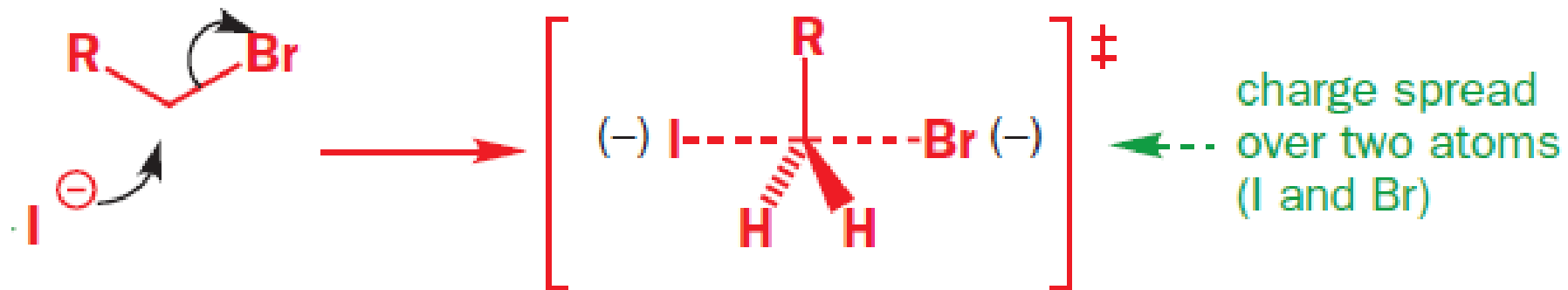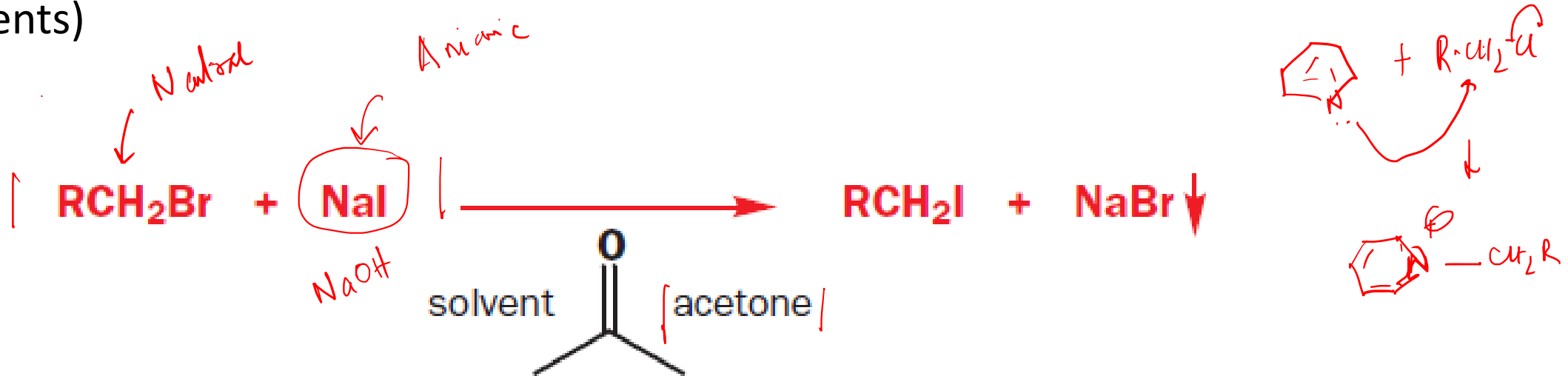