

Chapter 7

7.2 forces between chemical species

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electrostatic forces : ion-ion bonds, ion-dipole bonds, van der Waals forces
dipole-dipole bonds (H bond : O, N, F)

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secondary bonds : individually weak but collectively strong

7.3 solubility

non-ionic solutes : hydrocarbons & alkyl halides (nonpolar or weakly polar)

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dissolve in solvents of similar polarity.

(ligroin, benzene, CHCl_3 , CCl_4 , Et_2O)

not dissolved in H_2O .

$\text{R-OH} \implies$ Table 7.1 : detergent

↙

hydrophobic
lipophilic

↘

hydrophilic
lipophobic

ionic solutes :

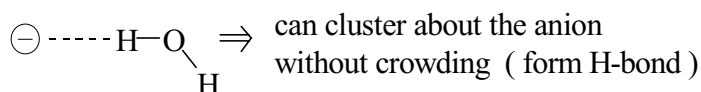
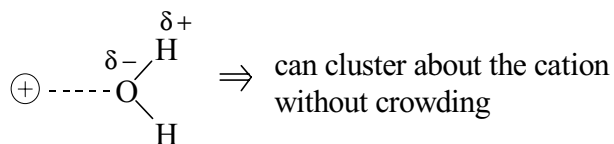
To dissolve ionic compds, a solvent should be polar and have a high

dielectric constant (insulating property)

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solvating power is required. \Leftarrow some liq with large dipole moments and high dielectric constants are poor solvents for ionic compds.

Water ;



CH₃OH dissolves ionic compounds through -OH group
but is inferior to H₂O (more crowded)

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protic solvent ⇒ solvates cations through unshared electrons
anions through hydrogen bonding

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dissolve ionic
compd through
solvating cations

⇐ aprotic solvent ex) DMSO, DMF, HMPT (HMPA)

⇓

negative pole is well-exposed ; solvate cations very strongly
positive pole is burried ; anions are solvated weakly

many organic rxns ⇒ rxns between organic (non-ionic) compds and ionic compds

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H₂O + CH₃OH or CH₃OH as a solvent

⇓

usually anion is attacking reagents to organic molecule

⇓

anion is hydrogen-bonded, strongly solvated, stabilized
and has lower reactivity

⇓

use aprotic solvent

⇓

anion is more naked, more basic and more nucleophilic

small ions are more strongly solvated than larger ions (with the same charge)

F⁻ > Cl⁻

Li⁺ > Na⁺

↑ ↑
hard soft

another view of the stabilization of an ion by a solvent ⇒ the more dispersed charge ⇒ the solvated ion gives some of its charge to solvent molecules

more important for
F⁻ or Li⁺ than
for I⁻ or Rb⁺

⇐

solvated ion feels the charge of
its counter - ion

⇒

ion pair < tight ion pair
loose ion pair

7.5

For S_N1 or S_N2 rxn

a bond is broken between carbon and leaving group \Rightarrow energy is required \Rightarrow Where does the energy come from?

\Downarrow

for $S_N2 \rightarrow$ from the forming bond

Where does the difference come from? \Leftarrow $\left(\begin{array}{l} \text{t-BuBr} \rightarrow \text{t-Bu}^+ + \text{Br}^- \\ \Delta H = 149 \text{ Kcal/mole} \quad \Leftarrow \text{ for } S_N1 \rightarrow ? \\ E_a \text{ for } S_N1 = 20 \sim 30 \text{ Kcal/mole} \end{array} \right.$

\Downarrow

reactant ; dipole moment

stabilizing effect

transition state ; greater dipole moment \Rightarrow solvated \Rightarrow stabilized by solvents \Rightarrow pdt \leftarrow transition state \leftarrow reactant

product ; ionic

\Rightarrow Fig 7.5 \Rightarrow cation : weak ion-dipole bonds due to dispersed charge

