I. Heterolytic Cleavages: The S_N1 – S_N2-Spectrum

The method of overlapping correlation lines, which allowed us to develop the comprehensive nucleophilicity and electrophilicity scales in section F, has analogously been employed to develop nucleofugality scales (leaving group abilities) (# 300). While it was already clear that nucleofugality is not the inverse of nucleophilicity, we have now found that differences in intrinsic barriers also account for the fact that electrofugality is not the inverse of electrophilicity (# 343).

Solvolysis rate constants of combinations of poor electrofuges with good nucleofuges as well as of good electrofuges with poor nucleofuges (Figure 4) have been determined to provide a semiquantitative scheme of heterolysis rates (Figure 5).

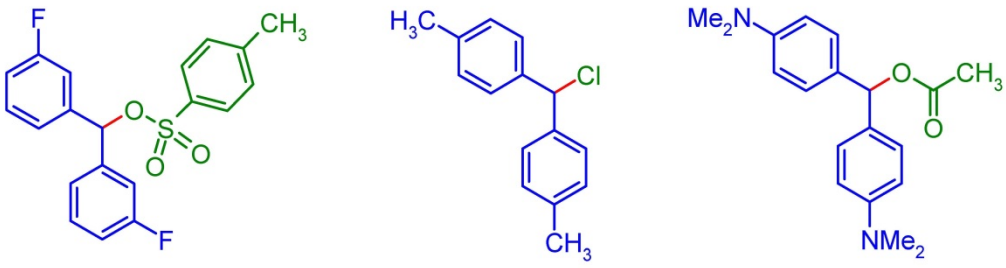

Figure 4. Electrofuge-nucleofuge combinations which dissociate with measurable rates

By developing a stopped-flow technique, which allows one to investigate solvolysis rate constants in the millisecond time scale (# 248), we have almost doubled the width of the green corridor of Figure 5, which indicates the experimentally accessible range.

As illustrated in Figure 6, it has become possible to quantitatively predict the mechanistic change from S_N2 reactions over ordinary S_N1 reactions with and without ion return to heterolytic cleavages with formation of persistent carbocations (# 272, 268). Studies with chiral allyl derivatives even allowed us to derive rate constants for internal and external ion-pair recombination (# 341).

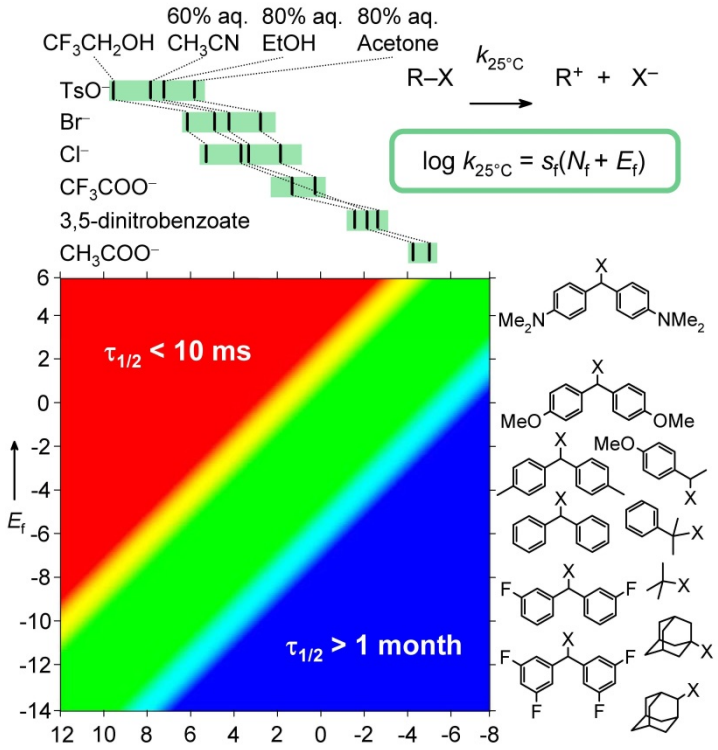

Figure 5. A practical guide for estimating rates of heterolysis reactions

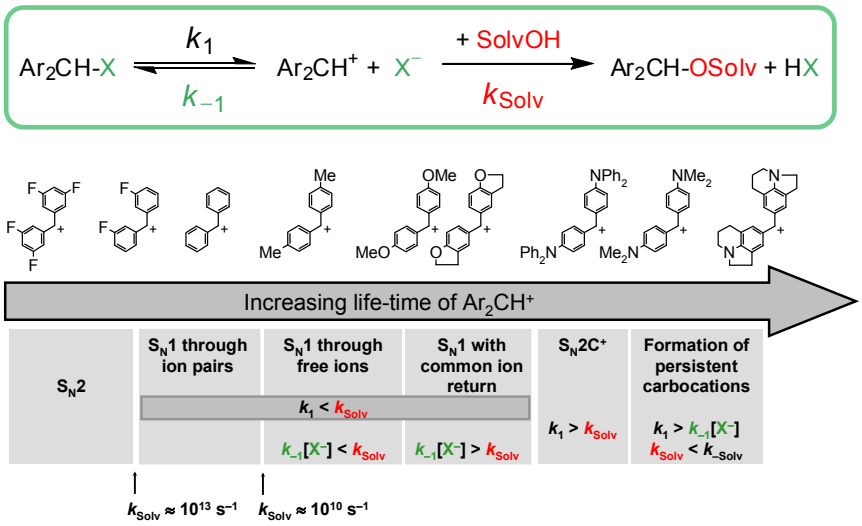

Figure 6. Changing Solvolysis Mechanisms

The newly developed methods have also been employed for studying solvolysis rates of trityl derivatives, which have only rarely been studied before because of the high rates of these heterolyses. Winstein-Grunwald *m*-values between 0.2 and 0.6 have been measured for these S_N1 reactions, showing that *m*-values cannot be used as a criterion to differentiate between S_N1 and S_N2 mechanisms (review # 332).