

How Constant Are Ritchie's "Constant Selectivity Relationships"? A General Reactivity Scale for n-, π -, and σ -Nucleophiles

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Abstract: The kinetics of 82 reactions of benzhydrylium ions (Ar_2CH^+) with n-nucleophiles has been determined at 20 °C. Evaluation by the equation $\log k = s(N + E)$ delivered the reactivity parameters N and s for 15 n-nucleophiles (water, hydroxide, amines, etc.). All nucleophiles except water ($s = 0.89$) and $^-\text{SCH}_2\text{CO}_2^-$ ($s = 0.43$) have closely similar slope parameters ($0.52 < s < 0.71$), indicating that the reactions of most n-nucleophiles approximately follow Ritchie's constant selectivity relationship ($s = \text{constant}$). The different slope parameter for water is recognized as the main reason for the deviations from the Ritchie relationship reported in 1986. Correlation analysis of the rate constants for the reactions of benzhydrylium ions with the n-nucleophiles (except H_2O) on the basis of Ritchie's equation $\log k = N_+ + \log k_0$ yields a statistically validated set of N_+ parameters for Ritchie-type nucleophiles and $\log k_0$ parameters for benzhydrylium ions. The N and s parameters of the n-nucleophiles derived from their reactions with benzhydrylium ions were combined with literature data for the reactions of these nucleophiles with other carbocations to yield electrophilicity parameters E for tritylium, tropylium, and xanthylium ions. While the E parameters for tropylium and xanthylium ions appear to be generally applicable, it is demonstrated that the E parameters of tritylium ions can be used to predict reactivities toward n-nucleophiles as well as hydride transfer rate constants but not rates for the reactions of tritylium ions with π -nucleophiles. It is now possible to merge the large data sets determined by Ritchie and others with our kinetic data and present a nucleophilicity scale comprising n- (e.g., amines), π - (e.g., alkenes and arenes), and σ -nucleophiles (e.g., hydrides).

Introduction

Ritchie's discovery that the rates of the reactions of stabilized carbocations and diazonium ions with water, alcohols, and several anions can be described by eq 1 marked a change of paradigm in Physical Organic Chemistry.¹

$$\log(k/k_0) = N_+ \quad (1)$$

$$\log k = N_+ + \log k_0 \quad (1a)$$

$\log k_0$ = electrophile-dependent parameter

N_+ = nucleophile-dependent parameter

Equation 1 implies that the relative reactivities of two nucleophiles are given by the differences of their N_+ values, which are independent of the electrophilicities of the reaction partners. It thus contradicts the previously accepted reactivity–selectivity principle, which postulates a decrease of selectivity

with increasing reactivity.² The so-called "constant selectivity relationship" (eq 1) found wide acceptance, but in 1986 Ritchie replaced the electrophile-independent parameters N_+ by several sets of N_+ values, which actually are relative reactivities toward malachite green, tris(*p*-methoxy)tritylium, pyronin-Y, or the *p*-(dimethylamino)phenyltropylium ion. Since then many authors either have been using the "largest revised set of N_+ parameters", which effectively are reactivities toward malachite green (or tris-*p*-methoxytritylium ion),³ or have been referring to Ritchie's original parameters¹ when analyzing new reactivity data.⁴

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Rearranging eq 1 leads to eq 1a, which emphasizes that $\log k_0$ in the Ritchie equation corresponds to a nucleophile-independent electrophilicity parameter that was initially defined as the rate constant for the reaction of an electrophile with water. During the past 15 years, we have been studying reactions of carbocations with π -nucleophiles,^{5–8} carbanions,⁹ and hydride donors^{10–12} and demonstrated that the rates of these reactions can be described by eq 2.

$$\log k(20\text{ }^\circ\text{C}) = s(N + E) \quad (2)$$

s = nucleophile-specific parameter

N = nucleophilicity parameter

E = electrophilicity parameter

Equation 2 differs from eq 1/1a by the use of an additional nucleophile-specific slope parameter, s . This parameter, which was set to $s = 1$ for 2-methyl-1-pentene,^{5,8} represents a correction term that improves the fit of data compared to eq 1. A theoretical interpretation of the physical meaning of s has recently been published.¹³ The Ritchie equation (eq 1/1a) can be considered as a special case of eq 2 that holds for reactions with groups of nucleophiles that have identical slope parameters s .

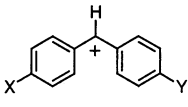
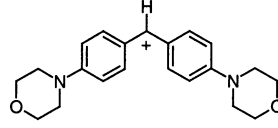
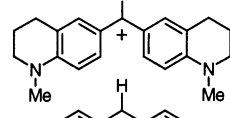
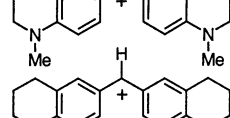
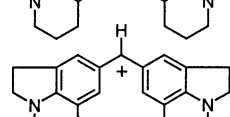
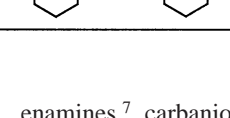
It was the goal of this work to investigate Ritchie-type reactions (carbocations + n -nucleophiles) with our methodology and to identify domains that can sufficiently be described by Ritchie's eq 1. In this way, it should become possible to search for relationships between the reactivity parameters of eqs 1 and 2 and to create a common reactivity scale for n -, π -, and σ -nucleophiles.

Method

Recently, we have recommended 22 differently substituted benzhydrylium ions as reference electrophiles for quantifying the reactivities of various types of nucleophiles.^{7,8} (Scheme 1)

We have demonstrated that the same electrophilicity parameters E can be used for describing the reactions of benzhydryl cations with alkenes, arenes, allylsilanes, allylstannanes, enol

Scheme 1. Abbreviations and Electrophilicity Parameters E of Benzhydrylium Ions

	X	Y	E^a
(pcp) ₂ CH ⁺	Cl	Cl	6.02
Ph ₂ CH ⁺	H	H	5.90
(pfp)PhCH ⁺	F	H	5.60
(tol)PhCH ⁺	CH ₃	H	4.59
(tol) ₂ CH ⁺	CH ₃	CH ₃	3.63
(pop)PhCH ⁺	OPh	H	2.90
(ani)PhCH ⁺	OCH ₃	H	2.11
(ani)(tol)CH ⁺	OCH ₃	CH ₃	1.48
(ani)(pop)CH ⁺	OCH ₃	OPh	0.61
(ani) ₂ CH ⁺	OCH ₃	OCH ₃	0.00
(fur) ₂ CH ⁺			-1.36
(pfa) ₂ CH ⁺	N(Ph)CH ₂ CF ₃	N(Ph)CH ₂ CF ₃	-3.14
(mfa) ₂ CH ⁺	N(CH ₃)CH ₂ CF ₃	N(CH ₃)CH ₂ CF ₃	-3.85
(dpa) ₂ CH ⁺	NPh ₂	NPh ₂	-4.72
(mor) ₂ CH ⁺			-5.53
(mpa) ₂ CH ⁺	N(Ph)CH ₃	N(Ph)CH ₃	-5.89
(dma) ₂ CH ⁺	N(CH ₃) ₂	N(CH ₃) ₂	-7.02
(pyr) ₂ CH ⁺	N(CH ₂) ₄	N(CH ₂) ₄	-7.69
(thq) ₂ CH ⁺			-8.22
(ind) ₂ CH ⁺			-8.76
(jul) ₂ CH ⁺			-9.45
(lil) ₂ CH ⁺			-10.04

^a From ref 8.

ethers, ketene acetals, enamines,⁷ carbanions,⁹ and hydride donors.^{10–12} We have now investigated the kinetics of the reactions of benzhydrylium ions with n -nucleophiles (Ritchie-type nucleophiles) and analyzed the observed second-order rate constants by eqs 1 and 2.

