

Effect of Solvent on Nucleophilic Subs. Reaction

Polar Aprotic Solvent

In contrast with protic solvents—which decrease the rates of S_N2 reactions by lowering the ground-state energy of the nucleophile—polar aprotic solvents increase the rates of S_N2 reactions by raising the ground-state energy of the nucleophile. Acetonitrile (CH_3CN), dimethylformamide [$(\text{CH}_3)_2\text{NCHO}$, abbreviated DMF], dimethyl sulfoxide [$(\text{CH}_3)_2\text{SO}$, abbreviated DMSO], and hexamethylphosphoramide [$(\text{CH}_3)_6\text{N}_3\text{PO}$, abbreviated HMPA] are particularly useful. These solvents can dissolve many salts because of their high polarity, but they tend to solvate metal cations rather than nucleophilic anions. As a result, the bare, unsolvated anions have a greater nucleophilicity and S_N2 reactions take place at correspondingly increased rates. For instance, a rate increase of 200,000 has been observed on changing from methanol to HMPA for the reaction of azide ion with 1-bromobutane.

