

8.2: Background

When determining whether a substitution/elimination reaction will proceed via an SN1/E1 or SN2/E2 reaction, one of the first questions that we ask concerns reaction conditions. Reactions run under high concentrations and with polar aprotic solvents tend to favor E2 and SN2 reactions. The underlying reason why high concentrations of reagents favor concerted substitutions and eliminations is due to kinetics. Specifically, SN2 and E2 reactions are bimolecular in nature and have a rate law (see equation 8.2.1) with terms including both the concentration of electrophile and nucleophile/base. This means that if we double the concentration of everything in the reaction, we would see a 4-fold increase in the rate of the reaction. Such a rate increase would not occur in a SN1/E1 reactions, which have a rate law that only includes a term for the concentration of the electrophile.

$$\text{Rate}_{\text{SN2/E2}} = k [\text{electrophile}][\text{nucleophile/base}] \quad (8.2.1)$$

$$\text{Rate}_{\text{SN1/E1}} = k [\text{electrophile}] \quad (8.2.2)$$

The use of polar aprotic solvents encourages SN2/E2 reactions by ensuring that the nucleophile/base is reactive, something that polar protic solvents will not be able to do. As shown in Figure 1, when a strong base and nucleophile such as sodium methoxide is dissolved in a polar aprotic solvent such as dimethylsulfoxide (DMSO) the lone pairs on the oxygen of DMSO can form stabilizing ion-dipole interactions with the sodium cation. The anion on oxygen, however, is unable to be stabilized effectively by lone pairs on DMSO. This means that the oxygen anion in sodium methoxide is reactive. If sodium methoxide were dissolved in a polar protic solvent, such as water, both the cation and the anion can be stabilized via intermolecular forces. Specifically, the sodium cation can be stabilized by ion-dipole interactions via lone pairs on the oxygen of water. The oxygen anion of sodium methoxide can also be stabilized by hydrogen bonding with the hydrogens on water molecules. This means that in water the nucleophile/base is stabilized, making it less reactive. Because an E2/SN2 reaction relies on a strong nucleophile/base, polar protic solvents slow down this bimolecular reaction.

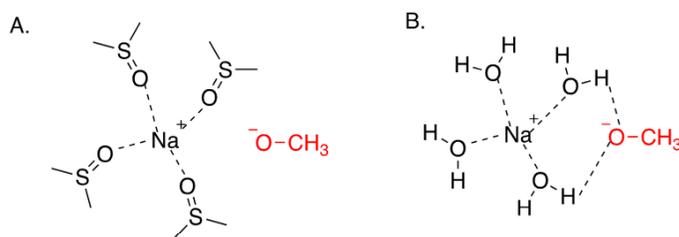


Figure 1A. Sodium methoxide solvated by (DMSO). Here the oxygen of the sulfoxide solvent can stabilize the sodium cation but unable to effectively stabilize the oxygen anion of the methoxide. **1B.** Sodium methoxide solvated by water. In this case both the sodium cation and oxygen anion of the compound are stabilized by intermolecular forces.

When talking reactivity in organic chemistry we often use a very qualitative description of stability. For example, a highly reactive species will be unstable and high in energy, while a stable species will be low in energy and less reactive. To determine how much more or less reactive one species is compared to another, energies can be calculated using quantum chemistry programs such as Orca. In the exercise that follows we calculate the thermodynamic values for an E2 reaction in a polar protic versus a polar aprotic solvent to help illustrate the role of solvation in SN2/E2 reactions.

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