

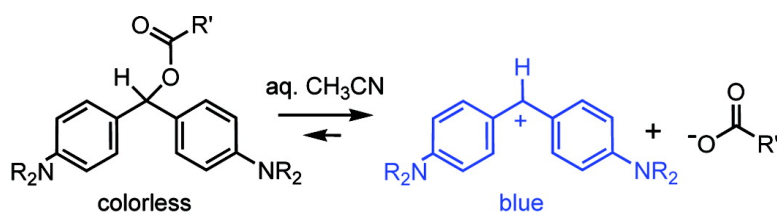
Article

## Direct Observation of the Ionization Step in Solvolysis Reactions: Electrophilicity versus Electrofugality of Carbocations

Heike F. Schaller, Alexander A. Tishkov, Xinliang Feng, and Herbert Mayr

*J. Am. Chem. Soc.*, **2008**, 130 (10), 3012-3022 • DOI: 10.1021/ja0765464

Downloaded from <http://pubs.acs.org> on February 8, 2009



Photometric determination of ionization rates

### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## Direct Observation of the Ionization Step in Solvolysis Reactions: Electrophilicity versus Electrofugality of Carbocations

Heike F. Schaller, Alexander A. Tishkov, Xinliang Feng, and Herbert Mayr\*

Department Chemie und Biochemie, Ludwig-Maximilians-Universität München,  
Butenandtstrasse 5–13 (Haus F), 81377 München, Germany

Received August 30, 2007; E-mail: Herbert.Mayr@cup.uni-muenchen.de

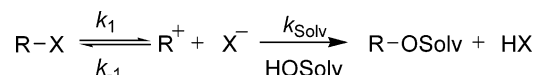
**Abstract:** Rates and equilibria of the reactions of highly stabilized amino-substituted benzhydrylium ions ( $\text{Ar}_2\text{CH}^+$ ) with carboxylate ions have been determined photometrically in acetone and acetonitrile solutions. Treatment of covalent benzhydryl carboxylates ( $\text{Ar}_2\text{CH}-\text{O}_2\text{CR}$ ) with aqueous acetone or acetonitrile leads to the regeneration of the colored amino-substituted benzhydrylium ions  $\text{Ar}_2\text{CH}^+$ , which do not undergo subsequent reactions with the solvent. One can, therefore, directly measure the first step of  $\text{S}_{\text{N}}1$  reactions. The electrofugality order, i.e., the relative ionization rates of benzhydryl esters  $\text{Ar}_2\text{CH}-\text{O}_2\text{CR}$  with the same anionic leaving group, does not correlate with the corresponding electrophilicity order, i.e., the relative reactivities of the corresponding benzhydrylium ions  $\text{Ar}_2\text{CH}^+$  toward a common nucleophile. Thus, benzhydrylium ions which are produced with equal rates by ionization of the corresponding covalent esters may differ by more than 2 orders of magnitude in their reactivities toward nucleophiles, e.g., carboxylate ions. Variable intrinsic barriers account for the breakdown of the rate–equilibrium relationships. Complete free-energy profiles for the ionization of benzhydryl carboxylates  $\text{Ar}_2\text{CH}-\text{O}_2\text{CR}$  are constructed, which demonstrate that the transition states of these ionizations are not carbocation-like. As a consequence, variation of the solvent-ionizing power  $Y$  has only a small effect on the ionization rate constant ( $m = 0.35$  to  $0.55$ ) indicating that small values of  $m$  in the Winstein–Grunwald equation do not necessarily imply an  $\text{S}_{\text{N}}2$  type mechanism.

### Introduction

Kinetic investigations of solvolysis reactions have been a major source for the development of electronic theory of Organic Chemistry.<sup>1</sup> In typical  $\text{S}_{\text{N}}1$  solvolysis reactions (Scheme 1), the carbocation  $\text{R}^+$  is formed as a short-lived intermediate, which undergoes rapid subsequent reactions with the solvent. Therefore, the rate of the ionization step is usually derived from the rate of the gross reaction, which is determined by analyzing the concentrations of the reactants  $\text{RX}$  or of the products  $\text{ROSolV}$  or  $\text{HX}$  as a function of time.