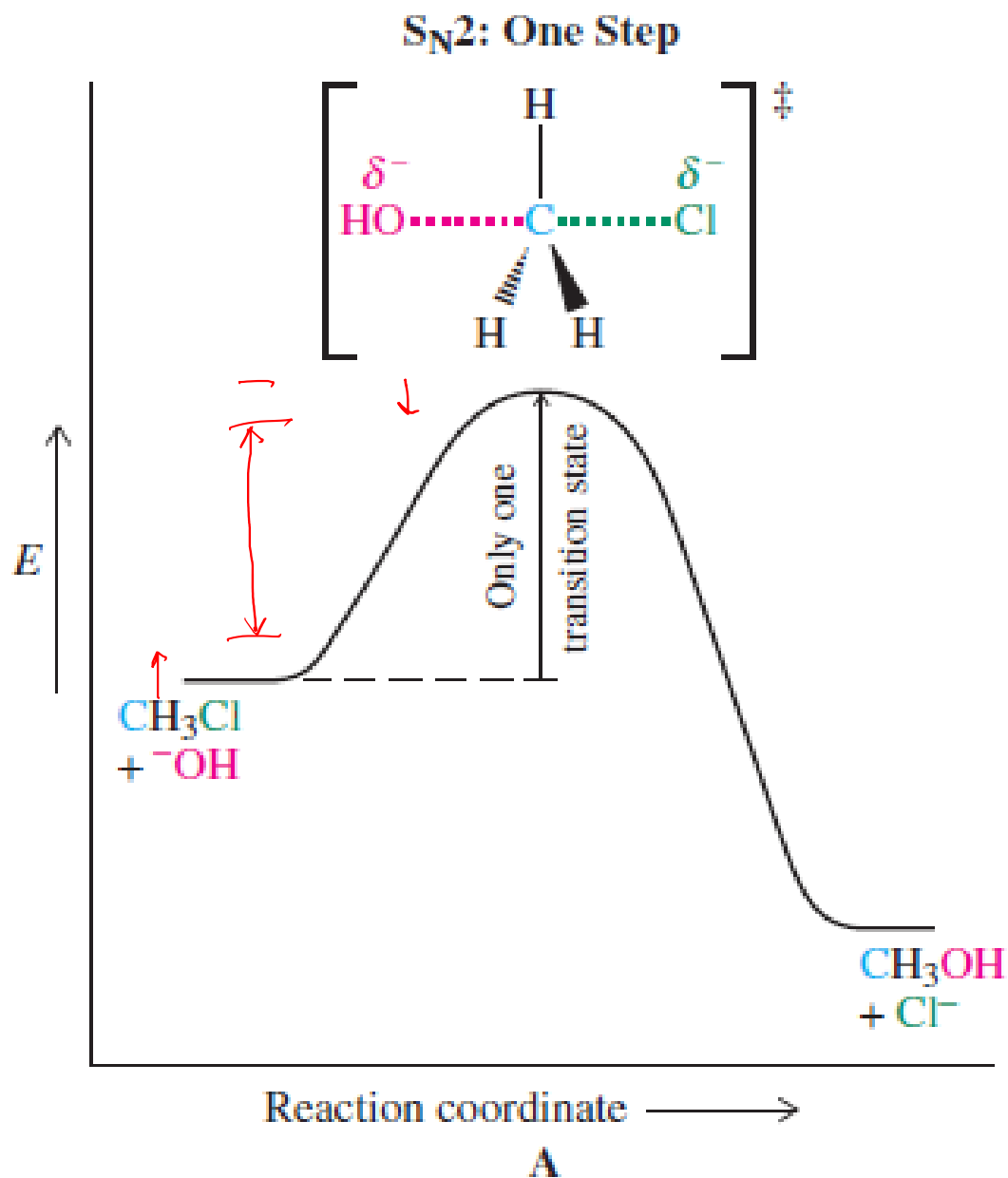# Solvent Effect: S_N2

