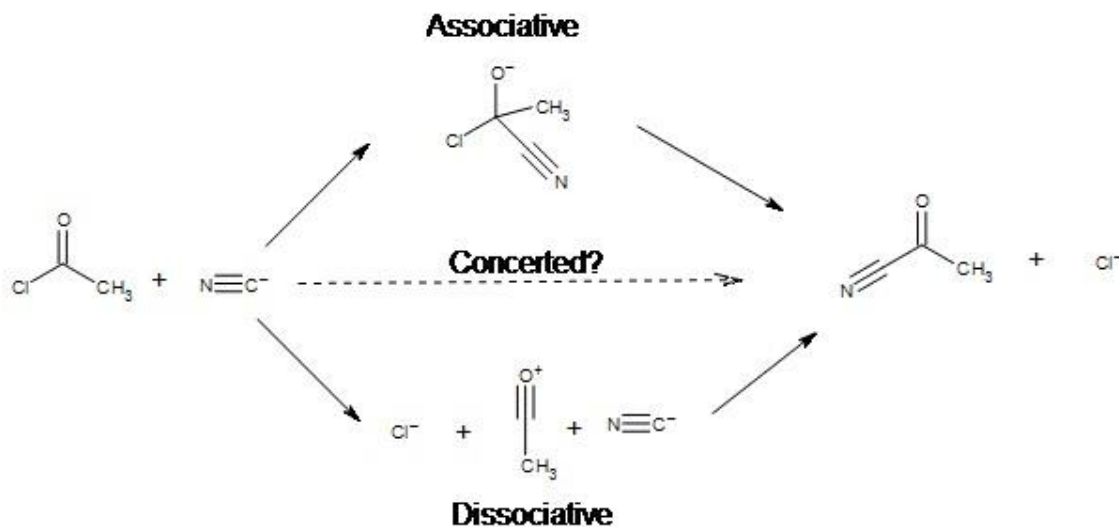


# Analyzing the Effects of a Better Leaving Group in Nucleophilic Acyl Substitution Using M06-2X and MP2

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The goal of this research is to analyze the effect of better leaving groups on nucleophilic acyl substitution reactions. By varying the stability of the leaving group, a concerted, associative, or dissociative reaction profile can be hypothesized (Figure 1). The leaving groups were chosen based on the gas phase acidity of their conjugate acids, with hydrogen chloride being approximately 60 kJ/mol more acidic than hydrogen cyanide ( $1433 \pm 4.6$  kJ/mol) and fluoroacetylene approximately 60 kJ/mol less acidic. Gas phase acidity calculations were also used to select the most appropriate method and basis set combination. Five electron correlation methods (MP2, MP3//MP2, MP4//MP2, CCSD//MP2, and CCSD(T)//MP2) and four density functional theory methods (M06-2X, M08-HX, MN15, and B3LYP) were tested with Dunning and Pople basis sets. The lowest mean unsigned error of all the DFT methods was M06-2X/aug-cc-pVDZ (17.9 kJ/mol) and MP4//MP2/aug-cc-pVTZ (8.6 kJ/mol) had the lowest MUE for the electron correlation methods. All structures were confirmed via frequency calculations using both method and basis set combinations. QST3 calculations were then performed to find transition states, which were confirmed by frequency and IRC calculations.



**Figure 1.** Potential reaction mechanisms for the nucleophilic acyl substitution reaction of ethanoyl chloride with hydrogen cyanide.