However, as initially pointed out by Winstein,<sup>2</sup> the observed gross rate constant  $k_{\text{obs}}$  often is a complex quantity. Since the  $\text{S}_{\text{N}}1$  reaction (Scheme 1) may be affected by nucleophilic solvent participation or accompanied by  $\text{S}_{\text{N}}2$  processes, there has been much controversy about the mechanism of solvolysis reactions, which is still ongoing.<sup>3,4</sup>

### Scheme 1

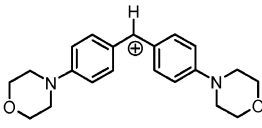
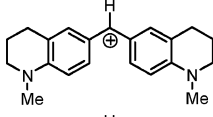
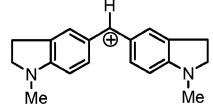
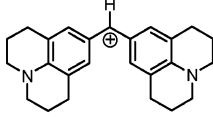
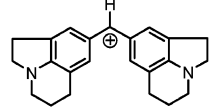


In recent work,<sup>5</sup> we have reported the change from the typical  $\text{S}_{\text{N}}1$  mechanism (Scheme 1,  $k_1 < k_{\text{solV}}$ ) to the so-called  $\text{S}_{\text{N}}2\text{C}^+$

- (1) (a) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962. (b) *Carbonium Ions*, Vol. 1–5; Olah, G. A., Schleyer, P. v. R., Eds.; Interscience: New York, 1968–1976. (c) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969. (d) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (e) *Advances in Carbocation Chemistry*, Vol. 1; Creary, X., Ed.; JAI Press: Greenwich, CT, 1989. (f) *Advances in Carbocation Chemistry*, Vol. 2; Coxon, J. M., Ed.; JAI Press: Greenwich, CT, 1995.
- (2) (a) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Heck, R.; Robinson, G. *C. J. Am. Chem. Soc.* **1956**, *78*, 328–335. (b) For a summary of Winstein's contributions, see: Bartlett, P. D. *J. Am. Chem. Soc.* **1972**, *94*, 2161–2170.

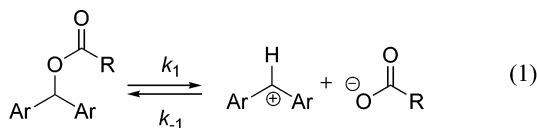
- (3) (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658–7666. (b) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7675. (c) Bentley, T. W.; Garley, M. S. *J. Phys. Org. Chem.* **2006**, *19*, 341–349. (d) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466–5475. (e) Richard, J. P.; Toteva, M. M.; Amyes, T. L. *Org. Lett.* **2001**, *3*, 2225–2228. (f) Tsuji, Y.; Toteva, M. M.; Amyes, T. L.; Richard, J. P. *Org. Lett.* **2004**, *6*, 3633–3636. (g) Gajewski, J. J. *J. Am. Chem. Soc.* **2001**, *123*, 10877–10883. (h) Peters, K. S.; Gasparrini, S.; Heeb, L. R. *J. Am. Chem. Soc.* **2005**, *127*, 13039–13047.
- (4) (a) Snee, R. A. *Acc. Chem. Res.* **1973**, *6*, 46–53. (b) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In *Ions and Ion Pairs in Organic Reactions*, Vol. 2; Szwarc, M., Ed.; Wiley: New York, 1974; pp 247–374. (c) Katritzky, A. R.; Musumarra, G.; Sakizadeh, K.; El-Shafie, S. M. M.; Jovanovic, B. *Tetrahedron Lett.* **1980**, *21*, 2697–2699. (d) Katritzky, A. R.; Brycki, B. *E. Chem. Soc. Rev.* **1990**, *19*, 83–105. (e) Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345–375. (f) Ta-Shma, R.; Rappoport, Z. *Adv. Phys. Org. Chem.* **1992**, *27*, 239–291. (g) Kevill, D. N. In *Advances in Quantitative Structure-Property Relationships*; Charton, M., Ed.; JAI Press: Greenwich, CT, 1996; Vol. 1, pp 81–115. (h) Yoh, S.-D.; Cheong, D.-Y.; Lee, C.-H.; Kim, S.-H.; Park, J.-H.; Fujio, M.; Tsuno, Y. *J. Phys. Org. Chem.* **2001**, *14*, 123–130. (i) Richard, J. P.; Amyes, T. L.; Toteva, M. M.; Tsuji, Y. *Adv. Phys. Org. Chem.* **2004**, *39*, 1–26. (j) Amyes, T. L.; Toteva, M. M.; Richard, J. P. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Maitland, J., Eds.; Wiley: New York, 2004; pp 41–68. (k) Tsuji, Y.; Richard, J. P. *Chem. Record* **2005**, *5*, 94–106. (l) Peters, K. S. *Acc. Chem. Res.* **2007**, *40*, 1–7. (m) Peters, K. S. *Chem. Rev.* **2007**, *107*, 859–873.
- (5) Denegri, B.; Minegishi, S.; Kronja, O.; Mayr, H. *Angew. Chem.* **2004**, *116*, 2353–2356; *Angew. Chem., Int. Ed.* **2004**, *43*, 2302–2305.