Experimental Section

Materials. Potassium hydroxide was purchased as an aqueous standard solution (Merck). 2,2,2-Trifluoroethanol (TFE), 2,2,2-trifluoroethylamine, semicarbazide hydrochloride, hydroxylamine hydrochloride, sodium sulfite (Na₂SO₃), sodium azide (NaN₃), aqueous hydrogen peroxide, phenol, and p -nitrophenol were reagent-grade chemicals from commercial sources and used without further purification. n -Propylamine, morpholine, and piperidine were commercial samples (Acros) and distilled over KOH before use. Aqueous hydrogen peroxide solutions were titrated with potassium permanganate solution. H₂NCH₂-CO₂Et was purchased as the hydrochloride salt, and the free base was

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liberated with NH_3 gas as described in ref 14. The free $\text{H}_2\text{NCH}_2\text{CO}_2\text{Et}$ was stored at -60°C , and its purity was checked by ^1H NMR before use. $\text{HSCH}_2\text{CO}_2\text{Na}$ was recrystallized from aqueous EtOH. Diazabicyclo-[2.2.2]octane (Dabco) was recrystallized from *n*-hexane. Sodium tetrafluoroborate (NaBF_4) was recrystallized from methanol.

Benzhydrylium tetrafluoroborates were prepared as previously described.⁸

Water was distilled and passed through a Milli-Q water purification system. Dimethyl sulfoxide (DMSO, Fluka, puriss., stored over molecular sieve, $\text{H}_2\text{O} \leq 0.01\%$) was used without further purification. Acetonitrile was distilled over diphenylketene.

Kinetics. The reactions of benzhydrylium ions with nucleophiles were studied in aqueous solution or in DMSO. The benzhydrylium salts used in this study are colored substances with absorption maxima in the range of 585–634 nm, which differ only slightly from those reported in CH_2Cl_2 ⁸ (Supporting Information Table S6). All amines were used as free bases. The anions $^-\text{SCH}_2\text{CO}_2^-$, HOO^- , PhO^- , and $(p\text{-NO}_2)_2\text{C}_6\text{H}_4\text{O}^-$ were generated in aqueous solution by treatment of the corresponding acids with KOH. Solutions of sulfite ion contained ca. 10^{-5} M hydroquinone (recrystallized from CH_3CN) to avoid decomposition.¹⁵

As the reactions of the colored benzhydrylium ions with *n*-nucleophiles gave rise to colorless products, the reactions could be followed by employing UV–vis spectroscopy.¹⁶ The rates of slow reactions ($\tau_{1/2} > 10$ s) were determined by using a J&M TIDAS diode array spectrophotometer, which was controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. The temperature of solutions during all kinetic studies was kept constant (usually $20 \pm 0.2^\circ\text{C}$) by using a circulating bath thermostat and monitored with a thermocouple probe that was inserted into the reaction mixture.

Hi-Tech SF-61DX2 stopped-flow spectrophotometer systems (controlled by Hi-Tech KinetAsyst2 software) were used for the investigation of rapid reactions of benzhydrylium ions with *n*-nucleophiles ($\tau_{1/2} < 10$ s at 20°C). The kinetic runs were initiated by mixing equal volumes of solutions of the nucleophile and the benzhydrylium salt. Nucleophile concentrations at least 10 times higher than the benzhydryl cation concentrations were usually employed, resulting in pseudo-first-order kinetics with an exponential decay of the benzhydryl cation concentration. First-order rate constants $k_{1\psi}$ (s^{-1}) were obtained by least-squares fitting of the absorbance data (averaged from at least four kinetic runs at each nucleophile concentration) to the single-exponential $A_t = A_0 \exp(-k_{1\psi}t) + C$.

As shown for the reaction of $(\text{liI})_2\text{CH}^+$ with OH^- in Figure 1, $k_{1\psi}$ increases linearly with the concentration of the nucleophile, and the slope of this correlation corresponds to the second-order rate constant (k_2). All second-order rate constants reported in this paper have analogously been derived from $k_{1\psi}$ vs [nucleophile]₀ plots.

As a consequence of the poor solubility of the benzhydrylium tetrafluoroborates, it was necessary to employ 0.4% (v/v) of a cosolvent (TFE or CH_3CN) for the kinetic investigations in water. Since aqueous solutions of benzhydrylium salts with an electrophilicity parameter $E > -7$ (Scheme 1) are not stable, the rates of the reactions of these electrophiles with OH^- or H_2O were determined by mixing solutions of benzhydrylium ions in CH_3CN with equal volumes of water or OH^-/water in the stopped-flow instrument. In some experiments with $(\text{dma})_2\text{CH}^+\text{BF}_4^-$ in water, small quantities of benzenesulfonic acid or *p*-toluenesulfonic acid were added to stabilize the aqueous solutions of the benzhydrylium salts. We were not able, however, to stabilize aqueous solutions of $(\text{mor})_2\text{CH}^+$ and $(\text{mfa})_2\text{CH}^+$ by the addition of

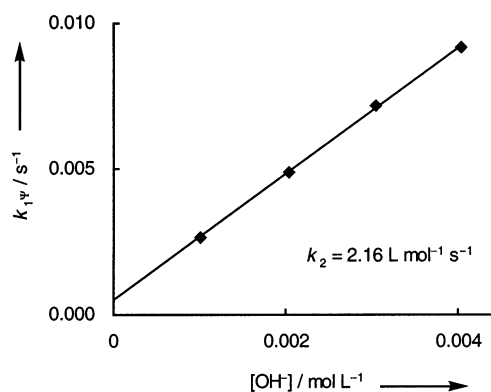


Figure 1. Determination of the second-order rate constant for the reaction of $(\text{liI})_2\text{CH}^+$ with OH^- in water (with 0.4% CH_3CN , 20°C).

sulfonic acids. Probably protonation at nitrogen and successive reaction with water resulted in a decolorization of the solutions.

Attempts to determine the reactivities of benzhydrylium ions with phenoxide ion in water failed, since none of the reactions of $(\text{liI})_2\text{CH}^+$, $(\text{jul})_2\text{CH}^+$, $(\text{thq})_2\text{CH}^+$, or $(\text{pyr})_2\text{CH}^+$ with an excess of phenoxide showed an exponential decay of the carbocation concentration. The reactions of *p*-nitrophenoxide with $(\text{ind})_2\text{CH}^+$ and $(\text{dma})_2\text{CH}^+$ were also examined, but precise rate constants could not be obtained because of the low reactivity of *p*-nitrophenoxide.

Product from $(\text{dma})_2\text{CH}^+$ with $\text{CF}_3\text{CH}_2\text{O}^-$ in Water. A solution of $(\text{dma})_2\text{CH}^+\text{BF}_4^-$ (200 mg, 0.588 mmol) in 10 mL of CH_3CN was added to a mixture of trifluoroethanol (TFE, 2 mL) and aqueous KOH (0.491 M, 1.4 mL) in 500 mL of water. After stirring at room temperature for 30 min, the organic layer was extracted with four 100-mL portions of CH_2Cl_2 . The combined organic layers were washed with water and dried with MgSO_4 . Then the solvent was evaporated to give 117 mg of a 7:1 mixture of $(\text{dma})_2\text{CHOCH}_2\text{CF}_3$ and $((\text{dma})_2\text{CH})_2\text{O}$ (according to ^1H NMR) as a pale blue solid.

Results

The combination of a benzhydrylium salt with more than 10 equiv of a nucleophile usually resulted in an exponential decay of the carbocation absorption, from which the pseudo-first-order rate constant $k_{1\psi}$ was derived. As shown for the reaction of $(\text{liI})_2\text{CH}^+$ with OH^- in Figure 1, $k_{1\psi}$ increases linearly with the concentration of the nucleophile, and the slope of this correlation corresponds to the second-order rate constant (k_2). All second-order rate constants reported in this paper have analogously been derived from $k_{1\psi}$ vs [nucleophile]₀ plots, as explicitly shown on pp S23–S77 in the Supporting Information.

In some cases, a bathochromic shift of the absorption maximum up to 5 nm was observed in the final stages of the reactions, when the carbocation concentrations became small (>95% conversion). Since the reason for this shift is not known, we have not evaluated the late stages of such reactions.

