Solvents in Organic Chemistry

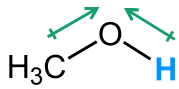
Solvents are selected based on their ability to **dissolve species in solution**, which is largely due to similarities in structure between solvent and reactant.

Described below are common classes of solvents and the roles that solvents can play in addition to dissolving reactants.

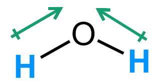
Classes of Common Solvents

1) ***Polar protic*** *(polar:* ***bond/molecular dipole****; protic:* ***hydrogen bonding****, H atoms bonded to O or N)*

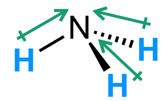
Examples:



methanol



water



ammonia

Solvents above dissolve other polar molecules through hydrogen bonding and dipole-dipole interactions

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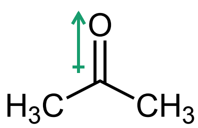
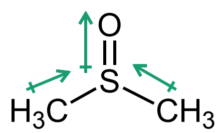
2) ***Polar aprotic*** *(polar:* ***bond/molecular dipole****; aprotic:* ***no*** *H-bonding, H atoms bonded to C)*

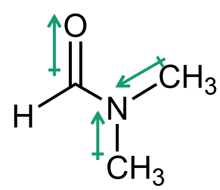
Examples:



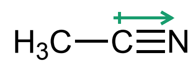
acetone



DMSO



DMF



acetonitrile

Solvents above dissolve other polar molecules through dipole-dipole interactions

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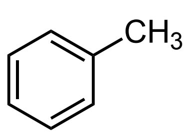
3) ***Nonpolar*** *(no significant bond dipoles, or all bond dipoles cancel)*

Examples:

hydrocarbons

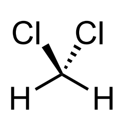


toluene

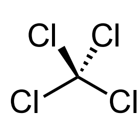
C_6H_{14}

hexane

chlorinated hydrocarbons

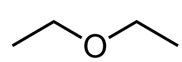


dichloromethane

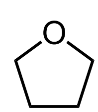


carbon tetrachloride

ethers



diethyl ether



THF

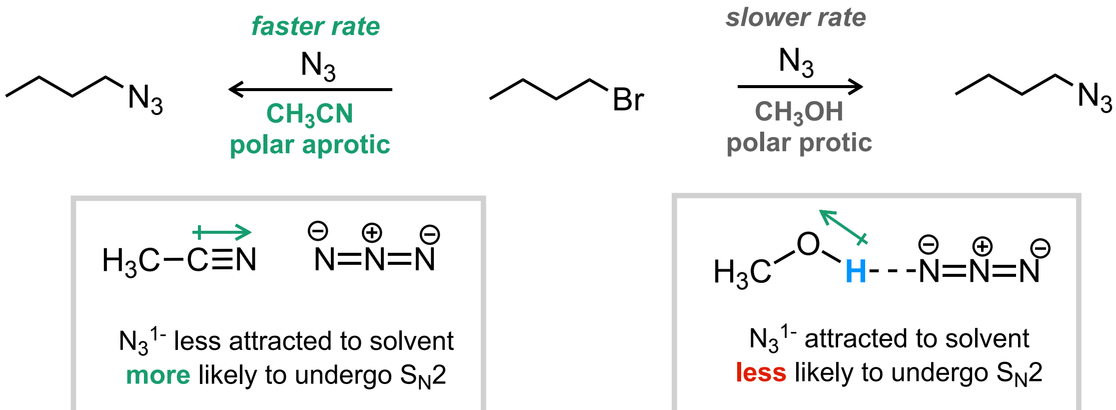
Role of Solvent

1. Solvents **dissolve reactants and products**

Solubility rule of thumb: “like dissolves like"

2. Solvents can **influence the rate of a reaction**

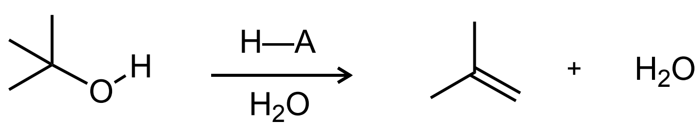
In the S_N2 reaction below, the choice of a polar **protic** solvent like CH_3OH slows the rate of the reaction because it effectively solvates (strong attraction) the nucleophile, thus keeping N_3^- from participating in the reaction