**Chart 1.** Benzhydrylium Ions  $\text{Ar}_2\text{CH}^+$  and Their Electrophilicity Parameters  $E^\circ$ 

$\text{Ar}_2\text{CH}^+$	X	Y	$E^\circ$
$(\text{pfa})_2\text{CH}^+$	$\text{N}(\text{Ph})\text{CH}_2\text{CF}_3$	$\text{N}(\text{Ph})\text{CH}_2\text{CF}_3$	-3.14
$(\text{mfa})_2\text{CH}^+$	$\text{N}(\text{CH}_3)\text{CH}_2\text{CF}_3$	$\text{N}(\text{CH}_3)\text{CH}_2\text{CF}_3$	-3.85
$(\text{dpa})_2\text{CH}^+$	$\text{NPh}_2$	$\text{NPh}_2$	-4.72
$(\text{mor})_2\text{CH}^+$			-5.53
$(\text{mpa})_2\text{CH}^+$	$\text{N}(\text{Ph})\text{CH}_3$	$\text{N}(\text{Ph})\text{CH}_3$	-5.89
$(\text{dma})_2\text{CH}^+$	$\text{N}(\text{CH}_3)_2$	$\text{N}(\text{CH}_3)_2$	-7.02
$(\text{pyr})_2\text{CH}^+$	$\text{N}(\text{CH}_2)_4$	$\text{N}(\text{CH}_2)_4$	-7.69
$(\text{thq})_2\text{CH}^+$			-8.22
$(\text{ind})_2\text{CH}^+$			-8.76
$(\text{jul})_2\text{CH}^+$			-9.45
$(\text{lil})_2\text{CH}^+$			-10.04

<sup>a</sup> Electrophilicity parameter as defined by eq 4 (from ref 9).

mechanism<sup>6</sup> (Scheme 1,  $k_1 > k_{\text{solv}}$ ), where ionization is faster than the subsequent reaction with the solvent. In the latter case, the intermediate carbocation  $\text{R}^+$  may accumulate. If the ionization equilibrium  $k_1/(k_{-1}[\text{X}^-])$  is favorable, it becomes possible to investigate the ionization step directly. We will now report on the direct UV-vis spectroscopic observation of the ionization of a series of benzhydryl carboxylates (eq 1) derived from the benzhydrylium ions listed in Chart 1.



In addition, we will report on the direct determination of the rates of the reverse reactions as well as of some of the relevant equilibrium constants. By combining these pieces of information we will arrive at complete free-energy profiles for solvolysis reactions of benzhydryl carboxylates, which allow us to determine the intrinsic barriers<sup>7,8</sup> for ionization processes. It will

- (6) Gelles, E.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1954**, 2918–2929.  
 (7) (a) Richard, J. P.; Amyes, T. L.; Toteva, M. M. *Acc. Chem. Res.* **2001**, *34*, 981–988. (b) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119–238. (c) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9–16. (d) Guthrie, J. P. *ChemPhysChem* **2003**, *4*, 809–816. (e) Guthrie, J. P.; Leandro, L.; Pitchko, V. *Can. J. Chem.* **2005**, *83*, 1654–1666.  
 (8) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301–308.

be shown that, in contrast to intuition and earlier assumptions,<sup>5</sup> there is no significant correlation between the rates of ionization of benzhydryl carboxylates and the electrophilic reactivities of the resulting carbocations.