The rates of cation–anion combinations are known to depend on ionic strength (I).¹⁷ However, Ritchie reported that for aqueous solutions, changes of ionic strength are negligible when $I < 0.1$ mol L^{-1} .¹⁸ In accord with this report, the second-order rate constant for the reaction of $(\text{liI})_2\text{CHBF}_4$ with OH^- remained almost unchanged when NaBF_4 was added to realize a constant ionic strength of $I = 0.005$ or 0.01 mol L^{-1} instead of $I =$

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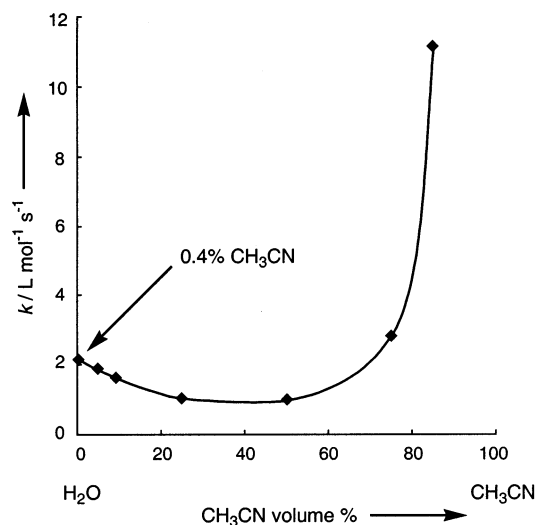


Figure 2. Solvent effect on the second-order rate constant of the reaction of $(\text{lil})_2\text{CH}^+$ with OH^- in acetonitrile–water mixtures (individual rate constants are given on pp S23–S28 of the Supporting Information). Because of the poor solubility of $(\text{lil})_2\text{CH}^+\text{BF}_4^-$, the rate constant in pure water cannot be measured.

Table 1. Influence of Ionic Strength (I) on the Rate Constant of the Reaction of $(\text{lil})_2\text{CH}^+\text{BF}_4^-$ ($1 \times 10^{-5} \text{ mol L}^{-1}$) + OH^- in Water (with 0.4% CH_3CN)

[KOH], mol L ⁻¹	[NaBF ₄], mol L ⁻¹	I , mol L ⁻¹	k_2 , L mol ⁻¹ s ⁻¹
0.001–0.004		0.001–0.004	2.16
0.001–0.004	0.004–0.001	0.005	2.24
0.001–0.004	0.009–0.006	0.01	1.93
0.002–0.008	0.048–0.042	0.05	1.18

0.001–0.004 mol L⁻¹ in the absence of the inert salt (Table 1). Only when the ionic strength was set to $I = 0.05 \text{ mol L}^{-1}$ by the addition of NaBF_4 did the second-order rate constant decrease to 50% of the value observed in the absence of an inert salt (Table 1). Since all reactions studied in this investigation were carried out at $I < 0.01 \text{ mol L}^{-1}$, we did not enforce constant ionic strength by adding inert salts.

To examine the influence of the cosolvents (trifluoroethanol or acetonitrile) on the rate constants in water, we have studied the reactivity of OH^- in water/acetonitrile mixtures of different composition. As shown in Figure 2, the second-order rate constant for the reaction of hydroxide with $(\text{lil})_2\text{CH}^+$ decreases from 2.16 to 1.03 L mol⁻¹ s⁻¹ when the acetonitrile content in water is increased from 0.4% to 50%. A dramatic enhancement of reactivity is observed when the acetonitrile content exceeds 75% (v/v) (11.2 L mol⁻¹ s⁻¹ for 15/85 (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{CN}$). An analogous solvent dependence has been reported for the reaction of malachite green with hydroxide ion¹⁹ and for the hydroxide-induced hydrolysis of *p*-nitrophenyl acetate in acetonitrile/water mixtures.²⁰ The small curvature of the graph in the water-rich section on the left of Figure 2 suggests an insignificant difference of reactivity in water and in 99.6/0.4 (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{CN}$. In accord with this interpretation, the rate constants measured for the reactions of benzhydrylium ions with semicarbazide, sulfite, hydroxylamine, or thiolatoacetate in aqueous solutions containing 0.4% of acetonitrile agreed with those determined in aqueous

solutions containing 0.4% TFE within a standard deviation of 3% (Table 2). For that reason, the presence of 0.4% of cosolvents in water will be neglected in the following discussion.

In the reactions of benzhydrylium ions with *n*-propylamine, hydrogen peroxide anion, or 2,2,2-trifluoroethoxide in water, competition of hydroxide with these nucleophiles has to be considered. As explicitly described for the reaction of $(\text{lil})_2\text{CH}^+$ with *n*-propylamine in water (Table 3), the pseudo-first-order rate constant reflects the reaction of the carbocation with *n*-propylamine and with OH^- (eq 3).

$$k_{1\Psi} = k_{2,\text{OH}^-}[\text{OH}^-] + k_{2,n\text{-PrNH}_2}[n\text{-PrNH}_2]_{\text{eff}} \quad (3)$$

Since the concentrations of *n*-propylamine and hydroxide ion can be calculated from the known $\text{p}K_{\text{a}}$ values^{21a} and the second-order rate constant for the reaction with OH^- has independently been determined in this work, one can easily derive the contribution of $k_{2,n\text{-PrNH}_2}$ to the observed pseudo-first-order rate constant. Table 3 shows that the corrections due to the contribution of OH^- are marginal (<2%), and $k_{2,n\text{-PrNH}_2}$ can again be derived from a plot of $k_{1\Psi,n\text{-PrNH}_2}$ vs $[n\text{-PrNH}_2]_{\text{eff}}$ (see Supporting Information, pp S49–S54).

Analogously, the observed pseudo-first-order rate constants for the reactions of benzhydrylium ions with trifluoroethoxide ($\text{p}K_{\text{a}} = 12.4$)³ and the anion of hydrogen peroxide ($\text{p}K_{\text{a}} = 11.8$)^{21b} are only slightly affected by the competing reaction with hydroxide. In accord with this interpretation, the reaction of $(\text{dma})_2\text{CH}^+\text{BF}_4^-$ with 99.6/0.4 (v/v) $\text{H}_2\text{O}/\text{TFE}$ in the presence of OH^- gave preferentially the trifluoroethyl ether.

In several cases, the equilibrium constant for product formation was relatively small, and the carbocation absorbance remained constant or only partially disappeared upon addition of the nucleophile. Thus, the reaction of $(\text{lil})_2\text{CH}^+$ with semicarbazide required a relatively large concentration of semicarbazide ($1.4 \times 10^{-3} \text{ mol L}^{-1}$) to achieve 90% of conversion (Supporting Information, p S35).

When $(\text{lil})_2\text{CH}^+$ or $(\text{jul})_2\text{CH}^+$ were combined with N_3^- in water,²² the carbocation absorbances decreased by less than 5%. The reactions of $(\text{thq})_2\text{CH}^+$ and $(\text{dma})_2\text{CH}^+$ with N_3^- were also incomplete in water,²³ but they proceeded so fast that we were not able to determine the rate constants. Only for the reaction of $(\text{lil})_2\text{CH}^+$ with N_3^- in DMSO, which proceeded with 65% conversion at $[\text{N}_3^-]_0 = 2.6 \times 10^{-5} \text{ mol L}^{-1}$, the combination rate constant could be determined (Table 2).

In previous work by McClelland and co-workers,^{24a,b} it has been shown that the first-order decay of benzhydrylium ions in acetonitrile/water mixtures increases with $[\text{H}_2\text{O}]$ at low water concentrations but remained almost constant for mixtures containing more than 20% water. In agreement with this report, we have found the pseudo-first-order rate constants for the consumption of $(\text{mfa})_2\text{CH}^+$ to increase by less than 16% when the solvent mixture was changed from 91/9 to 50/50 (v/v) $\text{H}_2\text{O}/$

(21) (a) Evans, A. G.; Hamann, S. D. *Trans. Faraday Soc.* **1951**, *47*, 34–40. (b) Evans, M. G.; Uri, N. *Trans. Faraday Soc.* **1949**, *45*, 224–230.

(22) (a) $[(\text{lil})_2\text{CH}^+]_0 = 1.5 \times 10^{-5} \text{ mol L}^{-1}$; $[\text{N}_3^-]_0 = (1-4) \times 10^{-3} \text{ mol L}^{-1}$. (b) $[(\text{jul})_2\text{CH}^+]_0 = 2.2 \times 10^{-5} \text{ mol L}^{-1}$; $[\text{N}_3^-]_0 = (0.4-1.4) \times 10^{-3} \text{ mol L}^{-1}$.

