

The Reaction of Acetyl Cyanide with Fluoroacetylide: Associative, Dissociative, and Concerted Pathways

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It is known that nucleophilic acyl substitution (NAS) reactions proceed through an associative pathway (below). This means that the compounds proceed through an anionic tetrahedral intermediate. It is also known that with a good leaving group (such as a really weak base) and a weak nucleophile, NAS reactions can occur in a dissociative manner where the leaving group leaves and forms a cationic intermediate prior to nucleophilic attack. The interest of this research is to explore the region between these two extremes where the reaction may be concerted. The concerted method shows a transition state where the nucleophile (fluoroacetylide) makes a bond with the carbonyl carbon simultaneously to the leaving group (cyanide) breaking its bond with the carbonyl carbon, thus making this reaction only one-step. The hypothesis is that the high gas phase acidity value of fluoroacetylene will create a less stable and more nucleophilic conjugate base (fluoroacetylide), which will then push the mechanism toward a more associative pathway than with a chloride or cyanide nucleophile. The energy of reactants, putative intermediates and products were calculated with the MP4//MP2 and M06-2X methods using the aug-cc-pVTZ basis set. Transition states were found using QST3 calculations and confirmed with frequency and IRC calculations. The reaction profiles were used to illustrate the reaction and compare to related reactions with weaker nucleophiles.

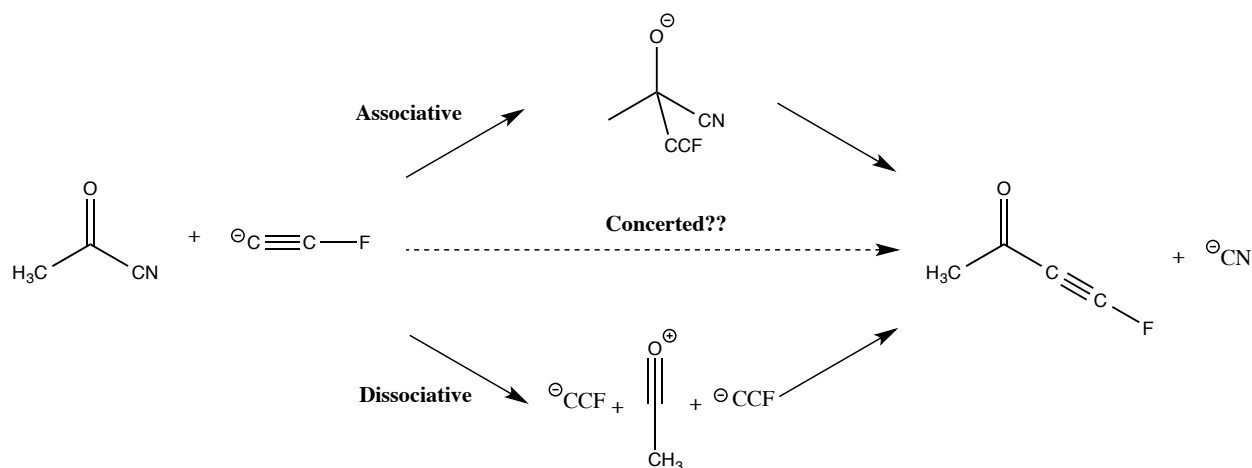


Figure 1. The proposed associative and dissociative pathways for the reaction of acetyl cyanide and fluoroacetylide.