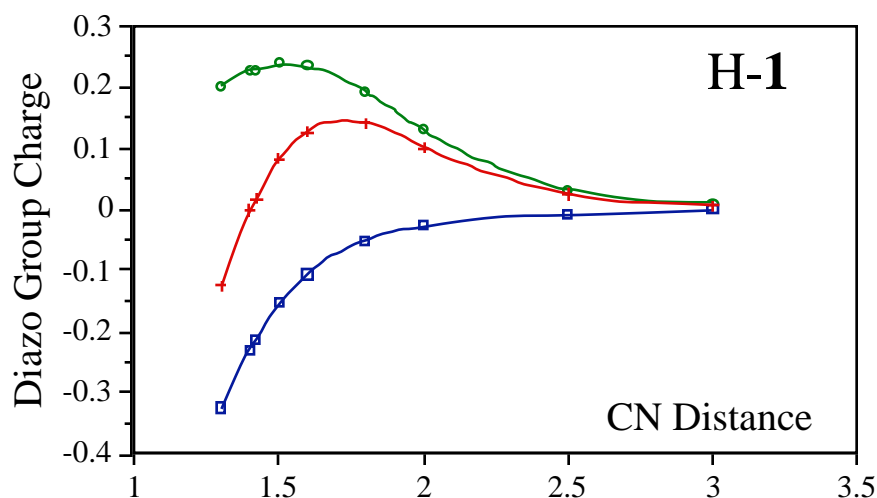


COMBINATION OF PHYSICAL-ORGANIC AND THEORETICAL METHODS IN ELECTRONIC STRUCTURE ANALYSIS. OPPOSING SIGN REACTION CONSTANTS IN DSP RELATIONS.

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Physical organic studies provide an extraordinary wealth of *experimental* data on electronic structure. The interpretation of the physical-organic data often is difficult and presents significant challenges that can only be met by combination of physical-organic and theoretical methods for electronic structure analysis. In this context, we will address a central question in physical-organic chemistry and the electronic structure theory of reaction kinetics: Why is $\rho_R/\rho_F = \lambda$ usually positive and close to unity and why are there only so very few exceptions?

$$\log(k_X/k_o) = \sigma_F\rho_F + \sigma_R\rho_R \text{ with } \rho_R/\rho_F = \lambda < 0$$



Dediazoniations are prominent representatives of the unusual reactions for which dual substituent parameter (DSP) relations yield reaction constants of opposing sign. The electronic relaxation has been studied of dediazoniations of a variety of substituted benzenediazonium ions with ab initio methods (up to QCISD(T)//MP2). The results are consistent with and provide additional support to the electron density based model that describes CN bonding in diazonium ions by synergistic π -donative N=C and π -backdonative C=N bonding. The analysis provides a theoretical basis for the interpretation of the opposing sign DSP relationship and, in addition, furnishes detail about the electronic structure that cannot be deduced from physical-organic studies alone.