## Experimental Section

**Materials.** Acetone and acetonitrile were distilled over  $\text{CaSO}_4$  and diphenylketene, respectively. Commercially available tetra-*n*-butylammonium acetate and benzoate (Fluka) were used without further purification. Tetra-*n*-butylammonium *p*-nitrobenzoate and 3,5-dinitrobenzoate were prepared from tetra-*n*-butylammonium hydroxide and the nitro-substituted benzoic acids as described previously.<sup>10</sup> The tetrafluoroborate salts of the benzhydrylium ions listed in Chart 1 were synthesized as reported in ref 9.

**Determination of Equilibrium Constants.** Equilibrium constants were measured by UV-vis spectroscopy in acetonitrile as follows: To solutions of the benzhydrylium tetrafluoroborates in acetonitrile, whose UV-vis maxima are reported in the Supporting Information, small volumes of stock solutions of tetra-*n*-butylammonium carboxylates were added, and the resulting absorbances were monitored. When the absorbance was constant (typically after 5 to 15 s), another portion of stock solution was added. This procedure was repeated four to five times for each benzhydrylium salt solution.

**Determination of the Rates of the Combinations of Benzhydrylium Ions with Carboxylate Ions ( $k_{-1}$  in eq 1).** Reactions of carboxylate ions with the colored benzhydrylium ions gave colorless products. The reactions were followed photometrically at the absorption maxima of  $\text{Ar}_2\text{CH}^+$  by UV-vis spectroscopy using a stopped-flow instrument (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software) in single- or double-mixing mode as described previously.<sup>9,11</sup> All experiments were performed under pseudo-first-order conditions (excess of  $n\text{-Bu}_4\text{N}^+\text{RCO}_2^-$ ) at 25 °C in acetonitrile, acetone, or mixtures of these solvents with water. First-order rate constants  $k_{\text{obs}}$  were obtained by least-squares fitting of the absorbance to the monoexponential function  $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ .

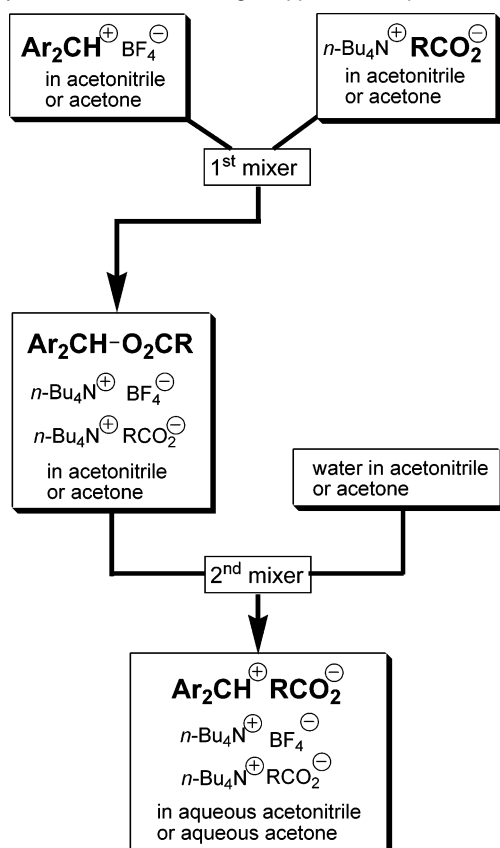
**Determination of Ionization Rates ( $k_1$  in eq 1).** Because benzhydrylium carboxylates  $\text{Ar}_2\text{CH}-\text{O}_2\text{CR}$ , which are derived from highly stabilized benzhydrylium ions, cannot be isolated, the double mixing technique illustrated in Scheme 2 was employed. In the first mixer, a solution of  $\text{Ar}_2\text{CH}^+ \text{BF}_4^-$  in acetonitrile or acetone is combined (stopped-flow instrument Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software in double-mixing mode) with a solution of 1–100 equiv of  $n\text{-Bu}_4\text{N}^+\text{RCO}_2^-$  in the same solvent. The resulting colorless solution is then combined with an equal volume of aqueous acetonitrile or acetone in a second mixer, which provokes the ionization of the pregenerated  $\text{Ar}_2\text{CH}-\text{O}_2\text{CR}$ . The ionizations are followed photometrically at the absorption maxima of  $\text{Ar}_2\text{CH}^+$ .