anion : solvation is important

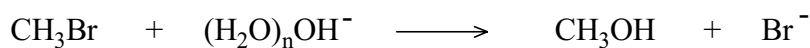
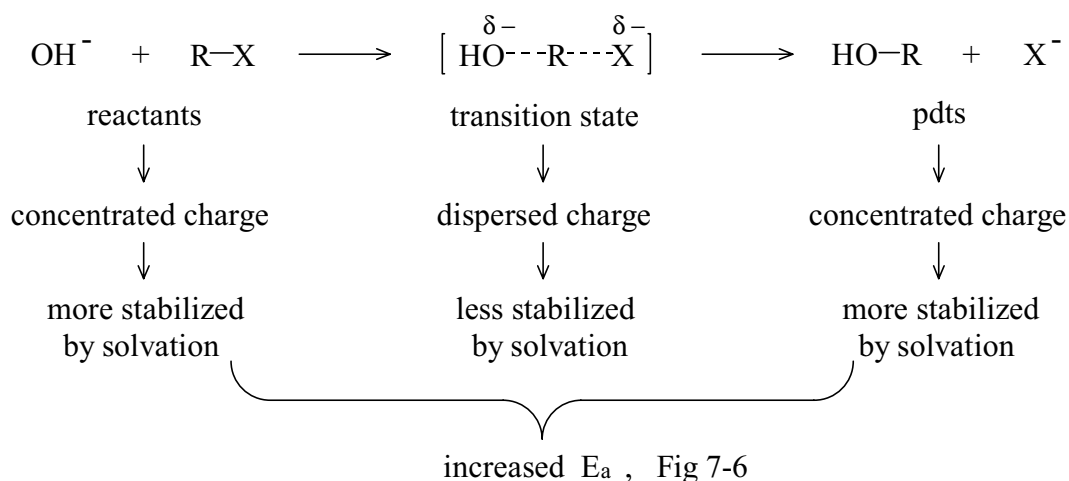
\Downarrow

protic solvents are better than aprotic \Rightarrow

the highest ionizing power is expected for the solvents to form the strongest H-bonds. (pull, cf push)

H_2O , CH_3OH , CF_3CH_2OH
 $HCOOH$, CF_3COOH etc.

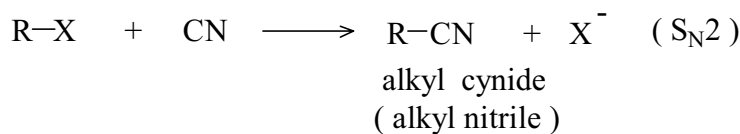
cf) DMF, DMSO, HMPT



relative rate ; p262 \Rightarrow the number of $\text{H}_2\text{O} \uparrow$ $E_a \uparrow$ rate \downarrow

relative reactivity in gas phase ; $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

relative reactivity in protic solvents ; $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$
(MeOH , H_2O , \dots)



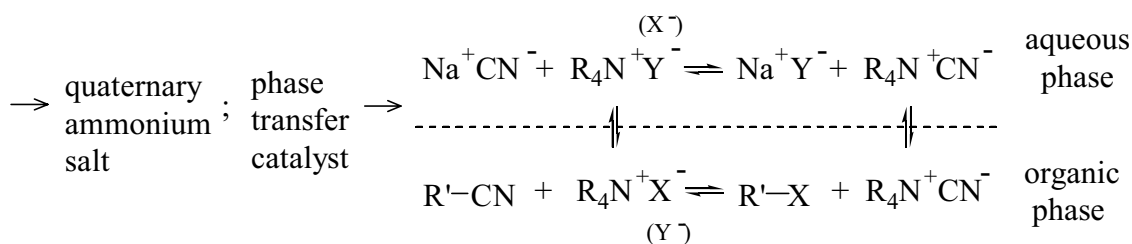
the less polar the solvent \longrightarrow the more highly reactive the nucleophile (CN^-),
the less soluble the nucleophile.

\downarrow

form two layers ; no rxn \longleftarrow how about using a nonpolar organic solvent
(RX is soluble) and H_2O (nucleophile is soluble) ?

\downarrow

add a catalytic amount of
a quaternary ammonium salt ($\text{R}_4\text{N}^+\text{Y}^-$) \longrightarrow the rxn proceeds fast with a high yield.



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PTC minimizes the forces ← CN⁻ is relatively free ← a loose ion pair
 deactivating an anion and reactive (not a tight ion pair)
 by solvation and ion-pairing

↓

another PTC ; crown ether

7.8 (p267)

S_N1 is favored by solvents of high ionizing power (polar, protic ; stabilize Nu most)

S_N2 is favored by aprotic solvents or solvents of
 low polarity + PTC (stabilize Nu least)