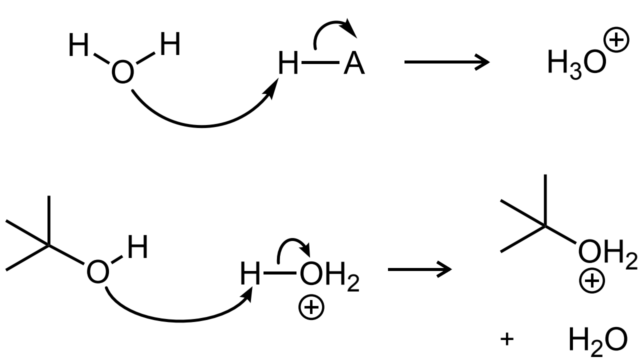
When using a polar **aprotic** solvent like CH_3CN for an S_N2 reaction, the lack of H-bonding in the solvent results in a weaker attraction to the nucleophile, therefore it is easier for N_3^{1-} to particpate in the reaction and the reaction rate is faster.

3. Solvents can be involved in **proton transfer**

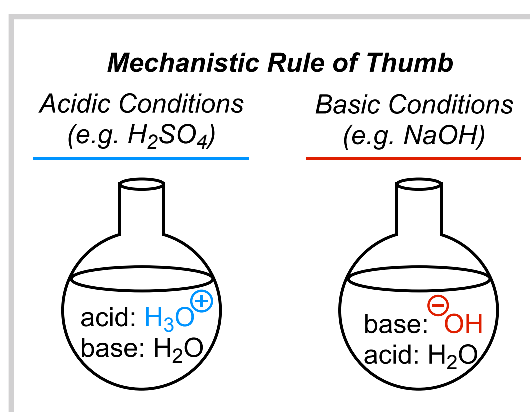
Example: **E_1 Dehydration**



Note: Strong acids (like H_2SO_4) form $H_3O^{\oplus}$ in H_2O

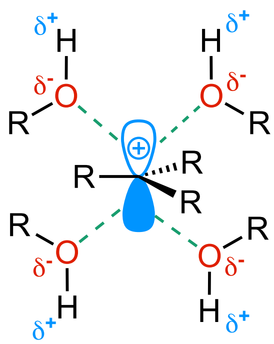


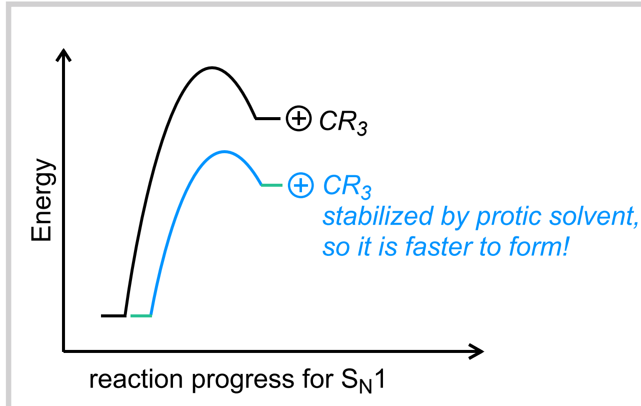
From this, we can say that the acid in solution in a mixture of strong acid and water is actually hydronium, H_3O^+



4. Solvents can **stabilize reactive intermediates**

Example:
stabilized carbocation *in S_N1 reaction*



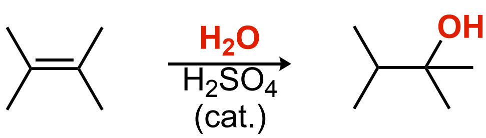


ROH solvent is oriented such that the **oxygen atom** stabilizes the **carbocation**

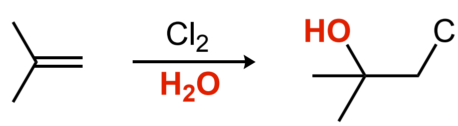
Note: **Dotted lines** are showing attractive interactions that are not true covalent bonds

5. In **rare** situations, often with water, the solvent can act as a reactant

Notable examples:



hydration of alkene



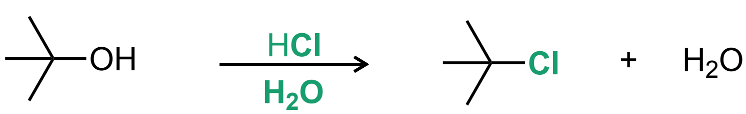
halohydrin formation

What if no solvent information is provided?

…then solvent is not important to the outcome of the reaction

Context clues can be used to identify solvent

When strong acids are used (HX, H_2SO_4, etc…), **H_2O** is assumed to be the solvent



When alkoxide bases are used, **the conjugate acid alcohol** is the solvent