✓ Typical choices: a less polar solvent for the S_N2 reaction (just polar enough to dissolve the ionic reagents)

S_N2: One Step

$CH_3Cl + ^-OH$

Only one transition state

$CH_3OH + Cl^-$

E

Reaction coordinate ⟶

A

✓ The most common S_N2 reactions use an anion as the nucleophile and the transition state is less polar than the localized anion as the charge is spread between two atoms

✓ A polar solvent solvates the anionic nucleophile and slows the reaction down

✓ A nonpolar solvent destabilizes the starting materials more than it destabilizes the transition state and speeds up the reaction

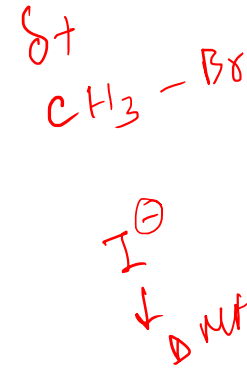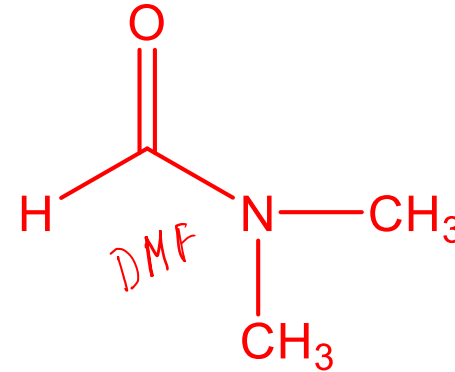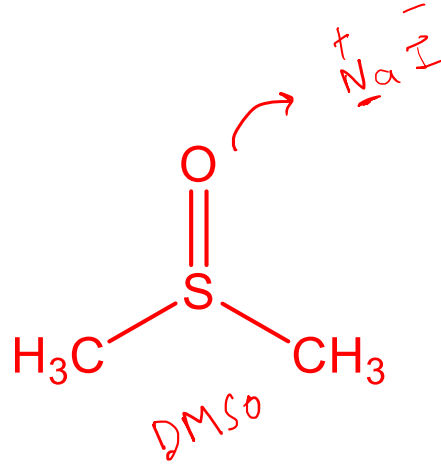*The following table presents rate data for the reactions of CH_3I with azide ion:*

$$CH_3I \xrightarrow{N_3^-} CH_3N_3$$
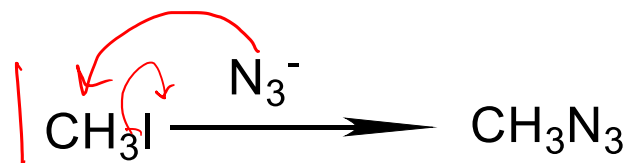
Solvent	Relative Rate	Dielectric Constant
Methanol	1	33
DMF	4.5×10^4	37

Polar protic solvents: (H$_2$O, ROH, RCO$_2$H |

✓ Are able to form hydrogen bonds (hydroxylic solvents)

✓ | They solvate both cations and anions well |

$\delta+$
$CH_3 - Br$

$I^{\ominus}$
$\downarrow$ DMF

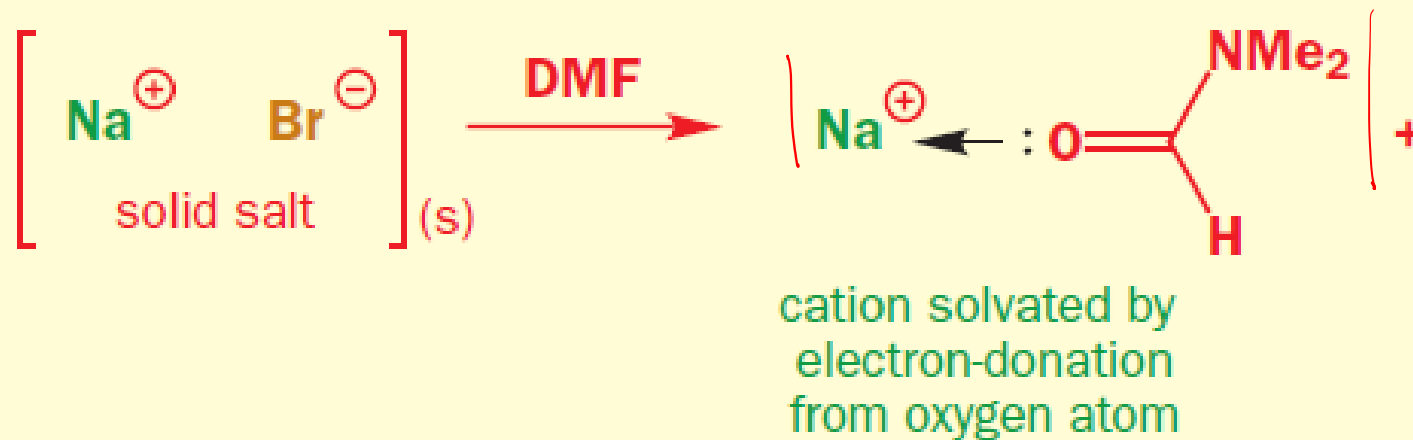Polar aprotic solvents:

