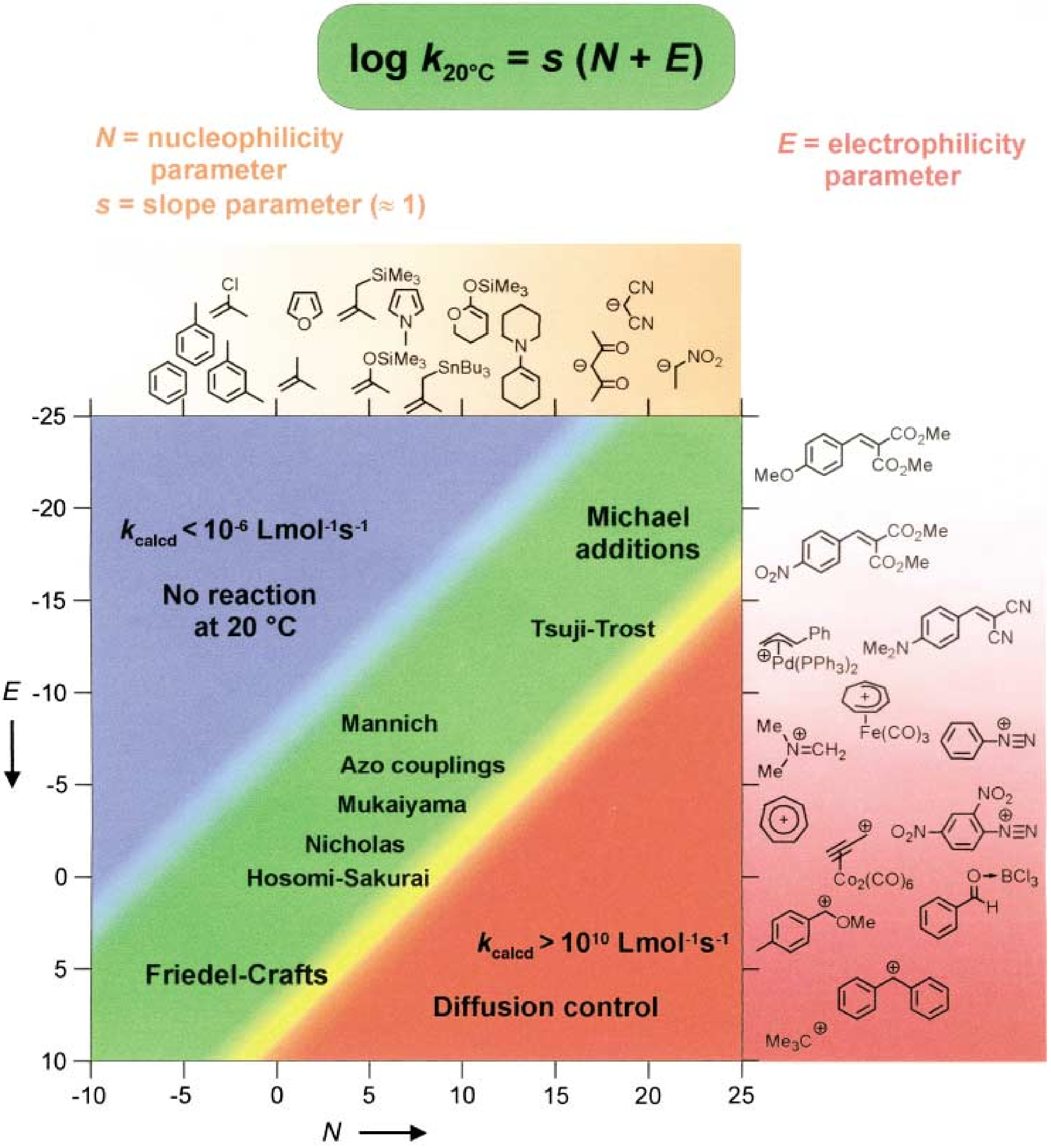
The kinetics of carbocation–carbanion combinations have been the missing link for a comprehensive model of polar organic reactivity.