By this protocol we have rapidly collected a large number of rate constants at different concentrations of  $n\text{-Bu}_4\text{N}^+\text{RCO}_2^-$  in different solvents. The reported ionization rates were obtained as the average from at least three different measurements.

## Results and Discussion

**Equilibrium Constants.** As a preliminary to kinetic studies, we determined the degree of ionization of covalent benzhydryl

- (9) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512.  
 (10) Kirby, J. P.; Roberts, J. A.; Nocera, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 9230–9236.  
 (11) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66–77.  
 (12) Pytela, O.; Kulhanek, J.; Ludwig, M.; Riha, V. *Coll. Czech. Chem. Commun.* **1994**, *59*, 627–638.  
 (13) Chantooni, M. K., Jr.; Kolthoff, I. M. *Anal. Chem.* **1979**, *51*, 133–140.  
 (14) Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3299–3305.  
 (15) Pilyugin, V. S.; Khrustaleva, L. Y.; Smirnova, S. L.; Ginzburg, M. E. *Zh. Obshch. Khim.* **1983**, *53*, 1391–1395.  
 (16) Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.* **1980**, *45*, 3305–3313.  
 (17) Dippy, J. F. J.; Hughes, S. R. C. *Tetrahedron* **1963**, *19*, 1527–1530.

**Scheme 2.** Generation and Subsequent Ionization of Benzhydryl Carboxylates in a Double-Mixing Stopped Flow Spectrometer

carboxylates (anions used:  $\text{AcO}^-$ ,  $\text{BzO}^-$ ,  $\text{PNB}^-$ , and  $\text{DNB}^-$ ) in pure acetonitrile (Scheme 3).

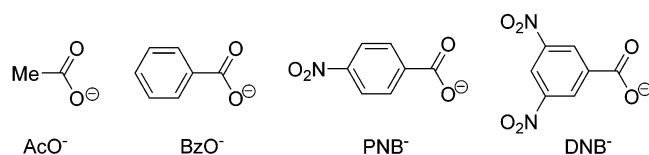
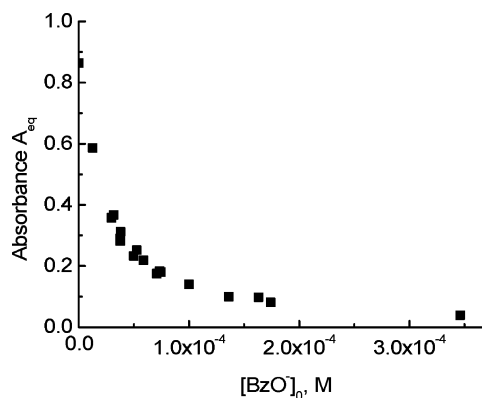


Figure 1 shows that the benzhydrylium ion absorbance at 632 nm decreases when increasing amounts of tetra-*n*-butylammonium benzoate ( $n\text{-Bu}_4\text{N}^+\text{BzO}^-$ ) are added to a solution of  $(\text{liI})_2\text{CH}^+\text{BF}_4^-$  in acetonitrile.