$\overset{+}{Na} \overset{-}{I}$

DMSO

DMF

✓ 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

$$\left[Na^{\oplus} \quad Br^{\ominus} \right]_{(s)}$$

solid salt

$\xrightarrow{\text{ROH}}$

$Na^{\oplus} \leftarrow :\overset{R}{\underset{H}{O}}$ + $\left(Br^{\ominus} \text{-----} H \overset{O}{\diagdown} R \right)$

cation solvated by electron-donation from oxygen atom

anion solvated by electron-acceptance through hydrogen bonding
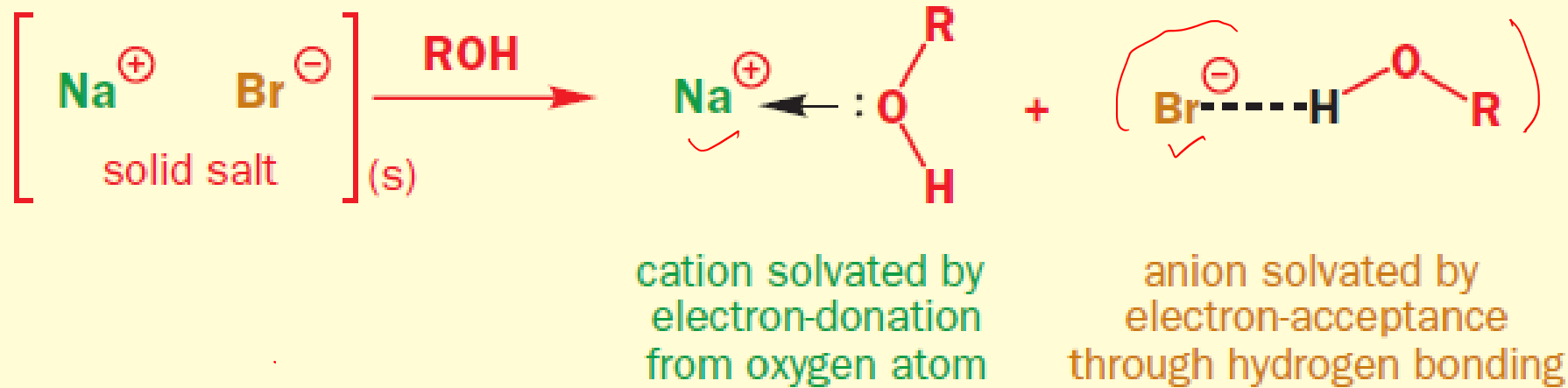
there are more than the one solvent molecule shown for each ion

solvation of salts by polar aprotic solvents

$$\left[Na^{\oplus} \quad Br^{\ominus} \right]_{(s)}$$

solid salt

$\xrightarrow{\text{DMF}}$

$\left| Na^{\oplus} \leftarrow :O = \overset{NMe_2}{\underset{H}{C}} \right|$ + $Br^{\ominus}$