The following pages show why only two parameters (E and N) are sufficient for a semiquantitative prediction of the rates of many polar organic reactions.

Kinetic Studies of Carbocation–Carbanion Combinations: Key to a General Concept of Polar Organic Reactivity**

Roland Lucius, Robert Loos, and Herbert Mayr*

Dedicated to Professor Lutz F. Tietze
on the occasion of his 60th birthday

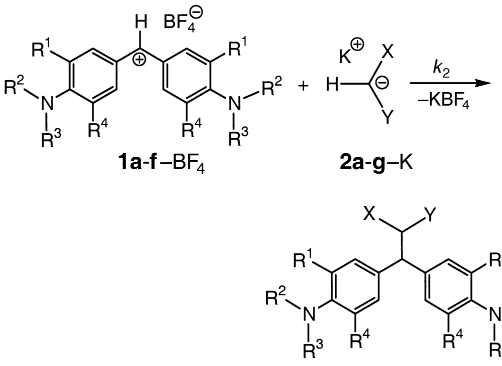
Organic chemistry is usually organized by the concept of functional groups. Although electrophile–nucleophile interactions are recognized as the key elements of many synthetic transformations, for example, electrophilic and nucleophilic aromatic substitutions as well as electrophilic and nucleophilic additions to ethylene derivatives and metal π complexes, these examples are usually treated as separate, seemingly unrelated reactions. This background explains the enthusiastic acceptance of qualitative perturbation molecular orbital theory (PMO theory), which treats a wide variety of organic reactions with a single principle: the interaction of the highest occupied molecular orbital of one reagent with the lowest unoccupied molecular orbital of the other.[1] Despite the wide applicability of PMO theory, quantitative predictions of rate constants can only be made within restricted series of reactions.

We recently showed that a modified linear free energy relationship approach [Eq. (1); s = nucleophile-specific slope parameter, N = nucleophilicity parameter, E = electrophilicity parameter], which employs benzhydryl cations (diaryl carbenium ions) as reference electrophiles, can be used to set up a general reactivity scale for π nucleophiles, including substituted benzenes and heteroarenes, alkenes, enol ethers, allylsilanes and -stannanes, ketene acetals, and enamines.[2a] Equation (1) even provides a direct comparison of π, n, and σ nucleophiles.[2]

$$\log k\,(20\,^\circ\mathrm{C}) = s(N+E) \qquad (1)$$

Although previous applications of Equation (1) were restricted to the reactions of cationic electrophiles with uncharged nucleophiles,[2] the reactions of carbanions with uncharged electrophiles were found to follow a similar pattern.[3] We now report the kinetics of the reactions of highly stabilized carbocations **1a**–**f** with carbanions **2a**–**g** ([Eq. (2), Table 1, and Table 3) and show that these data can be used to construct reactivity scales that combine the chemistry of carbocations with that of carbanions.[4, 5]

The fast reactions were investigated by using stopped-flow techniques with photometric detection of the blue carbocations **1a**–**f**. Usually, solutions of **1**–BF_4 (10^{-6}–10^{-5} M) in dimethyl sulfoxide (DMSO) were combined with solutions of **2**–K (10^{-5}–10^{-4} M) that contained [18]crown-6 (1.01–1.10 equivalents). Since in all cases a [**2**]/[**1**] ratio greater than ten was chosen, the almost constant carbanion concentration gave rise to pseudo-first-order kinetics, which was deduced from the exponential decay of the carbocation absorbance at λ_{max}(DMSO) = 616–643 nm.



