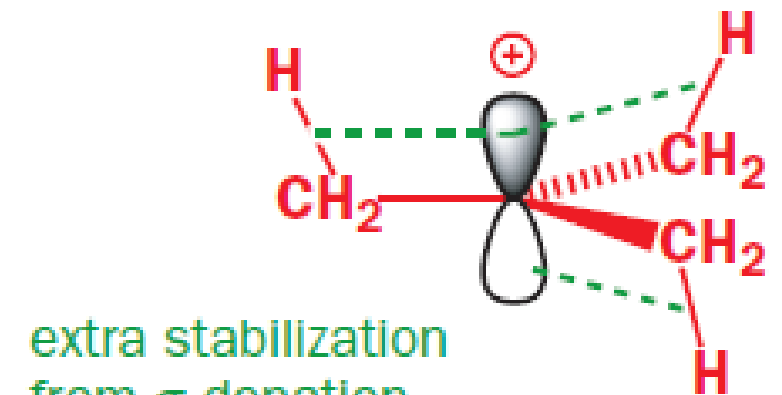
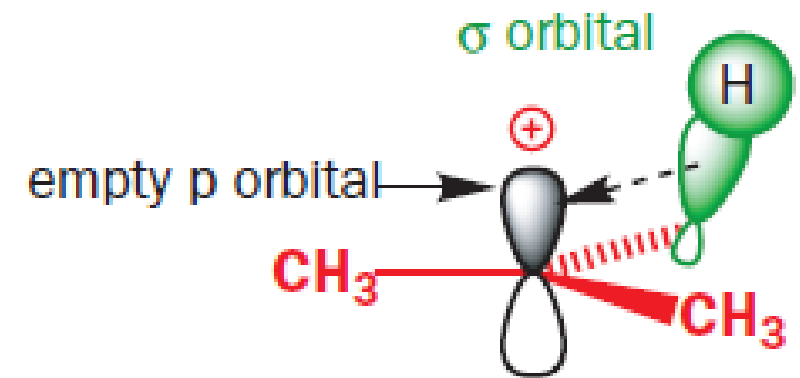
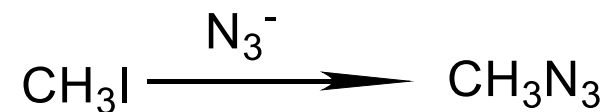


Q. There are 9 C-H bonds and each of them will interact with the vacant p orbital of the sp^2 hybridised carbon and will have a more stable C-H bond. Now my question is as we know that during the overlap of molecular orbital the overlap integral plays an important role. So in the case of tertiary carbocation the orientation of each C-H bond is different and the orientation of the vacant orbital is intact. So, how is it possible that the 9 of the C-H bond will get stabilised ? because there is a presence of a geometrical barrier (value of overlap integral is different) between the interaction of two orbitals.



extra stabilization
from σ donation
into empty p orbital
of planar carbocation

The following table presents rate data for the reactions of CH_3I with azide ion:



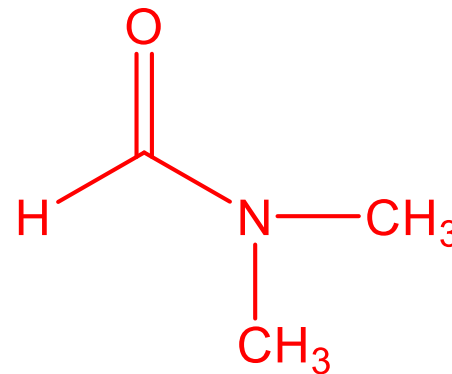
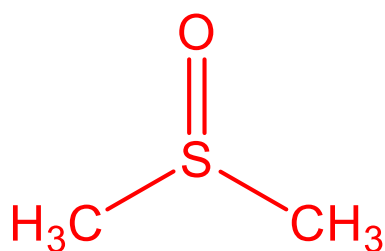
Solvent	Relative Rate	Dielectric Constant
Methanol	1	33
DMF	4.5×10^4	37