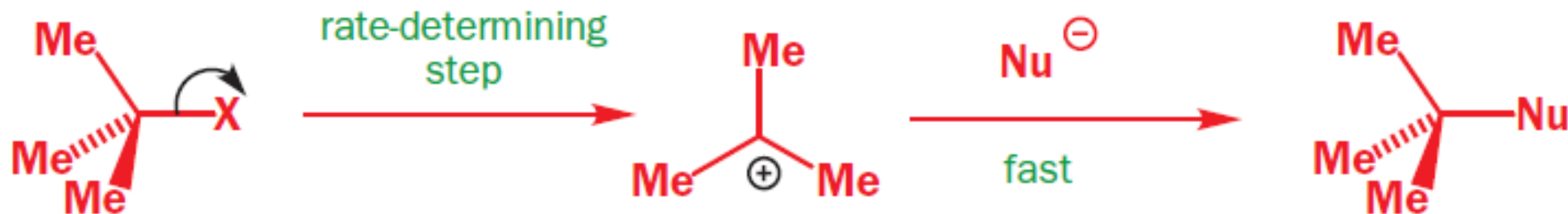**cation solvated by electron-donation from oxygen atom**

anion not solvated - no hydrogen bonding is possible the anion is "naked" and hence more nucleophilic

✓ *Can we rationalize the solvent effects based on the following equation?*

ΔE (interaction energy) : Σ sterics − Σ orbital overlap/(E_{LUMO} −E_{HOMO}) + Σ charge interaction

$$CH_3Cl + OH^{\ominus} \longrightarrow CH_3OH + Cl^{\ominus}$$

$$\longrightarrow CH_3OH \rightarrow ①$$

$$\longrightarrow DMF \rightarrow ②$$

C–Cl (σ^*)

HOMO of OH⁻

HOMO OH⁻

HOMO OH⁻

MeOH

DMF
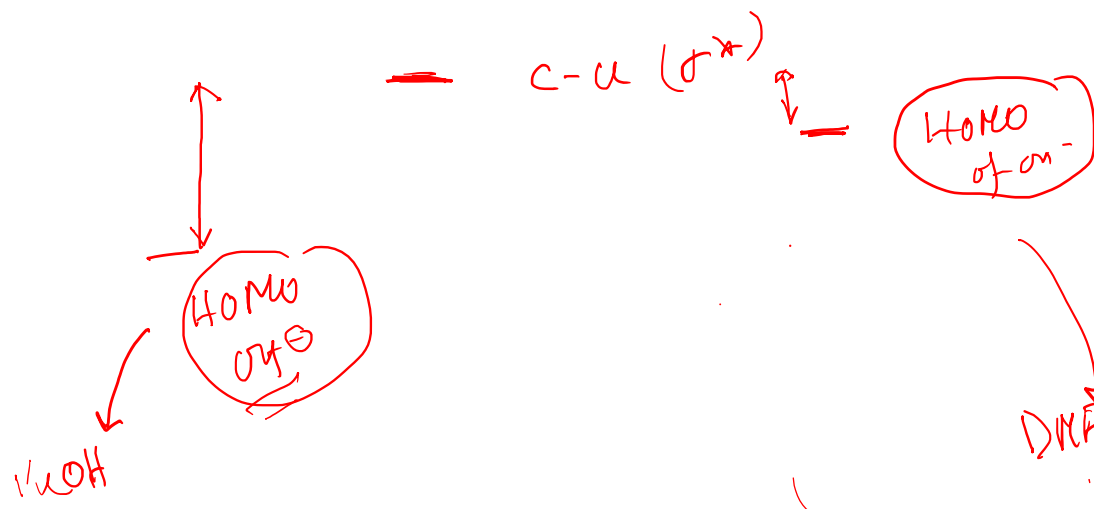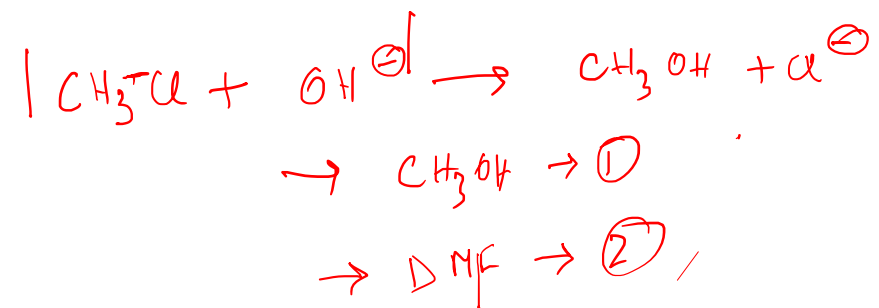
Solvent Effect: S$_N$1

