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?

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

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 $\sigma$-dative $N\rightarrow C$ and $C\rightarrow N$ $\pi$-backdative 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.