(23) (a) $[(\text{thq})_2\text{CH}^+]_0 = 1.2 \times 10^{-5} \text{ mol L}^{-1}$; $[\text{N}_3^-]_0 = (1-4) \times 10^{-3} \text{ mol L}^{-1}$. (b) $[(\text{dma})_2\text{CH}^+]_0 = 1.4 \times 10^{-5} \text{ mol L}^{-1}$; $[\text{N}_3^-]_0 = (0.4-1.4) \times 10^{-3} \text{ mol L}^{-1}$.

(24) (a) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. J. *Am. Chem. Soc.* **1989**, *111*, 3966–3972. (b) Pham, T. V.; McClelland, R. A. *Can. J. Chem.* **2001**, *79*, 1887–1897. (c) Minegishi, S.; Mayr, H. Unpublished results.

(19) Bunton, C. A.; Huang, S. K.; Paik, C. H. *Tetrahedron Lett.* **1976**, *18*, 1445–1448.

(20) Um, I.; Lee, G. J.; Yoon, H. W.; Kwon, D. S. *Tetrahedron Lett.* **1992**, *33*, 2023–2026.

Table 2. Kinetics of the Reactions of *n*-Nucleophiles with Benzhydrylium Tetrafluoroborates at 20 °C

nucleophile	electrophile	k_2 , L mol ⁻¹ s ⁻¹	solvent ^a	nucleophile	electrophile	k_2 , L mol ⁻¹ s ⁻¹	solvent ^a			
H ₂ O	(thq) ₂ CH ⁺	2.20×10^{-3} ^b	99.6/0.4 W/AN	<i>n</i> -PrNH ₂	(lil) ₂ CH ⁺	7.89×10^1	99.6/0.4 W/AN			
	(pyr) ₂ CH ⁺	5.57×10^{-3} ^b	99.6/0.4 W/AN		(ind) ₂ CH ⁺	3.07×10^2	99.6/0.4 W/AN			
	(dma) ₂ CH ⁺	2.6×10^{-2} ^{b,c}	W		(pyr) ₂ CH ⁺	1.23×10^3	99.6/0.4 W/AN			
	(mor) ₂ CH ⁺	3.31×10^{-1} ^b	50/50 W/AN		(dma) ₂ CH ⁺	3.12×10^3	99.6/0.4 W/AN			
	(mfa) ₂ CH ⁺	3.78 ^b	50/50 W/AN		(mor) ₂ CH ⁺	2.44×10^4 ^d	91/9 W/AN			
	(ani) ₂ CH ⁺	1.3×10^5 ^{b,c}	67/33 W/AN		(pfa) ₂ CH ⁺	1.87×10^5 ^d	91/9 W/AN			
	ani(tol)CH ⁺	9.1×10^5 ^{b,c}	67/33 W/AN		H ₂ NCH ₂ CO ₂ Et	(lil) ₂ CH ⁺	7.78×10^2	DMSO		
	ani(Ph)CH ⁺	2.1×10^6 ^{b,c}	67/33 W/AN			(jul) ₂ CH ⁺	2.05×10^3	DMSO		
	(tol) ₂ CH ⁺	3.2×10^7 ^{b,c}	67/33 W/AN			(ind) ₂ CH ⁺	3.99×10^3	DMSO		
	OH ⁻	(lil) ₂ CH ⁺	2.16			99.6/0.4 W/AN	(thq) ₂ CH ⁺	1.33×10^4	DMSO	
		1.90	95/5 W/AN	(dma) ₂ CH ⁺		8.43×10^4	DMSO			
		1.65	91/9 W/AN	(lil) ₂ CH ⁺		9.43×10^2	99.6/0.4 W/AN			
		1.05	80/20 W/AN	(ind) ₂ CH ⁺		4.22×10^3	99.6/0.4 W/AN			
		1.03	50/50 W/AN	(dma) ₂ CH ⁺		4.31×10^4	99.6/0.4 W/AN			
		2.81	25/75 W/AN	<i>n</i> -PrNH ₂		(lil) ₂ CH ⁺	3.93×10^3	DMSO		
		1.12×10^1	15/85 W/AN			(jul) ₂ CH ⁺	1.12×10^4	DMSO		
(jul) ₂ CH ⁺		3.44	99.6/0.4 W/AN		(ind) ₂ CH ⁺	2.06×10^4	DMSO			
(ind) ₂ CH ⁺		1.08×10^1	99.6/0.4 W/AN		(thq) ₂ CH ⁺	6.61×10^4	DMSO			
		8.56	50/50 W/AN		SO ₃ ²⁻	(lil) ₂ CH ⁺	7.72×10^3	99.6/0.4 W/TFE		
(pyr) ₂ CH ⁺	4.85×10^1	99.6/0.4 W/AN	(jul) ₂ CH ⁺			7.50×10^3	99.6/0.4 W/AN			
(dma) ₂ CH ⁺	1.31×10^2	99.6/0.4 W/AN	(ind) ₂ CH ⁺			1.20×10^4	99.6/0.4 W/TFE			
	9.83×10^1	50/50 W/AN	(thq) ₂ CH ⁺			3.83×10^4	99.6/0.4 W/TFE			
(mor) ₂ CH ⁺	1.06×10^3	50/50 W/AN	(pyr) ₂ CH ⁺			7.06×10^4	99.6/0.4 W/TFE			
(mfa) ₂ CH ⁺	6.67×10^3	50/50 W/AN	(pyr) ₂ CH ⁺			1.50×10^5	99.6/0.4 W/TFE			
H ₂ NNHCONH ₂	(lil) ₂ CH ⁺	3.32	99.6/0.4 W/TFE	morpholine		(lil) ₂ CH ⁺	4.62×10^4	DMSO		
	(thq) ₂ CH ⁺	2.86×10^1	99.6/0.4 W/TFE			(jul) ₂ CH ⁺	1.17×10^5	DMSO		
	(pyr) ₂ CH ⁺	5.56×10^1	99.6/0.4 W/TFE			(ind) ₂ CH ⁺	3.23×10^5	DMSO		
	(dma) ₂ CH ⁺	1.20×10^2	99.6/0.4 W/TFE			(thq) ₂ CH ⁺	7.94×10^5	DMSO		
		1.20×10^2	99.6/0.4 W/AN		piperidine	(lil) ₂ CH ⁺	1.13×10^5	DMSO		
	HONH ₂	(lil) ₂ CH ⁺	6.59			99.6/0.4 W/TFE	(jul) ₂ CH ⁺	3.19×10^5	DMSO	
			6.37			99.6/0.4 W/AN	(ind) ₂ CH ⁺	6.67×10^5	DMSO	
		(jul) ₂ CH ⁺	9.58			99.6/0.4 W/TFE	(thq) ₂ CH ⁺	2.51×10^6	DMSO	
		(ind) ₂ CH ⁺	2.94×10^1			99.6/0.4 W/TFE	-SCH ₂ CO ₂ ⁻	(lil) ₂ CH ⁺	2.88×10^5	99.6/0.4 W/TFE
		(pyr) ₂ CH ⁺	1.24×10^2			99.6/0.4 W/TFE		(jul) ₂ CH ⁺	3.09×10^5	99.6/0.4 W/AN
(dma) ₂ CH ⁺		2.52×10^2	99.6/0.4 W/TFE	(ind) ₂ CH ⁺		3.87×10^5		99.6/0.4 W/TFE		
(mor) ₂ CH ⁺		2.26×10^1	DMSO	(thq) ₂ CH ⁺		9.67×10^5		99.6/0.4 W/TFE		
(ind) ₂ CH ⁺		1.44×10^2	DMSO	N ₃ ⁻		(lil) ₂ CH ⁺		1.61×10^6	99.6/0.4 W/TFE	
(dma) ₂ CH ⁺		3.09×10^3	DMSO			(lil) ₂ CH ⁺		1.68×10^6	DMSO	
(mor) ₂ CH ⁺		1.65×10^4	DMSO		(jul) ₂ CH ⁺	$>2 \times 10^6$		DMSO		
CF ₃ CH ₂ NH ₂	(lil) ₂ CH ⁺	3.79×10^1	99.6/0.4 W/TFE							
	(jul) ₂ CH ⁺	7.06×10^1	99.6/0.4 W/TFE							
	(thq) ₂ CH ⁺	4.35×10^2	99.6/0.4 W/TFE							
	(dma) ₂ CH ⁺	2.14×10^3	99.6/0.4 W/TFE							

^a Mixtures of solvents are given as ratios (v/v). Solvents: W = water, AN = acetonitrile, TFE = trifluoroethanol. ^b Unit is s⁻¹. ^c Counterion is 4-cyanophenolate or acetate.^{24a} ^d These experiments have been performed during late stages of this investigation. For that reason, they are not considered in Tables S1, S2, and S3.