✓ 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$_N$1 reaction.

✓ *The rate-determining step usually involves the formation of ions and the rate of this process will be increased by a polar solvent*
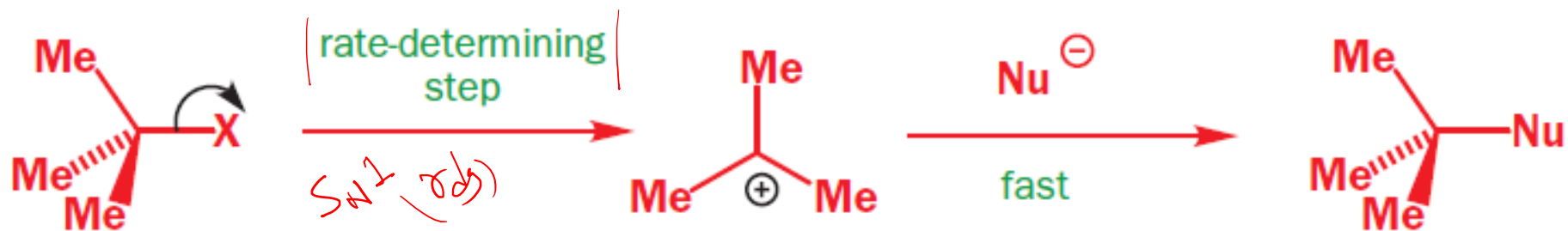
We have covered so far:

1. Structural factors (sterics)

2. Solvent effects

We will now look at two other factors:

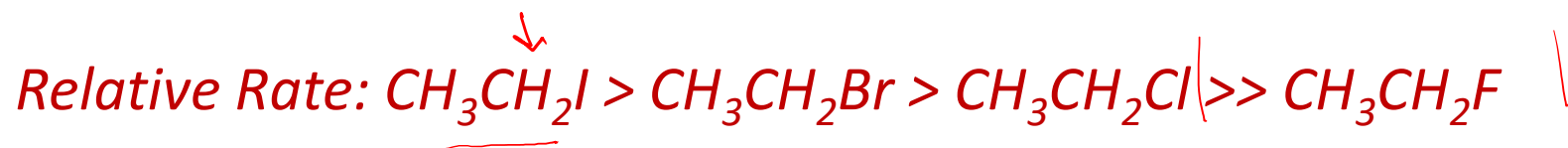Leaving groups

The Leaving Group

Me,
Me''''   X
Me

SN1 (rds)

rate-determining step

Me
Me ⊕ Me

Nu⊖

fast

Me,
Me''''   Nu
Me

Nu⊖   Me—X

rate-determining step

Nu—Me   +   X⊖

Table 17.4 Halide leaving groups in the S$_N$2 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$^-$
fluorine	118
chlorine	81
bromine	67
iodine	54

C–F

C–I

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

Relative Rate: CH$_3$CH$_2$I > CH$_3$CH$_2$Br > CH$_3$CH$_2$Cl >> CH$_3$CH$_2$F

✓ 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

10

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