✓ The dielectric constant (ϵ) of a solvent is a measure of its polarity

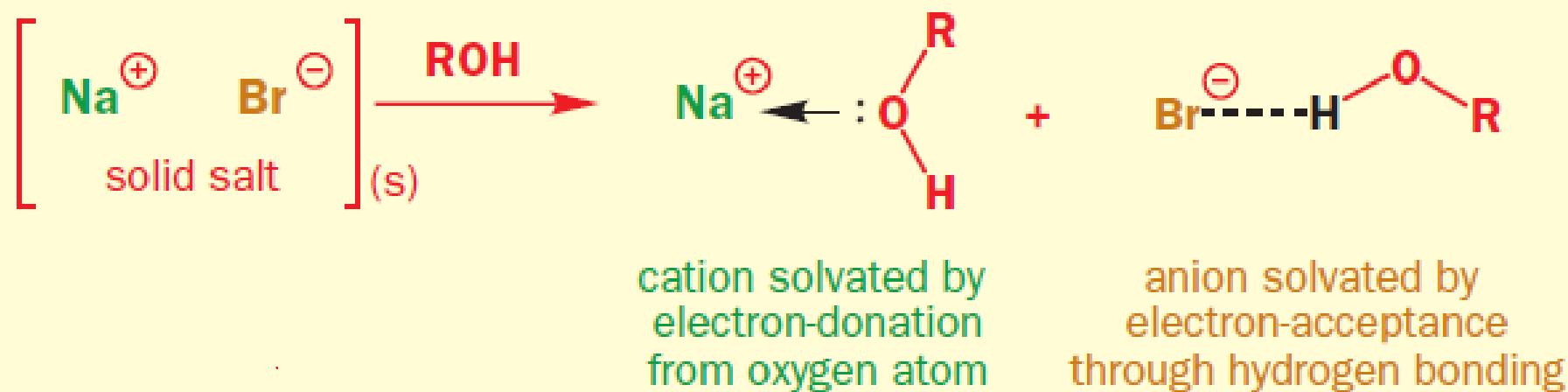
Polar protic solvents: H_2O , ROH , RCO_2H

- ✓ Are able to form hydrogen bonds (hydroxylic solvents)
- ✓ They solvate both cations and anions well

Polar aprotic solvents:

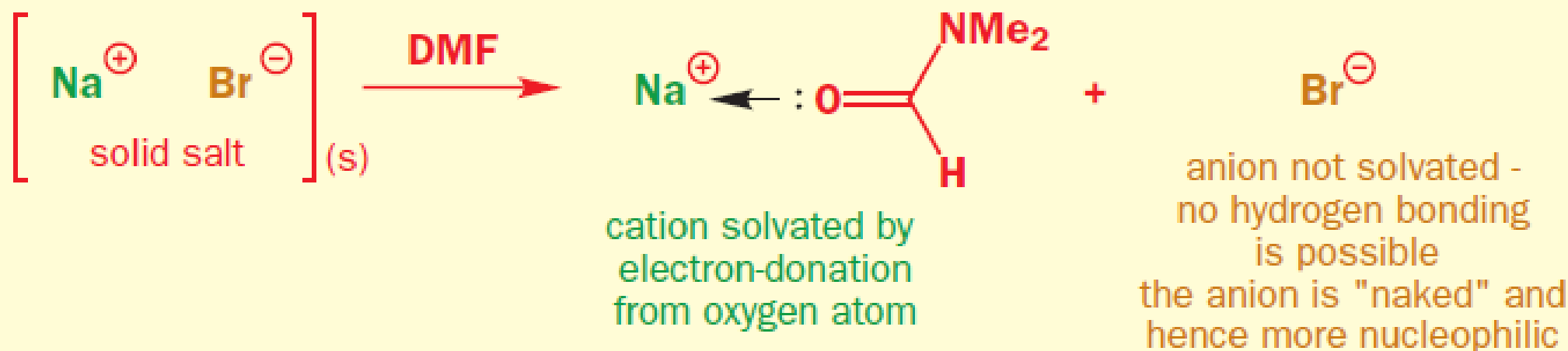


- ✓ Polar aprotic solvents, on the other hand, have dipole moments and are still able to solvate cations by electron donation from an oxygen atom
- ✓ They don't solvate the anions