Table 3. Competing Reaction of *n*-Propylamine and OH⁻ with (lil)₂CH⁺ (7.39×10^{-6} mol L⁻¹) in Water at 20 °C

[<i>n</i> -PrNH ₂] ₀ , mol L ⁻¹	$k_{1\text{pr}}$, s ⁻¹	[OH ⁻] _{eff} , ^a mol L ⁻¹	[<i>n</i> -PrNH ₂] _{eff} , mol L ⁻¹	$k_{2,\text{OH}}[\text{OH}^-]_{\text{eff}}$, s ⁻¹	$k_{2,\text{n-PrNH}_2}[\text{n-PrNH}_2]_{\text{eff}}$, s ⁻¹
1.29×10^{-3}	5.63×10^{-2}	5.96×10^{-4}	6.93×10^{-4}	1.30×10^{-3}	5.50×10^{-2}
2.15×10^{-3}	1.05×10^{-1}	8.24×10^{-4}	1.32×10^{-3}	1.78×10^{-3}	1.03×10^{-1}
3.01×10^{-3}	1.59×10^{-1}	1.01×10^{-3}	2.00×10^{-3}	2.19×10^{-3}	1.57×10^{-1}
4.30×10^{-3}	2.39×10^{-1}	1.25×10^{-3}	3.05×10^{-3}	2.70×10^{-3}	2.36×10^{-1}
5.16×10^{-3}	3.02×10^{-1}	1.39×10^{-3}	3.77×10^{-3}	3.01×10^{-3}	2.99×10^{-1}

^a Calculated from $\text{p}K_{\text{a}}(\text{n-PrNH}_3^+) = 10.7$; ref 21a.

CH₃CN.^{24c} For that reason, the first-order rate constants for the reactions with water in Table 2 referring to different water/acetonitrile mixtures can directly be compared with each other.

Discussion

Figure 3 shows that the rate constants of the reactions of *n*-nucleophiles with benzhydrylium ions correlate linearly with the electrophilicity parameters *E*, which have been derived from the reactions of these benzhydrylium ions with a set of π -nucleophiles.⁸

It was, therefore, possible to derive *N* and *s* parameters for *n*-nucleophiles from the rate constants given in Table 2 and the

previously published *E* parameters (Scheme 1) by linear regressions on the basis of eq 2 (Table 4).

The small value of the standard deviation (factor 1.14) between experimental rate constants and those calculated by eq 2 from *E* (Scheme 1)⁸ and the *N* and *s* values given in Table 4 corroborates the suitability of the previously published electrophilicity parameters *E*⁸ for describing reactions with *n*-nucleophiles. Comparisons between calculated and experimental rate constants can be found in Table S1 of the Supporting Information.

Table 4 shows that, with the exception of water (*s* = 0.89) and 2-thiolatoacetate in water (*s* = 0.43), all nucleophiles

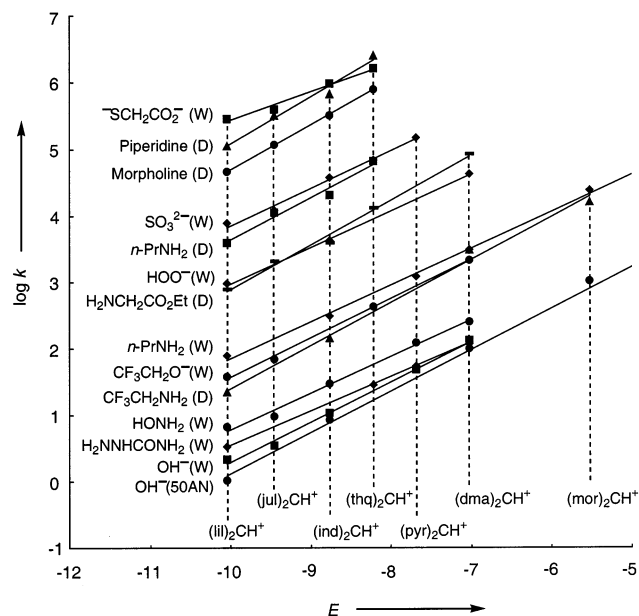


Figure 3. Correlation of the rate constants (20 °C) for the reactions of *n*-nucleophiles with benzhydrylium ions (Ar_2CH^+) toward the electrophilicity parameters E . Solvents: W = water, D = dimethyl sulfoxide, 50AN = 50/50 (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{CN}$. Data from Table 2.

Table 4. Nucleophilicity (N) and Slope (s) Parameters for 15 Ritchie-type Nucleophile Solvent Systems

nucleophile (solvent)	N	s
H_2O (water)	5.11 ^a	0.89 ^a
OH^- (50AN) ^b	10.19	0.62
OH^- (water)	10.47	0.61
$\text{H}_2\text{NNHCONH}_2$ (water)	11.05	0.52
HONH_2 (water)	11.41	0.55
$\text{CF}_3\text{CH}_2\text{NH}_2$ (DMSO)	12.15	0.65
$\text{CF}_3\text{CH}_2\text{O}^-$ (water)	12.66	0.59
<i>n</i> -PrNH ₂ (water)	13.33 ^c	0.56 ^c
$\text{H}_2\text{NCH}_2\text{CO}_2\text{Et}$ (DMSO)	14.30	0.67
HOO^- (water)	15.40	0.55
<i>n</i> -PrNH ₂ (DMSO)	15.70	0.64
SO_3^{2-} (water)	16.83	0.56
morpholine (DMSO)	16.96	0.67
piperidine (DMSO)	17.19	0.71
$\text{SCH}_2\text{CO}_2^-$ (water)	22.62	0.43

^a From first-order rate constants; correlation not shown in Figure 3. ^b 50/50 (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{CN}$. ^c These numbers have been corrected after performing the correlation analysis. For the calculations in Tables S1 and S3, $N = 13.57$ and $s = 0.53$ were used, which have been derived from the rate constants in Table 2 without the rate constants for *n*-PrNH₂ + (mor)₂CH⁺ and (mf)₂CH⁺.

investigated in this work have slope parameters of $0.52 < s < 0.71$, indicating that most carbocation nucleophile combinations follow almost constant selectivity relationships: For constant values of s , eq 2 transforms into eq 1/1a. The exceptionally high value of s for water given in Table 4 is consistent with Ritchie's report that in reactions of tritylium ions the ratio $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$ decreases as the electrophilicities of the tritylium ions increase.³

The narrow range that embraces most s parameters in Table 4 suggests evaluating the rate constants of Table 2 by the Ritchie equation (eq 1/1a, Figure 4). When water with the different s parameter is excluded, the standard deviation between calculated (eq 1) and experimental rate constants is somewhat larger (factor 1.20) than that obtained by employing eq 2 (factor 1.14), despite the fact that the linear regression according to eq 2 uses the

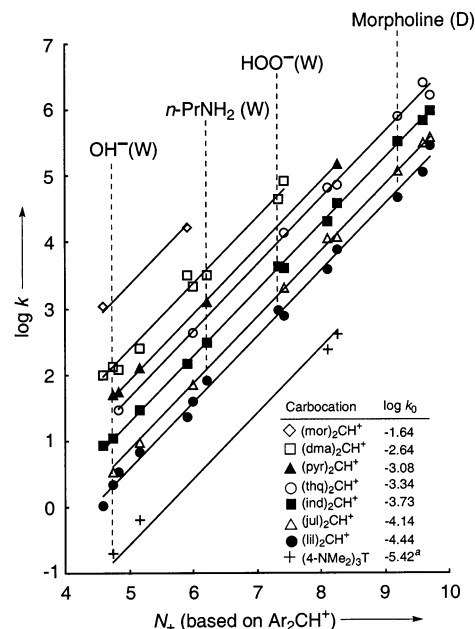


Figure 4. Analysis of the rate constants for the reactions of benzhydrylium ions with *n*-nucleophiles in water (W) or dimethyl sulfoxide (D) according to the Ritchie formalism (eq 1/1a) compared with crystal violet (4-NMe₂)₃T. ^a Data for (4-NMe₂)₃T from ref 3 and Table S3; all other data from Table 2.