(2)

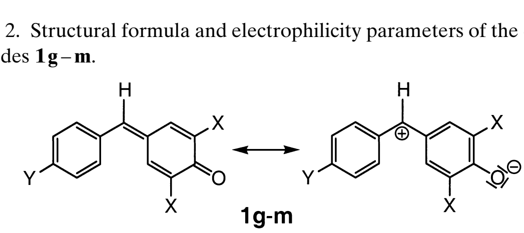
Table 1. Substitution pattern and electrophilicity parameters of the benzhydryl cations **1a**–**f** [Eq. (2)].

	R^1	R^2	R^3	R^4	E[a]
1a	H	CH_3	CH_3	H	–7.02
1b	H	($CH_2CH_2CH_2CH_2$)		H	–7.69
1c	($CH_2CH_2CH_2$)		CH_3	H	–8.22
1d	(CH_2CH_2)		CH_3	H	–8.76
1e	($CH_2CH_2CH_2$)		($CH_2CH_2CH_2$)		–9.45
1f	(CH_2CH_2)		($CH_2CH_2CH_2$)		–10.04

[a] Electrophilicity parameters taken from ref. [2a].

From the ion-pair dissociation constants of the potassium salts **2**–K in DMSO,[6] one can derive that ion pairing is negligible at the concentrations of the kinetic experiments, in accord with our previous report that the same rate constants were found for the reactions of **1j** (Table 2) with **2f**–NBu_4, **2f**–K, **2f**–K/[18]crown-6, and **2f**–K/Kryptofix 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane).[3] For that reason, the observed pseudo-first-order rate constants can be divided by the carbanion concentration to give the second-order rate constants k (Table 3). The high oxidation potentials of the carbanions **2b**–**g**,[7a,b] indicate that the

Table 2. Structural formula and electrophilicity parameters of the quinone methides **1g**–**m**.



1g-**m**

	Y	X	E[a]
1g	OCH_3	Br	–8.63
1h	OCH_3	C_6H_5	–12.18
1i	$N(CH_3)_2$	C_6H_5	–13.39
1j	CH_3	$C(CH_3)_3$	–15.83
1k	OCH_3	$C(CH_3)_3$	–16.11
1l	$N(CH_3)_2$	$C(CH_3)_3$	–17.29
1m	[b]	$C(CH_3)_3$	–17.90

[a] Electrophilicity parameters from correlation analysis in this work. [b] Y-C_6H_4 = Julolidin-9-yl (Figure 1).

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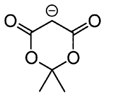
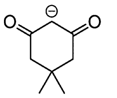
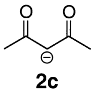
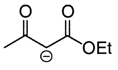
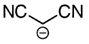
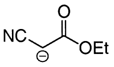
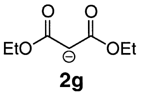
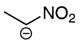
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

reactions occur through a polar mechanism. In contrast to carbocation–carbanion combinations previously investigated,[8] single electron transfer processes do not play a role in this case.[7c]

Table 3. Experimental second-order rate constants k (20 °C) and calculated values k_{calcd} from Equation (1) for the reactions of electrophiles **1a–i** with carbanions **2a–g**.[a]