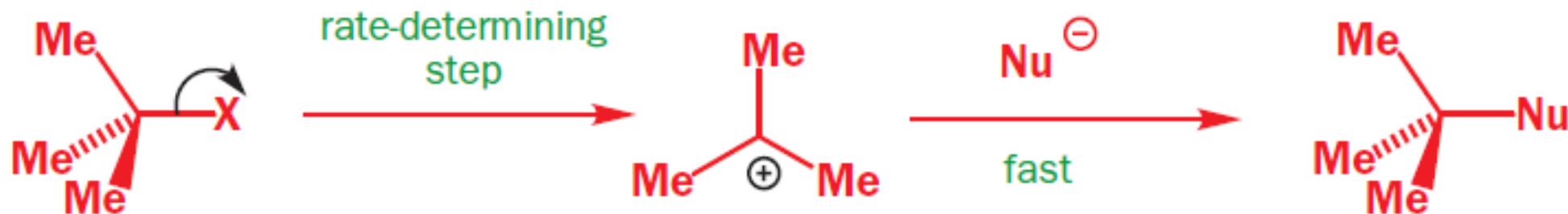


there are more than the one solvent molecule shown for each ion

solvation of salts by polar aprotic solvents



Solvent Effect: S_N1



- ✓ The transition state is more polar than the starting materials and so is stabilized by the polar solvent
- ✓ A polar protic solvent for the S_N1 reaction.
- ✓ *The rate-determining step usually involves the formation of ions and the rate of this process will be increased by a polar solvent*

We have covered so far:

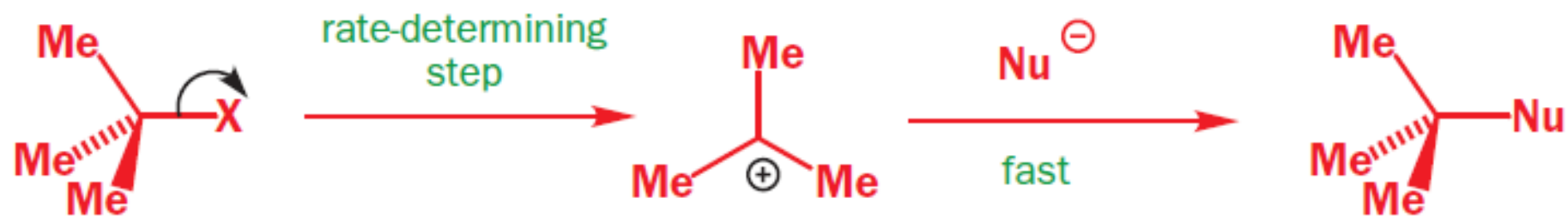
1. Structural factors (sterics)
2. Solvent effects

We will now look at two other factors:

Leaving groups

Nucleophilicity

The Leaving Group



Halide leaving groups in the S_N2 reaction

Halide X in MeX	pK _a of conjugate acid HX	Rate of reaction with NaOH
F	+3	very slow indeed
Cl	-7	moderate
Br	-9	fast
I	-10	very fast

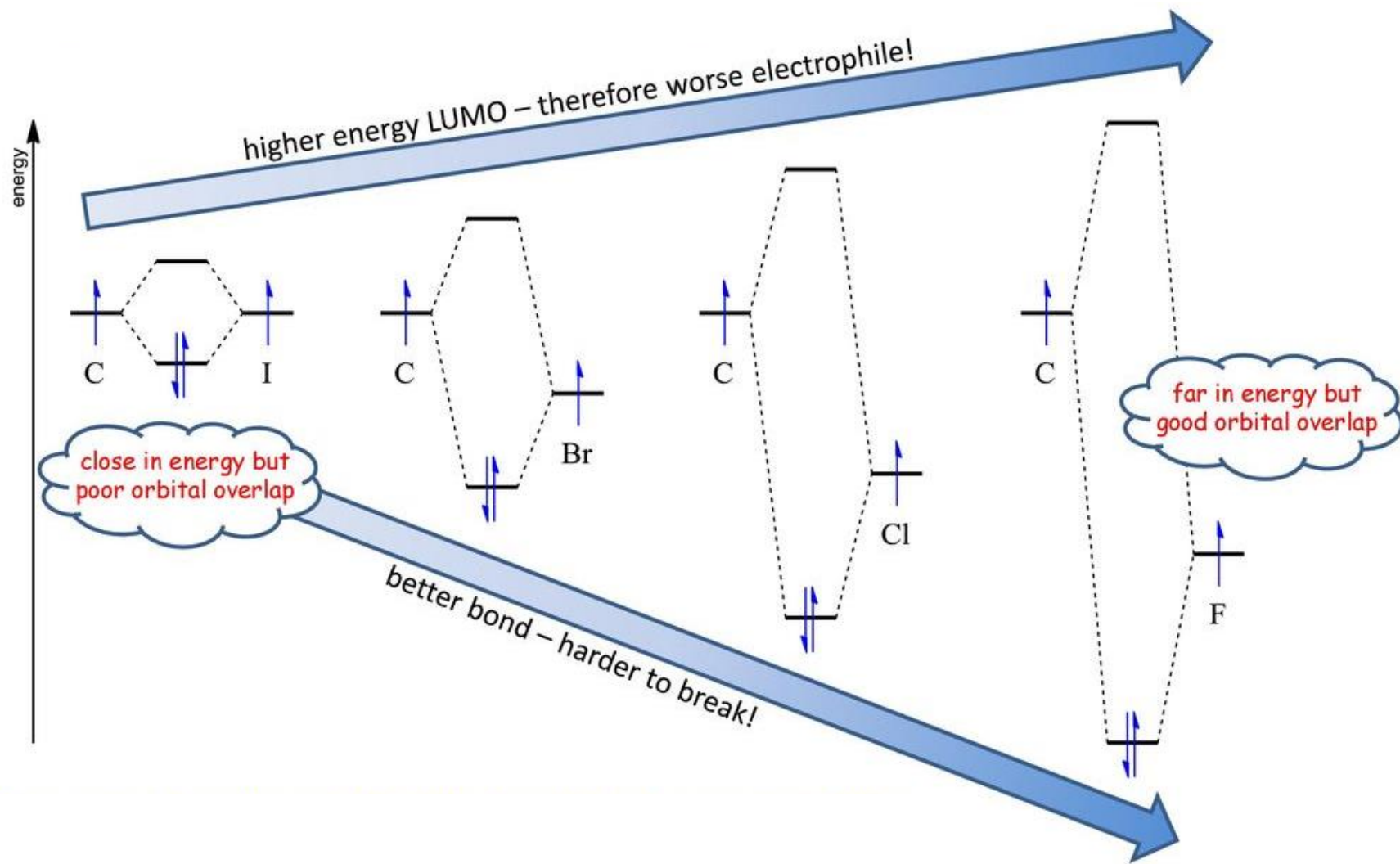
Halide (X)	Strength of C-X bond, kJ mol ⁻¹
fluorine	467
chlorine	346
bromine	290
iodine	228