Table 5. Comparison of N_+ Values for *n*-Nucleophiles with Respect to Different Series of Electrophiles

nucleophile (solvent)	Ar_2CH^+ ^a	Ar_3C^+ ^b	Pyronin-Y ^c	Ar-Trop ^d
OH^- (water)	=4.75 (5)	=4.75	=4.75	=4.75
OH^- (50AN) ^e	4.60 (4)			
$\text{H}_2\text{NNHCONH}_2$ (water)	4.83 (4)	3.73		3.42
HONH_2 (water)	5.16 (5)	5.05		3.82
$\text{CF}_3\text{CH}_2\text{NH}_2$ (DMSO)	5.92 (4)	4.86	4.70	
$\text{CF}_3\text{CH}_2\text{O}^-$ (water)	5.99 (4)	5.06		5.66
<i>n</i> -PrNH ₂ (water)	6.22 (4)			
HOO^- (water)	7.35 (3)	8.52	7.33	7.20
$\text{H}_2\text{NCH}_2\text{CO}_2\text{Et}$ (DMSO)	7.43 (5)	6.54		
<i>n</i> -PrNH ₂ (DMSO)	8.11 (4)	7.88	8.40	
SO_3^{2-} (water)	8.26 (5)	8.01	7.91	7.50
morpholine (DMSO)	9.20 (4)		9.17	
piperidine (DMSO)	9.61 (4)		9.32	
$\text{SCH}_2\text{CO}_2^-$ (water)	9.72 (4)	9.09		

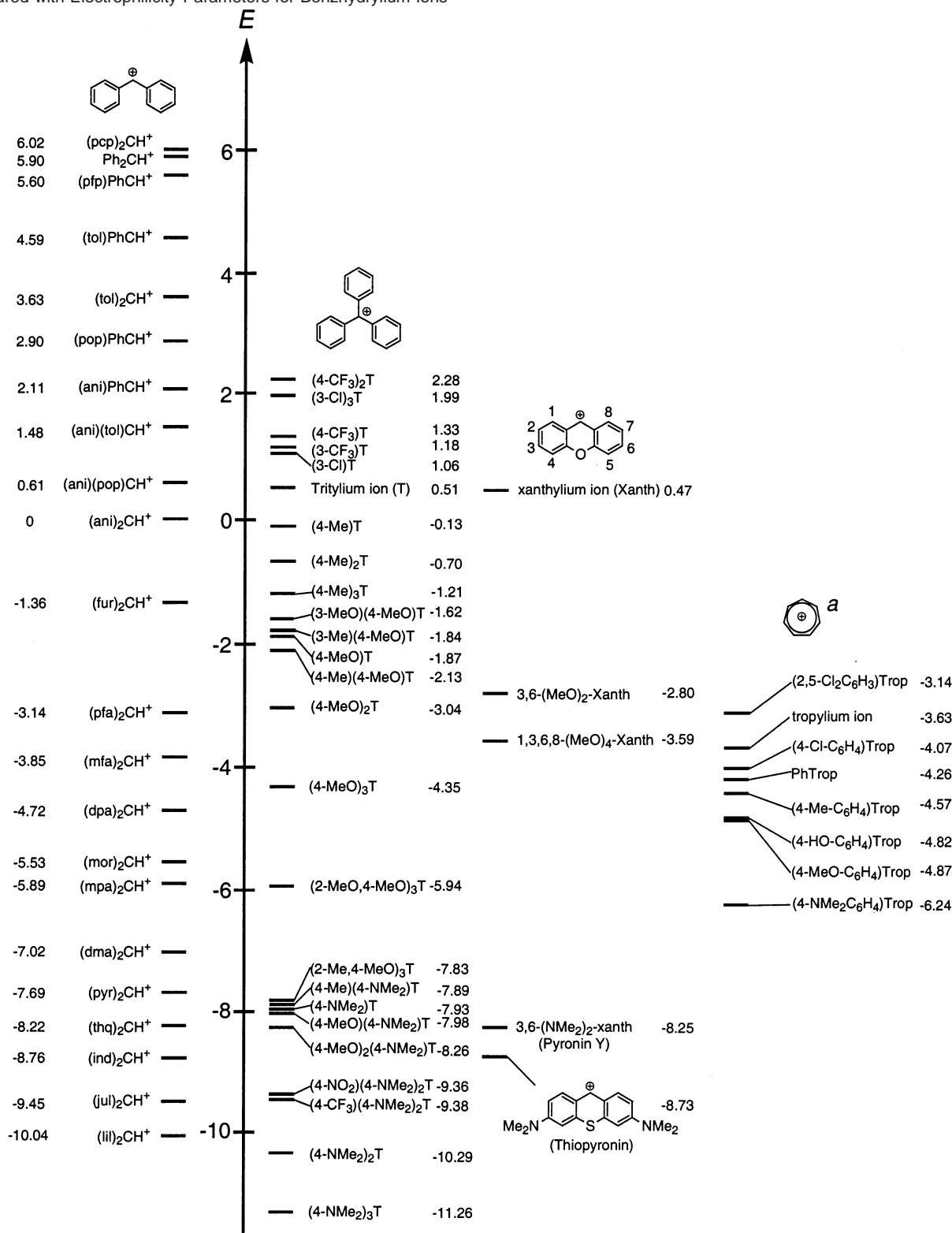
^a This work; least-squares fit; number of reactions given in parentheses. ^b From ref 3, relative reactivities toward malachite green. ^c From ref 3. ^d From ref 3, relative reactivities toward the *p*-(dimethylamino)phenyltropylium ion. ^e Solvent mixture, 50/50 (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{CN}$.

fixed E parameters from ref 8, while the $\log k_0$ parameters in eq 1 are fully optimized for the data of this investigation. Table S2 in the Supporting Information gives an explicit comparison of the experimental rate constants with those calculated from $\log k_0$ (Figure 4) and N_+ (Table 5) by the Ritchie eq 1/1a.

As expected, the N_+ values thus derived from the reactions of the *n*-nucleophiles with benzhydrylium ions differ only slightly from those reported by Ritchie (Table 5). Since the different N_+ values given in Ritchie's 1986 paper³ for reactions with tritylium ions, tropylium ions, and pyronines are not based on rate constants for series of reactions but refer to only a single electrophile of each class, we will not attempt an interpretation of the differences of N_+ from different sources.

Evaluation of the kinetic data in Table 2 by the Ritchie equation eq 1/1a also provides $\log k_0$ values for benzhydrylium ions (Figure 4), which allow us to compare the benzhydrylium

Scheme 2. Electrophilicity Parameters E (according to Eq 2) for Ritchie's Electrophiles from Reactions with n -Nucleophiles (at $I < 0.1$) Compared with Electrophilicity Parameters for Benzhydrylium Ions^b



^a For further tropylium ions, see Table S3 (Supporting Information). ^b The E parameters for tritylium ions given in this scheme must not be used for predicting reactivities toward π -systems (see the text).

ions studied in this work with those electrophiles previously investigated by Ritchie (Table S2).