Nucleophile(*N*/*s*)	Electrophile	k [$L\,mol^{-1}\,s^{-1}$][b]	k_{calcd} [$L\,mol^{-1}\,s^{-1}$][c]
 **2a** (13.91/0.856)	**1a**–BF_4^-	$(5.78 \pm 0.07) \times 10^5$	7.84×10^5
	1b–BF_4^-	$(2.57 \pm 0.03) \times 10^5$	2.09×10^5
	1c–BF_4^-	$(7.37 \pm 0.05) \times 10^4$	7.34×10^4
	1d–BF_4^-	$(2.17 \pm 0.01) \times 10^4$	2.55×10^4
	1e–BF_4^-	$(7.42 \pm 0.10) \times 10^3$	6.50×10^3
	1f–BF_4^-	$(2.56 \pm 0.01) \times 10^3$	2.05×10^3
	1g	$(3.50 \pm 0.08) \times 10^4$	3.28×10^4
	1h	$(2.37 \pm 0.11) \times 10^1$[d]	3.03×10^1
	1i	3.08 ± 0.05	2.80
 **2b** (16.27/0.767)	**1a**–BF_4^-	$(1.24 \pm 0.02) \times 10^7$	1.24×10^7
	1b–BF_4^-	$(5.75 \pm 0.13) \times 10^6$	3.80×10^6
	1c–BF_4^-	$(1.76 \pm 0.02) \times 10^6$	1.49×10^6
	1d–BF_4^-	$(5.03 \pm 0.06) \times 10^5$	5.76×10^5
	1e–BF_4^-	$(1.97 \pm 0.02) \times 10^5$	1.69×10^5
	1f–BF_4^-	$(6.08 \pm 0.02) \times 10^4$	6.03×10^4
	1g	$(5.85 \pm 0.45) \times 10^5$	7.24×10^5
	1h	$(8.99 \pm 0.19) \times 10^2$[d]	1.38×10^3
	1i	$(1.23 \pm 0.03) \times 10^2$	1.63×10^2
 **2c** (17.64/0.729)	**1b**–BF_4^-	$(2.03 \pm 0.30) \times 10^7$	1.78×10^7
	1c–BF_4^-	$(6.79 \pm 0.07) \times 10^6$	7.29×10^6
	1d–BF_4^-	$(2.52 \pm 0.04) \times 10^6$	2.96×10^6
	1e–BF_4^-	$(8.33 \pm 0.09) \times 10^5$	9.23×10^5
	1f–BF_4^-	$(3.29 \pm 0.01) \times 10^5$	3.46×10^5
	1g	$(4.25 \pm 0.45) \times 10^6$[d]	3.67×10^6
	1h	$(1.01 \pm 0.01) \times 10^4$[d]	9.50×10^3
	1i	$(1.30 \pm 0.01) \times 10^3$	1.25×10^3
 **2d** (18.82/0.688)	**1c**–BF_4^-	$(1.72 \pm 0.07) \times 10^7$	1.97×10^7
	1d–BF_4^-	$(7.15 \pm 0.24) \times 10^6$	8.42×10^6
	1e–BF_4^-	$(3.09 \pm 0.05) \times 10^6$	2.80×10^6
	1f–BF_4^-	$(1.20 \pm 0.02) \times 10^6$	1.11×10^6
	1h	$(4.46 \pm 0.06) \times 10^4$[d]	3.73×10^4
	1i	$(5.48 \pm 0.02) \times 10^3$	5.48×10^3
 **2e** (19.36/0.671)	**1e**–BF_4^-	$(4.32 \pm 0.03) \times 10^6$	4.44×10^6
	1f–BF_4^-	$(1.76 \pm 0.01) \times 10^6$	1.80×10^6
	1h	$(6.80 \pm 0.04) \times 10^4$[d]	6.59×10^4
	1i	$(1.14 \pm 0.01) \times 10^4$	1.02×10^4
 **2f** (19.62/0.668)	**1e**–BF_4^-	$(5.89 \pm 0.06) \times 10^6$	6.17×10^6
	1f–BF_4^-	$(2.40 \pm 0.04) \times 10^6$	2.51×10^6
	1h	$(1.05 \pm 0.01) \times 10^5$[c]	9.32×10^4
	1i	$(1.49 \pm 0.01) \times 10^4$	1.45×10^4
 **2g** (20.22/0.654)	**1e**–BF_4^-	$(9.13 \pm 0.23) \times 10^6$	1.10×10^7
	1f–BF_4^-	$(4.11 \pm 0.06) \times 10^6$	4.56×10^6
	1h	$(2.59 \pm 0.11) \times 10^5$[d]	1.81×10^5
	1i	$(2.96 \pm 0.08) \times 10^4$	2.93×10^4
 **2h** (21.93/0.568)	[e]		

