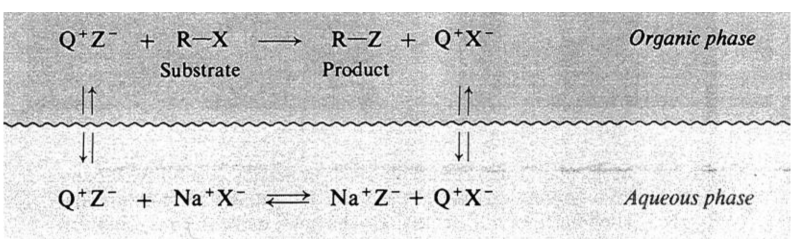

Figure 7.7 Phase-transfer catalysis. The quaternary ammonium ion (Q^+) is both hydrophilic and lipophilic. It shuttles back and forth between the aqueous phase and the organic phase, taking an anion with it: the nucleophile (Z^-) or the leaving group (X^-). In the organic phase, the nucleophile is virtually unsolvated and reacts rapidly with the substrate (R—X).

Solvolysis: A special case where the nucleophile is also the solvent.