Due to the possible coexistence of covalent benzhydryl carboxylates with different types of ion pairs and free ions, the mathematical expression for the equilibrium constants may not be trivial. However, our experiments show that eq 2 provides a satisfactory description of the equilibria in acetonitrile at the low concentrations used (ionic strengths from  $2.82 \times 10^{-5}$  to  $1.96 \times 10^{-3}$ ). The drifts of  $K$  with increasing carboxylate concentration, which were observed in some cases (see Supporting Information), were so small that an explicit treatment of these effects was not attempted.

$$K = \frac{[\text{Ar}_2\text{CH}-\text{O}_2\text{CR}]_{\text{eq}}}{[\text{Ar}_2\text{CH}^+]_{\text{eq}}[\text{RCO}_2^-]_{\text{eq}}} = \frac{[\text{Ar}_2\text{CH}^+]_0 - [\text{Ar}_2\text{CH}^+]_{\text{eq}}}{[\text{Ar}_2\text{CH}^+]_{\text{eq}}([\text{RCO}_2^-]_0 - [\text{Ar}_2\text{CH}^+]_0 + [\text{Ar}_2\text{CH}^+]_{\text{eq}})} \quad (2)$$

**Figure 1.** Determination of the equilibrium constant for the reaction of  $n\text{-Bu}_4\text{N}^+\text{BzO}^-$  with  $(\text{liI})_2\text{CH}^+\text{BF}_4^-$  [ $(1.43\text{--}1.46) \times 10^{-5}$  M] in acetonitrile at 25 °C.  $-A_{\text{eq}} = \epsilon \times [\text{Ar}_2\text{CH}^+] \times d$ .**Scheme 3**

From the initial concentrations,  $[\text{Ar}_2\text{CH}^+]_0$  and  $[\text{RCO}_2^-]_0$ , and the absorbance of  $\text{Ar}_2\text{CH}^+\text{BF}_4^-$  ( $A = \epsilon \times [\text{Ar}_2\text{CH}^+] \times d$ ), the equilibrium concentrations  $[\text{Ar}_2\text{CH}^+]_{\text{eq}}$ ,  $[\text{RCO}_2^-]_{\text{eq}}$ , and  $[\text{Ar}_2\text{CH}-\text{O}_2\text{CR}]_{\text{eq}}$  were calculated. Substitution into eq 2 yielded the equilibrium constants  $K$  listed in Table 1.

As the equilibrium constants  $K$  defined by eq 2 reflect the relative Lewis basicities of these carboxylate ions toward benzhydrylium ions in acetonitrile, while  $\text{p}K_{\text{a}}$  values reflect the relative basicities of these anions toward the proton (Scheme 4), a comparison between these two quantities is appropriate (Figure 2).

The vertical ordering of the correlation lines provides a direct comparison of the affinities of the benzoate ions  $\text{BzO}^-$ ,  $\text{PNB}^-$ ,  $\text{DNB}^-$  toward benzhydrylium ions and the proton in different solvents. It is obvious that the benzoates possess a higher affinity toward the proton in acetonitrile and DMSO than toward  $(\text{dma})_2\text{CH}^+$  and better stabilized benzhydrylium ions in acetonitrile.

The similarity of the slopes indicates the internal consistency of the equilibrium constants. They also show that substituents in the benzoate ions affect their Lewis basicities toward benzhydrylium ions in the same way as their Brønsted basicities in acetonitrile and in DMSO.

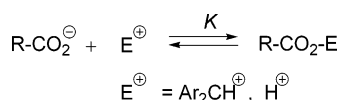
From the equilibrium constants in Table 1 one can derive that, at high carboxylate concentration in acetonitrile, the equilibrium lies further toward the covalent benzhydryl carboxylates. Therefore, the rate constants  $k_{-1}$  for the combinations of the corresponding benzhydrylium ions with carboxylate ions in acetonitrile should be accessible.

**Second-Order Rate Constants for Carbocation Carboxylate Combinations.** The decays of the benzhydrylium absorbances, which were observed after mixing solutions of benzhydrylium tetrafluoroborates with more than 6 equiv of tetrabutylammonium carboxylates, followed single exponentials from which the concentration-dependent first-order rate constants  $k_{\text{obs}}$  were derived. As illustrated in Figure 3,  $k_{\text{obs}}$  increases linearly with the concentration of  $n\text{-Bu}_4\text{N}^+\text{RCO}_2^-$ , indicating that only a small percentage of cations can be paired with  $\text{RCO}_2^-$ . Since

**Table 1.** Equilibrium Constants  $K$  ( $M^{-1}$ ) for Reactions of Benzhydrylium Ions with Carboxylate Ions in Acetonitrile at 25 °C

