
The reactivity scales developed in Section F have been employed for a rigorous examination of common concepts of Organic Chemistry. Though the reactivity selectivity principle has been abandoned as a general rule more than 30 years ago through the work of several authors, many chemists still believe that it is generally applicable rule, violated just by a few exceptions. In a review, we have shown, why it is impossible that selectivity generally decreases with increasing reactivity and in which cases a decrease of selectivity with increasing reactivity can reliably be expected (# 228).

Detailed experimental studies on the ambident reactivities of \( \text{SCN}^- \) (# 204), \( \text{CN}^- \) (# 215), \( \text{NO}_2^- \) (# 221), \( \text{OCN}^- \) (# 256), \( \text{PhSO}_2^- \) (# 283), pyridone anions (# 297), hydrazines (# 317), and hydrazones (# 356) showed that the “principle of hard and soft acids and bases” or the related Klopman-Salem concept of “frontier- and charge controlled reactions” does not even correctly describe the regioselectivities of the prototypes of ambident nucleophiles. In a quantum chemical investigation we have demonstrated that a consistent description of activation-controlled can be based on Marcus theory (# 288).

An extensive review on ambident reactivity provides a consistent analysis of ambident reactivity on the basis of Figure 8 and demonstrates that the application of PMO theory on reactivities of ambident anions toward carbocations often implies extrapolations to transition states of reactions, which do not have a transition state as they undergo diffusion-controlled combinations (review # 305).

![Figure 8. A systematic analysis of ambident reactivity.](image)

The question polar reactivity versus SET processes, which has been attracting our attention for many years (# 130, 198), has recently been examined for the reactions of quinones with a variety of \( \pi \)-nucleophiles and amines (# 355, 364).

Another long lasting research interest, the differentiation between concerted and stepwise cycloadditions (# 146, 171, 189, see also Section C) has recently gained
new actuality by our demonstration that the rate constants of stepwise 1,3-dipolar cycloadditions are correctly reproduced by our reactivity parameters (# 357, 359). For that reason, the energy of concert can be derived from the ratio of measured vs. calculated (by eq. 1) rate constants.