[a] The reactions were carried out in DMSO at 20 °C in the presence of [18]crown-6 (1.01–1.10 equiv). The nucleophilicity parameters *N* and the slope parameters *s* were determined by correlation analysis, as described in the text. [b] The listed rate constants are averages from three to five experiments with different anion concentrations. [c] The values of k_{calcd} were calculated with more decimals of *E*, *N*, and *s* than those indicated in the table. The use of *E*, *N*, and *s* from Tables 1–3 leads to slightly deviating values. [d] Without the addition of 18[crown]-6. [e] The *N* and *s* parameters of **2h** were derived from its reactivity towards quinone methides (ref. [3]).

To bridge the gap between the weakest cationic electrophile **1f**[2a] and the most reactive quinone methide studied so far, **1j**,[3] we have also investigated the kinetics of the reactions of the carbanions **2a–g** with the more electrophilic quinone methides **1g–i** (Table 3), which may be considered as highly stabilized benzhydryl cations.[9]

All the rate constants of the reactions of carbanions **2a–h** listed in ref. [3] and in Table 3 were used to calculate the *E* parameters of quinone methides **1g–m** and the *N* and *s* parameters of carbanions **2a–h**, as defined by Equation (1). For this purpose, Δ^2 [Eq. (3)] was minimized.[10]

$$\Delta^2 = \Sigma(\log k - \log k_{calcd})^2 = \Sigma(\log k - s(E+N))^2 \qquad (3)$$

The new reactivity parameters were coupled to those previously determined for carbocations and neutral nucleophiles[2a] by keeping the *E* parameters for the benzhydryl cations **1a–f** constant in the least-squares fit. Thus, the *N* and *s* parameters for the carbanions **2a–h** as well as the *E* parameters for the neutral electrophiles **1g–m** reported herein correspond to the same references as the previously reported scales, that is, $E = 0.0$ for the bis(*p*-methoxyphenyl)carbenium ion and $s = 1.0$ for 2-methyl-1-pentene.[2a] The good agreement between the calculated and the experimental rate constants in Tables 3 and S1 in the Supporting Information (standard deviation: factor 1.16) proves that Equation (1) is also suitable for describing the reactivity of the carbanions towards charged and uncharged π electrophiles. The close similarity between the slope parameters for the carbanions (Table 3) and the uncharged π nucleophiles[2a] indicates that a change in the charge does not change the mechanism of the interaction.

With the determination of the *N* and *s* parameters for the carbanions and of the *E* parameters for the quinone methides, the reactivity range covered by Equation (1) has been extended to almost 30 orders of magnitude (Figure 1). The transition from carbocation chemistry on the left side of Figure 1 to carbanion chemistry on the right includes a change of the reference solvent from dichloromethane to dimethyl sulfoxide. To refer to free carbanions, dimethyl sulfoxide has also been selected as the reference solvent for carbocation–carbanion combinations. Because the *E* parameters of benzhydryl cations determined in CH_2Cl_2 were adopted unchanged for DMSO, we have defined *E* parameters as solvent-independent. As a consequence, the *N* and *s* parameters depend on the solvent and refer to dichloromethane for neutral π nucleophiles,[11] and to dimethyl sulfoxide for carbanions.

Combinations of neutral electrophiles with neutral nucleophiles have not been used for establishing these reactivity scales and the question arises whether the reactivity parameters thus defined can also be used to predict the rate constants for the reactions of neutral electrophiles with neutral nucleophiles. Table S2 and Figure S1 in the Supporting Information show that the rate constants determined for the reactions of quinone methides **1g** and **1h** with piperidinocyclohexene (**3a**) and piperidinocyclopentene (**3b**) in dichloromethane and in DMSO deviate from those calculated by using Equation (1) by less than a factor of 4. It should be noted, however, that larger deviations have to be expected for the