$Ar_2CH^+$	$K, M^{-1}$		
	$BzO^-^a$	$PNB^-^b$	$DNB^-^c$
$(lil)_2CH^+$	$(6.20 \pm 0.40) \times 10^4$	$(5.79 \pm 0.16) \times 10^2$	
$(jul)_2CH^+$	$(5.38 \pm 1.06) \times 10^4$	$(5.18 \pm 0.11) \times 10^2$	
$(ind)_2CH^+$		$(1.08 \pm 0.08) \times 10^4$	$(1.99 \pm 0.25) \times 10^2$
$(thq)_2CH^+$		$(1.13 \pm 0.17) \times 10^4$	$(2.33 \pm 0.28) \times 10^2$
$(pyr)_2CH^+$		$(3.20 \pm 0.10) \times 10^4$	$(5.48 \pm 0.25) \times 10^2$
$(dma)_2CH^+$		$(4.32 \pm 0.33) \times 10^5$	$(5.46 \pm 0.16) \times 10^3$

<sup>a</sup>  $BzO^-$  = benzoate. <sup>b</sup>  $PNB^-$  = 4-nitrobenzoate. <sup>c</sup>  $DNB^-$  = 3,5-dinitrobenzoate.

**Scheme 4**

the ion combinations studied in this work are slow compared with the diffusional processes which interconvert free ions and ion pairs, the Curtin–Hammett principle allows us to neglect the formation of ion pairs prior to bond formation. The second-order rate constants  $k_{-1}$  can, therefore, be obtained as the slopes of the plots of  $k_{obs}$  versus the concentration of  $n-Bu_4N^+ RCO_2^-$ .

Some plots of  $k_{obs}$  against the carboxylate concentrations show considerable intercepts on the ordinate as illustrated on pp S25–S26 in the Supporting Information. In pure acetonitrile and acetone, i.e., solvents which do not react with the benzhydrylium ions under consideration, this situation is observed when the cation anion combinations reach an equilibrium. The observed rate constants for reversible reactions equal the sum of forward and backward reactions as expressed by eq 3.<sup>18</sup>

$$k_{obs} = k_1 + k_{-1}[R-CO_2^-] \quad (3)$$

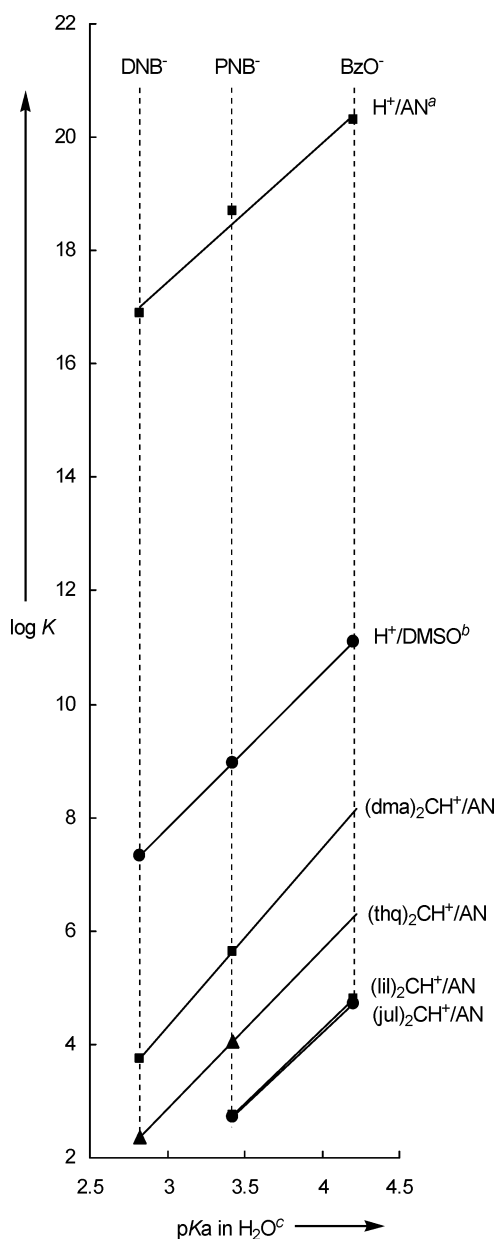
For the reaction of  $(ind)_2CH^+ BF_4^-$  with  $n-Bu_4N^+ PNB^-$  in acetonitrile the intercept of the plot of  $k_{obs}$  against the carboxylate concentration is  $11.1 s^{-1}$  (see Supporting Information). This value closely resembles the ionization rate constant  $k_1 = 9.07 s^{-1}$  calculated from the ratio of the ion combination rate constant  $k_{-1} = 9.80 \times 10^4 M^{-1} s^{-1}$  and the equilibrium constant  $K = 1.08 \times 10^4 M^{-1}$  (Table 1). As expected, the ionization rate constants derived from the intercepts of the ion combination reactions are less precise when the intercepts are small compared with  $k_{obs}$ .

