K.   General Concepts of Organic Chemistry.

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 SCN^- (# 204), CN^- (# 215), NO_2^- (# 221), OCN^- (# 256), $PhSO_2^-$ (# 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 ambient reactivity provides a consistent analysis of ambient reactivity on the basis of Figure 8 and demonstrates that the application of PMO theory on reactivities of ambient 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).
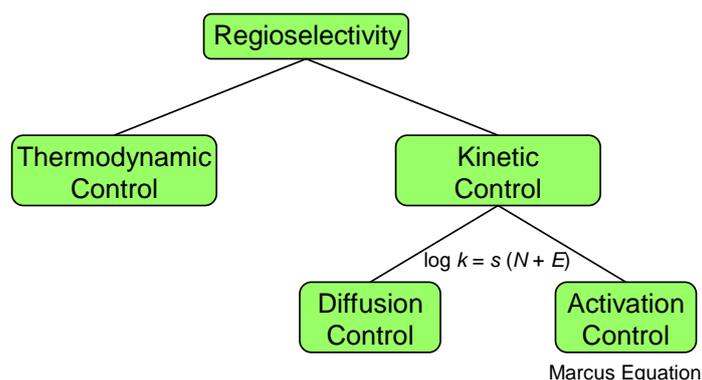
Figure 8. A systematic analysis of ambient reactivity.

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 π-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.