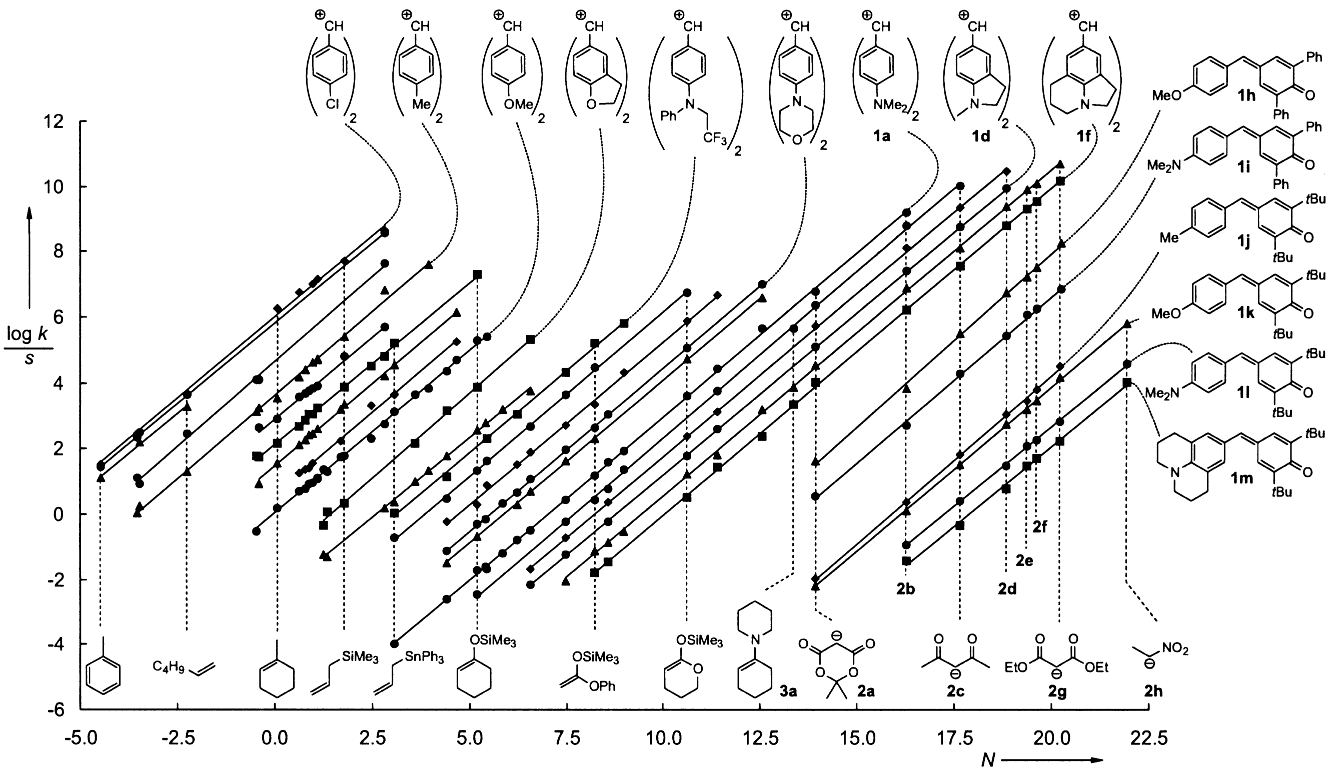


Figure 1. Plot of $(\log k)/s$ versus the nucleophilicity parameter N for the reactions of benzhydryl cations and quinone methides with π nucleophiles and carbanions (correlation line for **1g** not depicted).

reactions of neutral nucleophiles with neutral electrophiles that undergo a large change in dipole moment and therefore show a larger solvent dependence[12] than the reactions of quinone methides with enamines.