However, because of the much wider applicability of eq 2 compared to eq 1 (in contrast to eq 1, eq 2 also holds for reactions with π -systems), it is more advantageous not to employ

$\log k_0$ (Figure 4) but to use the electrophilicity parameters E as defined by eq 2 for comparing electrophiles of different type. Therefore, the previously reported rate constants for the reactions of tritylium, tropylium, and xanthylium ions with the 15 nucleophile systems characterized in this work (Table 4) were

Table 6. Comparison between Calculated and Experimental Rate Constants for the Reactions of Tritylium Ions with Hydride Donors

electrophile (<i>E</i>) ^a	nucleophile (<i>N</i> , <i>s</i>) ^b	<i>k</i> _{calc} (20 °C), ^c L mol ⁻¹ s ⁻¹	<i>k</i> _{exp} , L mol ⁻¹ s ⁻¹
(4-MeO) ₃ T (-4.35)	cycloheptatriene (0.52, 0.97)	1.9 × 10 ⁻⁴	1.6 × 10 ^{-3 d} (80 °C, CH ₃ CN)
(4-MeO) ₂ T (-3.04)	cycloheptatriene (0.52, 0.97)	3.6 × 10 ⁻³	1.1 × 10 ^{-3 d} (23 °C, CH ₃ CN)
(4-MeO)T (-1.87)	cycloheptatriene (0.52, 0.97)	4.9 × 10 ⁻²	2.0 × 10 ^{-2 d} (23 °C, CH ₃ CN)
(4-Me) ₃ T (-1.21)	cycloheptatriene (0.52, 0.97)	2.1 × 10 ⁻¹	2.7 × 10 ^{-2 d} (23 °C, CH ₃ CN)
T (0.51)	1,4-cyclohexadiene (0.09, 0.98)	3.9	3.2 × 10 ^{-1 e} (20 °C, CH ₂ Cl ₂)
	1,4-dihydronaphthalene (-0.07, 1.03)	2.8	8.2 × 10 ^{-2 e} (20 °C, CH ₂ Cl ₂)
	9,10-dihydroanthracene (-0.86, 0.92)	4.8 × 10 ⁻¹	1.4 × 10 ^{-2 e} (20 °C, CH ₂ Cl ₂)
	cycloheptatriene (0.52, 0.97)	1.0 × 10 ¹	1.8 ^f (20 °C, CH ₂ Cl ₂)
	HSiEt ₃ (3.64, 0.65)	5.0 × 10 ²	1.2 × 10 ^{2 g} (20 °C, CH ₂ Cl ₂)
	HSiMe ₂ Ph (3.27, 0.73)	5.7 × 10 ²	2.1 × 10 ^{2 g} (25 °C, CH ₂ Cl ₂)
	HSiBu ₃ (4.45, 0.64)	1.5 × 10 ³	2.4 × 10 ^{2 g} (20 °C, CH ₂ Cl ₂)
(3-Cl)T (1.06)	1,4-cyclohexadiene (0.09, 0.98)	1.3 × 10 ¹	2.3 ^f (20 °C, CH ₂ Cl ₂)
(3-Cl) ₃ T (1.99)	1,4-cyclohexadiene (0.09, 0.98)	1.1 × 10 ²	5.4 × 10 ^{1 e} (20 °C, CH ₂ Cl ₂)
	H ₃ SiPh (0.25, 0.67)	3.2 × 10 ¹	4.6 ^f (20 °C, CH ₂ Cl ₂)

^a From Scheme 2. ^b From ref 8 or 12. ^c Calculated according to eq 2. ^d From ref 25. ^e From ref 26. ^f From ref 27. ^g From ref 28; for HSiEt₃: $\Delta H^\ddagger = 29.3$ kJ mol⁻¹, $\Delta S^\ddagger = -105$ J K⁻¹ mol⁻¹; for HSiBu₃: $\Delta H^\ddagger = 26.4$ kJ mol⁻¹, $\Delta S^\ddagger = -109$ J K⁻¹ mol⁻¹.

subjected to a correlation analysis on the basis of eq 2. When calculating the *E* parameters of these electrophiles by a least squares minimization of the deviations between observed and calculated rate constants (Table S3), the *N* and *s* values of Table 4, which were derived from reactions with reference electrophiles, were kept as fixed parameters. In Scheme 2 only those *E* parameters are listed that could be derived from kinetics at an ionic strength of *I* < 0.1.

Though calculated and experimental rate constants for reactions with tropylium ions often differ by 1 order of magnitude (Table S3), the *E* parameter derived for the parent tropylium ion from reactions with *n*-nucleophiles (-3.63, Scheme 2) differs only slightly from that derived from the reactions of this electrophile with the reference π -nucleophiles (-3.72).⁸ One can, therefore, expect that all *E* parameters for tropylium ions given in Scheme 2 can be used for calculating reactivities of these electrophiles toward all types of nucleophiles, i.e., also for reactions with alkenes, arenes, or hydrides.

The applicability of the *E* parameters of tritylium ions is more limited, however, since the sensitivity of bulky reagents toward variation of the steric requirements of the reaction partner will be large. Because our approach, like Ritchie's, does not explicitly treat steric effects, we have recommended that reactions of bulky reagents should not be treated with eq 2.^{5,8} The satisfactory agreement between calculated (eq 2) and experimental rate constants in Table S3 indicates, however, that reactivities of tritylium ions toward *n*-nucleophiles can generally be reproduced by eq 2, in accord with Ritchie's previous work.

When the *E* parameters of tritylium ions given in Scheme 2 are used to calculate rate constants of hydride abstractions, however, *k*_{calc} is usually somewhat larger than *k*_{obs}, indicating that the transition states of hydride transfer reactions have higher steric requirements than the reactions of carbocations with *n*-nucleophiles (Table 6). This result is surprising in view of the almost linear C-H-X arrangement in the corresponding transition states.²⁹ However, since the deviation between *k*_{calc} and *k*_{obs} in Table 6 rarely exceeds 1 order of magnitude, it is possible to combine all *E* parameters presented in Scheme 2

Table 7. Approximate Nucleophilicity Parameters *N* and *s* of Nucleophiles from Reactions with Ritchie's Electrophiles (Scheme 2)^a

nucleophile (solvent)	<i>N</i>	<i>s</i>
MeOH (methanol)	6.02 ^b	1.01 ^b
CF ₃ CH ₂ NH ₂ (water)	8.70	0.68
CN ⁻ (water)	9.19	0.60
NH ₃ (water)	9.26	0.66
CH ₃ ONH ₂ (water)	9.81	0.63
H ₂ NCH ₂ CONHCH ₂ CO ₂ ⁻ (water)	10.28	0.77
H ₂ NCH ₂ CO ₂ Et (water)	10.28	0.70
NCCH ₂ CH ₂ NH ₂ (water)	10.33	0.63
H ₂ NCH ₂ CH ₂ NH ₂ (water)	10.37	0.82
PhNHNH ₂ (water)	10.83	0.64
BH ₃ CN ⁻ (water)	11.02	0.59
H ₂ NCH ₂ CO ₂ ⁻ (water)	11.15	0.74
<i>n</i> -BuNH ₂ (water)	11.69	0.65
MeOCH ₂ CH ₂ NH ₂ (water)	11.81	0.57
BH ₄ ⁻ (water)	12.23	0.78
EtNH ₂ (water)	12.24	0.61
H ₂ NNH ₂ (water)	12.45	0.61
<i>N</i> -benzylidihydronicotinamide (water)	12.48	0.66
Me ₃ N ⁺ CH ₂ CH ₂ O ⁻ (water)	12.66	0.56
HC≡CCH ₂ O ⁻ (water)	12.77	0.57
CH ₃ O ⁻ (methanol)	13.59	0.90
HOCH ₂ CH ₂ S ⁻ (water)	15.62	0.78
MeO ₂ CCH ₂ CH ₂ S ⁻ (water)	15.82	0.81

^a The *N* and *s* parameters listed here are those from Table S5 and refer to correlations covering at least 3 orders of magnitude in rate constants. These *N* and *s* parameters are less accurate than those in Table 4 because of the indirect evaluation. ^b Based on first-order rate constants.

with the *N* and *s* parameters of hydride donors^{8,12} for estimating the rates of hydride transfer reactions.