✓ In the Ethyl halide series, the rate follows the order:

Relative Rate: CH₃CH₂I > CH₃CH₂Br > CH₃CH₂Cl >> CH₃CH₂F

✓ It is clearly easiest to break a C-I bond and most difficult to break a C-F bond. Iodide sounds like the best leaving group

ΔE (interaction energy) : Σ sterics – Σ orbital overlap / $(E_{\text{LUMO}} - E_{\text{HOMO}})$ + Σ charge interaction



Nucleophiles and Bases

- ✓ It is generally expected that nucleophilicity can be correlated to basicity since both involve the availability of electron pairs and the ease with which they are donated
 - ✓ However, basicity involves electron pair donation to **hydrogen** (Bronsted sense) whereas nucleophilicity involves electron pair donation to another atom **usually carbon**
 - ✓ Basicity is likely to be little affected by steric influences, whereas nucleophilicity may be significantly affected
-
- ✓ **Hard base**: high electronegativity of the donor atom and low polarizability: OH^- , OR^- , R_3N
 - ✓ **Soft base**: low electronegativity of the donor atom and high polarizability: RS^- , I^- , SCN^-

Nucleophiles in S_N1 Reaction

- ✓ We have established that the nucleophile is not important in the *rate* of an S_N1 reaction
- ✓ A better nucleophile will not accelerate the S_N1 reaction but it may determine which product is formed

Nucleophiles in S_N2 reactions

Relative rates (water = 1) of reaction with MeBr in EtOH

Nucleophile X	pK _a of HX	Relative rate
HO ⁻	15.7	1.2×10^4
PhO ⁻	10.0	2.0×10^3
AcO ⁻	4.8	9×10^2
H ₂ O	-1.7	1.0
ClO ₄ ⁻	-10	0



Nucleophilicity parallels basicity

Relative rates (water = 1) of reaction with MeBr in EtOH

Nucleophile X	pK _a of HX	Relative rate
PhS ⁻	6.4	5.0×10^7
PhO ⁻	10.0	2.0×10^3



Nucleophilicity does not parallel basicity

✓ How do we explain these trends?

Relative rates (water = 1) of
reaction with MeBr in EtOH

Nucleophile X	pK_a of HX	Relative rate
HO^-	15.7	1.2×10^4
PhO^-	10.0	2.0×10^3
AcO^-	4.8	9×10^2
H_2O	-1.7	1.0
ClO_4^-	-10	0

- ✓ If the atom that is forming the new bond to carbon is the same over a range of nucleophiles—it might be oxygen, for example, and the nucleophiles might be HO^- , PhO^- , AcO^- , and TsO^- , *then nucleophilicity does parallel basicity*