Previous work has demonstrated that the N and s parameters of neutral π nucleophiles derived from their reactions with benzhydryl cations are widely applicable and also hold for the reactions of π nucleophiles with other types of carbocations, cationic metal π complexes, and diazonium ions.[2] Analogously, Lemek found that the reactivity parameters for the carbanions reported herein also hold for their reactions with typical Michael acceptors, for example, benzylidene malononitriles or benzylidene malonic esters.[13a] The accuracy of the predictions from Equation (1) decreases when benzhydryl cations are replaced by other types of electrophiles, because the steric situation around the electrophilic reaction centers is not any longer constant. However, the deviations are so moderate[14] that a comprehensive representation of electrophile–nucleophile combinations becomes possible with Equation (1).

In Figure 2, the nucleophiles are ordered in increasing reactivity from left to right, and electrophiles are ordered in increasing reactivity from top to bottom. In this arrangement, the diagonal line identifies electrophile–nucleophile combinations that proceed with a rate constant of $1\,\mathrm{L\,mol^{-1}\,s^{-1}}$ at 20 °C ($E+N=0$). Three domains are differentiated with color; the diffuse borders are partially a result of the variable magnitude of s. The blue sector (cold) identifies combinations of electrophiles with nucleophiles that are too slow to occur at room temperature, whereas red (hot) indicates diffusion-controlled reactions with rate constants of 10^{9}–$10^{10}\,\mathrm{L\,mol^{-1}\,s^{-1}}$. Reactions that have rate constants between 10^{-6} and $10^{10}\,\mathrm{L\,mol^{-1}\,s^{-1}}$ are found in the green and yellow zones. When moving from left to right or from top to bottom in the green zone, the increase in reactivity is predominately a result of a decrease in $\Delta H^{\ddagger}$,[15b] which becomes zero in the yellow strip. The yellow domain encompasses reactions that are not diffusion controlled with $\Delta H^{\ddagger}=0$ (entropy-controlled reactions).[15]

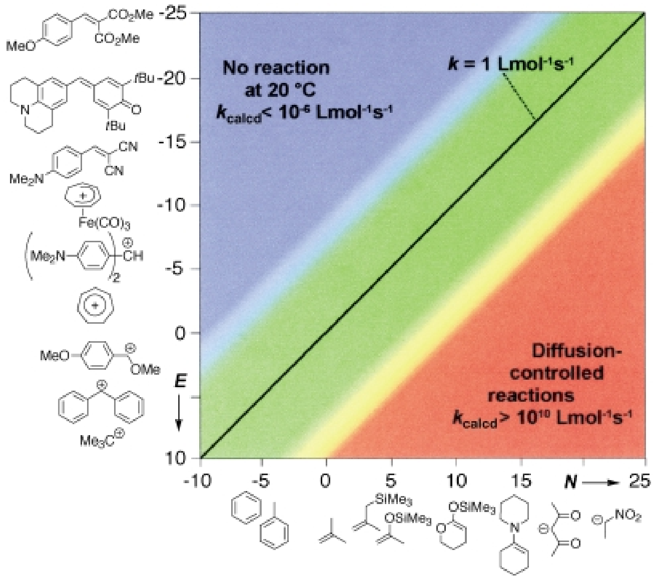


Figure 2. From inertness to diffusion control: a semiquantitative model of polar organic reactivity.

Equation (1), which was previously used to describe the rate constants for the reactions of carbocations with neutral nucleophiles,[2] has now also been demonstrated to hold for reactions of carbocations with carbanions and for reactions of carbanions with neutral electrophiles. It thus became possible to combine the chemistry of carbocations with that of carbanions, and to construct electrophilicity and nucleophilicity scales that cover almost 30 orders of magnitude.