As expected, the reactions of π -nucleophiles with tritylium ions are considerably slower than predicted by eq 2 (Table S4). For the reactions of tritylium ions with 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (*N* = 9.00, *s* = 0.98),⁸ the rate constants calculated by eq 2 are 4–6 orders of magnitude higher than experimentally observed by Fukuzumi.³⁰ Since the large steric demand of both reagents enforces a reaction at the *p*-position of a phenyl group at tritylium, the steric effect for attack at the tertiary carbenium center is even larger than derived from the ratio *k*_{calc}/*k*_{obs}. Furthermore, Fukuzumi³⁰ reported rate constants for the reactions of 1-ethoxy-1-(triethylsiloxy)ethene and *tert*-butyldimethylsiloxy-1-ethoxyethene that are 2 orders of magnitude smaller than the prediction of eq 2 for reactions of tritylium ions with the less nucleophilic 1-phenoxy-1-

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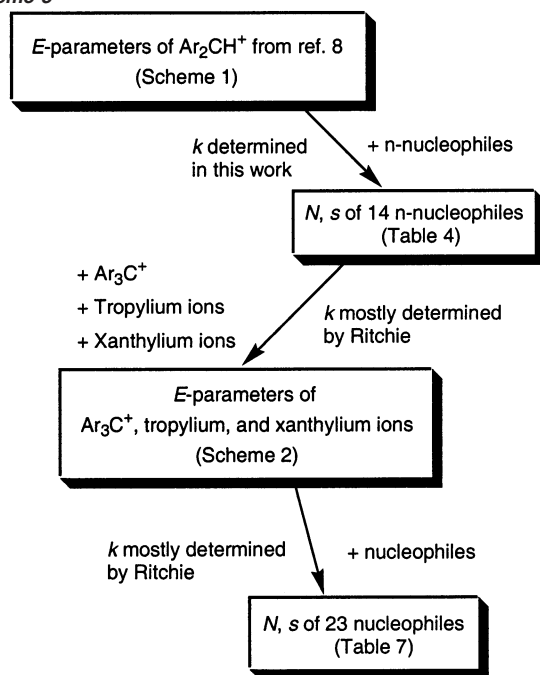
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Scheme 3

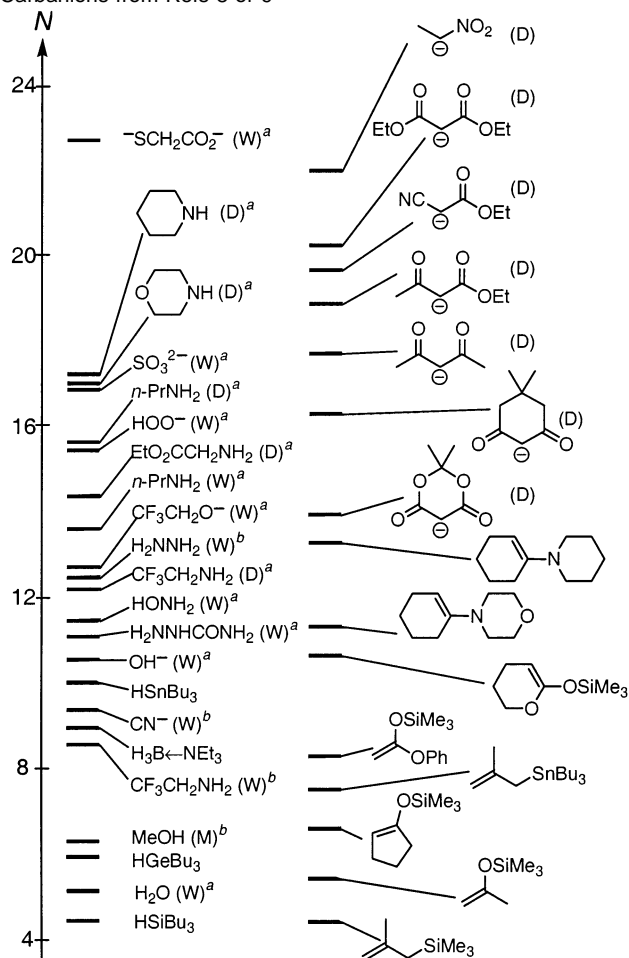


(trimethylsilyloxy)ethene ($N = 8.23$, $s = 0.81$).⁸ These examples demonstrate that reactions of tritylium ions with π -nucleophiles cannot be described by eq 2, and we explicitly advise not using the E parameters of tritylium ions listed in Scheme 2 for calculating reactivities toward π -nucleophiles.

The previously mentioned suitability of the N and s parameters for the n -nucleophiles in Table 4 for calculating their reactivities toward benzhydrylium, tritylium, tropylium, and xanthylum ions indicates that differential steric effects are not important in the reactions of O-, S-, and N-nucleophiles with these carbocations. The nucleophilicity parameters N and s of many additional n -nucleophiles (and hydride donors) can, therefore, be derived from the published rate constants of their reactions with tritylium, tropylium, and xanthylum ions and the corresponding E parameters given in Scheme 2. As shown in Table S5 and the plots in Figure S1 (Supporting Information, pp S18–S19), 33 nucleophiles have been characterized in this way. Because of the uncertainty of slopes for “short” correlation lines, only the N and s parameters of 23 of these nucleophiles for which rate constants over more than three log k units were available, have been listed in Table 7.

Readers not familiar with our recent papers^{7,8,12} may be wondering why the stepwise procedure summarized in Scheme 3 has been used to determine the electrophilicity parameters of Scheme 2 and the nucleophilicity parameters of Table 7 instead of subjecting all available rate constants for the reactions of nucleophiles with carbocations to a single correlation analysis.

As previously discussed in detail,⁸ only the unequal treatment of data from different sources allows us to systematically extend our reactivity scales without the necessity to continuously revise the entire sets of electrophilicity and nucleophilicity parameters. It is thus possible to employ preliminary numbers in some cases, which can be replaced by more reliable data at a later stage without affecting the “established” parameters. This procedure also allows us to define reactivity parameters that can only be used for certain types of reactions (e.g., E parameters of Ar_3C^+ for their reactions with n -nucleophiles and hydride donors),

Scheme 4. Comparison of the Nucleophilic Reactivities of n -Nucleophiles with Typical π -Nucleophiles, Hydride Donors, and Carbanions from Refs 8 or 9^c

^a From Table 4. ^b From Table 7. ^c The solvent was CH_2Cl_2 , unless noted otherwise: H_2O (W), DMSO (D), methanol (M).

which would be impossible if all reactions would be treated equally. Inclusion of reactivity data for more reactive carbocations is in progress.³¹

Conclusion

We have demonstrated that the problem with “constant selectivity relationships” reported by Ritchie in 1986 is predominantly caused by the widely deviating slope parameter s of water. By employing eq 2 instead of eq 1, we can describe all reactions of tritylium, tropylium, and xanthylum ions with n -nucleophiles with a single set of parameters. Since eq 2 has previously been demonstrated to hold for the reactions of carbocations with π - and σ -nucleophiles, it has now become possible to combine kinetic data from different sources and create a nucleophilicity scale that directly compares n -, π -, and σ -nucleophiles (Scheme 4).

Though the data of Table 4 indicate a fair correlation between N and s for n -nucleophiles, the situation becomes more complicated when π -nucleophiles and hydride donors are

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included. It is evident that most π -nucleophiles are characterized by higher values of s than n-nucleophiles, even when compounds of similar N values are compared. As a consequence, more reactive carbocations (harder electrophiles) will show a relative preference for π -nucleophiles over n-nucleophiles compared to less reactive carbocations (softer electrophiles). Since alkoxides and amines are considered as hard bases in contrast to alkenes and arenes (soft bases), we must conclude that the Hard Soft Acid Base Principle³² is not useful for describing our correlations.

According to a recent theoretical analysis,¹³ slope parameters of approximately 0.67, as found for most nucleophiles in this investigation, are indicative of constant intrinsic barriers within a reaction series. A more detailed analysis considering absolute

intrinsic barriers of these reactions^{4b,33} is now needed to reveal the physical background of these correlations.

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Supporting Information Available: Correlation of electrophile–nucleophile reactions, details of the kinetic experiments, and absorption maxima of benzhydryl cations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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