

Prof. Herbert Mayr

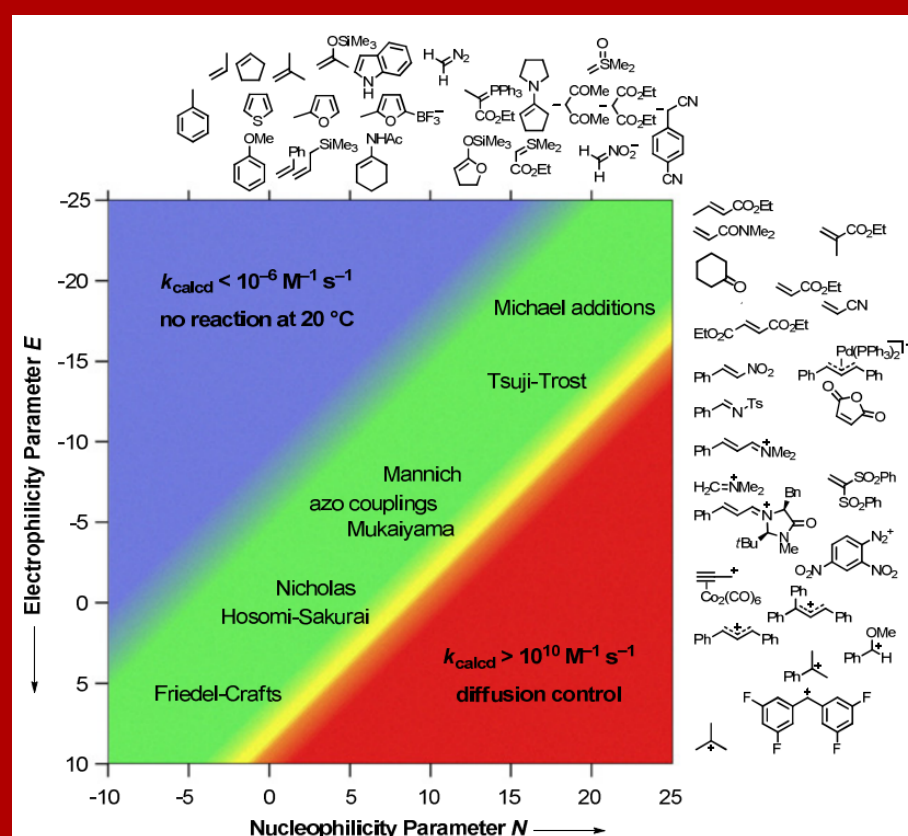
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*Quantifying Polar Organic Reactivity by
Nucleophilicity and Electrophilicity Scales*Martedì 02 Maggio 2023
ore 16.00, Aula A

In a historic review, the development of nucleophilicity and electrophilicity scales from the 1950s to the 1970s will be described. Kinetic investigations of S_N2 reactions by Swain and Scott (1953) and Ritchie's studies of the rates of the reactions of tritylium and tropylium ions with amines, alkoxides and related anions (1972) are the most prominent examples. In the early 1980s we discovered methods for the selective formation of 1:1-products by additions of carbocations to olefins and used the kinetics of these reactions to generate the first nucleophilicity scales for π -systems. We found that the second-order rate constants of these reactions can be expressed by equation (1), where electrophiles are characterized by one parameter (E) and nucleophiles are characterized by two solvent-dependent parameters, the nucleophilicity N and the susceptibility s_N (typically $0.6 < s_N < 1.1$).

$$\lg k_{20^\circ\text{C}} = s_N (E + N) \quad (1)$$

By using para- and meta-substituted benzhydrylium ions (Ar_2CH^+) and structurally related quinone methides as reference electrophiles which differ widely in reactivity, we have created the most comprehensive nucleophilicity scales presently available. In this way a direct comparison of the nucleophilicities of alkenes, allylsilanes and -stannanes, enol ethers and enamines, carbo- and heterocyclic arenes, carbanions, ylids, diazoalkanes, N-heterocyclic carbenes, isonitriles, O-, N-, S- and P-centered nucleophiles, as well as hydride donors became available which are summarized in a freely accessible database: <https://www.cup.lmu.de/oc/mayr/DBintro.html>. In combination with analogously derived electrophilicity parameters, absolute rate constants for polar reactions can be calculated with an accuracy of factor 10-100 in a reactivity range of more than forty orders of magnitude. In this way it has become possible to predict inter- and intramolecular selectivities, in particular whether projected reactions will take place at all and whether they will proceed with activation or diffusion control.



La presenza della S. V. sarà molto gradita.

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