A three-parameter equation that neglects steric effects can certainly not be expected to provide accurate rate constants. However, it has been shown for reactions of carbocations with π nucleophiles that the deviation between calculated and experimental rate constants seldom exceeds a factor of 30 when bulky reagents are excluded[14]—a remarkable agreement in view of the many orders of magnitude covered by this model. Since this precision is sufficient for planning organic syntheses, a common set of reactivity parameters E, N, and s can be used to describe reactions as different as Friedel–Crafts alkylations,[16] Hosomi–Sakurai allylations,[17] Nicholas propargylations,[18] Mukaiyama aldol reactions,[19] Mannich aminoalkylations,[20] azo couplings,[21] palladium-catalyzed allylations,[22] Michael additions,[23] and many others. Multicenter reactions, including S_N2-type reactions, are excluded.

This model does not only allow one to determine whether a certain reaction is likely to take place, but also identifies diffusion-controlled reactions of reactive intermediates, which may be associated with a breakdown of regio- and stereoselectivity.[24] Whereas small differences between k and k_{calcd} from Equation (1) cannot be interpreted, deviations of several orders of magnitude have mechanistic significance. A common feature of the reactions that follow Equation (1) is the formation of one new single bond in the rate-determining step. Strong deviations may therefore indicate an alternative reaction mechanism or be a result of special stabilizing or destabilizing interactions in the transition states, as expected from Pearson's hard and soft acids and bases principle.[25]

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[3] R. Lucius, H. Mayr, *Angew. Chem.* **2000**, *112*, 2086–2089; *Angew. Chem. Int. Ed.* **2000**, *39*, 1995–1997.

[4] Thermodynamics of carbocation carbanion combinations: a) K. Okamoto, K. Takeuchi, T. Kitagawa, *Adv. Phys. Org. Chem.* **1995**, *30*, 173–221; b) T. Kitagawa, K. Takeuchi, *J. Phys. Org. Chem.* **1998**, *11*, 157–170.

[5] Previous investigations on the kinetics of carbocation–carbanion combinations: E. M. Arnett, K. E. Molter, *Acc. Chem. Res.* **1985**, *18*, 339–346.

[6] a) V. M. DePalma, E. M. Arnett, *J. Am. Chem. Soc.* **1978**, *100*, 3514–3525; b) W. N. Olmstead, F. G. Bordwell, *J. Org. Chem.* **1980**, *45*, 3299–3305.

[7] a) F. G. Bordwell, J. A. Harrelson, Jr., A. V. Satish, *J. Org. Chem.* **1989**, *54*, 3101–3105; b) F. G. Bordwell, J. A. Harrelson, Jr., X. Zhang, *J. Org. Chem.* **1991**, *56*, 4448–4450; c) from the oxidation potentials of $+0.7$ to $+0.9$ V for **2b–g** (ref. [7a,b]; values for **2a** and **2h** are not available) and the irreversible reduction potentials of -0.3 to -0.4 V for **1c–e** (R. Lucius, unpublished results), one can estimate SET rate constants considerably smaller than those actually observed.

[8] E. B. Troughton, K. E. Molter, E. M. Arnett, *J. Am. Chem. Soc.* **1984**, *106*, 6726–6735.

[9] J. P. Richard, M. M. Toteva, J. Crugeiras, *J. Am. Chem. Soc.* **2000**, *122*, 1664–1674.

[10] Δ^2 [Eq. (3)] was minimized by means of "*What'sBest!* 4.0 Commercial" by LINDO Systems Inc. by solving the model several times with different initial values of E, N, and s. The program's nonlinear solver employs both successive linear programming and generalized reduced gradient algorithms.

[11] It has been shown, however, that the rates of reactions of carbocations with uncharged π nucleophiles are only slightly affected by solvent polarities; see ref. [2].

[12] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 1st ed., VCH, Weinheim, **1988**, pp. 147–160.

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[14] See Tables 2 and 3 in ref. [2a]. Steric factors cannot be neglected in reactions with bulky reagents, for example, tritylium (see ref. [15c]) or alkyldiaryl carbenium ions (M. Roth, H. Mayr, R. Faust, *Macromolecules* **1996**, *29*, 6110–6113).

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