

Intrinsic Reactivity and α -effect in Elimination Reactions and Competing Mechanisms in the Gas-phase

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Chemical reaction rates are strongly influenced by noncovalent interactions. Gas-phase studies allow the factors inherent to reactants to be revealed in the absence of solvent effects, and the true relationship between the intrinsic character and solvent effects can be understood. One of the most complex areas of interest is the α -effect (the enhanced reactivity relative to a given basicity for nucleophiles with a lone pair of electrons adjacent to the attacking atom). Our current work focuses on the α -effect in the gas-phase reaction of a series of systems to elucidate the nature of the α -effect and to allow these effects to be compared to those in solution. Computational studies are also employed to support discussions of intrinsic differences among anions.

The experiments were carried out using the tandem flowing afterglow-selected ion flow tube (FA-SIFT). Ions were generated by chemical ionization method, and then mass-selected using a quadrupole mass filter and injected into the reaction flow tube. Ions were thermalized through collisions with He buffer gas, and allowed to react with the neutral reagent, which were introduced through multiple inlets along the length of the reaction flow tube. Ionic reactants and products are analyzed in the detection region using a triple-quadrupole mass filter and an electron multiplier. The rate constants, product branching ratios, and reaction efficiencies were obtained. Theoretical calculations were performed to support the experimental studies.

We investigate the reactivity trends and α -effect for a series of reactions in single-channel reaction substrates (tert-butyl chloride and methyl chloride), as well as two competitive reaction systems (dimethyl methylphosphonate and methyl formate). A Brønsted-type correlation is employed to discern differences in reactivity as a function of proton affinity in the E2 reactions of a series of anions with tert-butyl chloride. To refine our assessment of intrinsic differences, we narrowed our focus to reagent pairing of normal and α nucleophiles of nearly identical proton affinity ($\text{FCH}_2\text{CH}_2\text{O}^-$, PhCH_2O^- , $(\text{CH}_3)_3\text{COO}^-$) in the E2 reaction with tert-butyl chloride and the $\text{S}_{\text{N}}2$ reaction with methyl chloride. We then expand our reagent pairing (HOO^- versus HO^- , CH_3O^- , $\text{C}_2\text{H}_5\text{O}^-$, and $(\text{CH}_3)_2\text{CHO}^-$) in the competing reactions of dimethyl methylphosphonate and methyl formate to assess the relationship between product distributions and the magnitude of the α -effect.

While our results do not indicate significant deviations between the α -anions and the normal anions for the E2 mechanism, enhanced nucleophilicity is observed for both $(\text{CH}_3)_3\text{COO}^-$ and HOO^- . Unlike condensed phase studies, the magnitude of the α -effect in the methyl formate reactions at the sp^3 carbon (nucleophilic substitution, $\text{S}_{\text{N}}2$) and the sp^2 carbon (addition-elimination at the carbonyl center, $\text{B}_{\text{AC}}2$) are nearly identical. The behavior of the α -nucleophiles can be rationalized by “soft” base behavior (in the context of hard and soft acids and bases).