In aqueous solvents, the kinetics of the reactions of benzhydrylium ions with carboxylate ions often did not show a monoexponential decay of the carbocations due to the reversibility of the carbocation anion combinations and the competing reactions of the carbocations with the solvents. However, in cases where monoexponential decays of the carbocation absorbances were observed, rate constants for the combinations of benzhydrylium ions with carboxylate ions could be determined (Table 2). In Table 2 values of rate constants given in parentheses are approximate, with typical errors of 8–10%.

In previous work,<sup>9,11,19</sup> we have shown that reactions of carbocations with nucleophiles can be described by eq 4,

$$\log k = s(N + E) \quad (4)$$

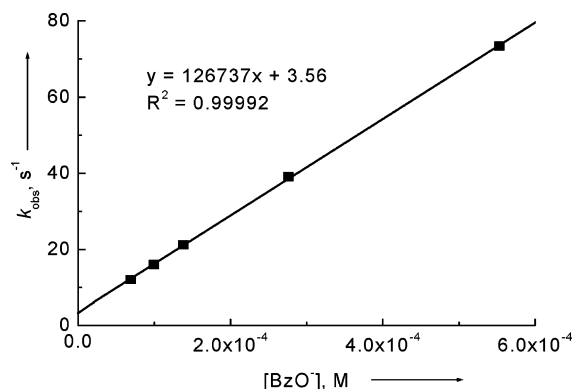
where  $k$  is the second-order rate constant,  $E$  is a nucleophile-independent electrophilicity parameter, and  $N$  and  $s$  are elec-



**Figure 2.** Comparison of the equilibrium constants (25 °C) for reactions of benzhydrylium ions with benzoate ( $BzO^-$ ), 4-nitrobenzoate ( $PNB^-$ ), and 3,5-dinitrobenzoate ( $DNB^-$ ) ions with the  $pK_a$  values of the corresponding carboxylic acids in different solvents (AN: acetonitrile). <sup>a</sup>  $pK_a$ (in AN) = 20.3 (benzoic acid, from ref 12), 18.7 (4-nitrobenzoic acid, from ref 13), and 16.9 (3,5-dinitrobenzoic acid, from ref 13). <sup>b</sup>  $pK_a$ (in DMSO) = 11.0 (benzoic acid, from ref 14), 9.0 (*p*-nitrobenzoic acid, from ref 15), and 7.3 (3,5-dinitrobenzoic acid, from ref 16). <sup>c</sup>  $pK_a$ (in  $H_2O$ ) = 4.2 (benzoic acid, from ref 17), 3.4 (*p*-nitrobenzoic acid, from ref 17), 2.8 (3,5-dinitrobenzoic acid, from ref 17).

trophile-independent nucleophilicity parameters. Figure 4 correlates some of the second-order rate constants listed in Table 2 with the previously reported electrophilicity parameters of benzhydrylium ions<sup>9,11</sup> and shows that the reactions of the

- (18) (a) Maskill, H. *The Investigation of Organic Reactions and Their Mechanisms*; Blackwell Publishing: Oxford, 2006. (b) Schmid, R.; Sapunov, V. N. *Non-Formal Kinetics*; Verlag Chemie: Weinheim, 1982. (19) (a) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990–1010; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938–957. (b) Mayr, H.; Ofial, A. R. In *Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; Wiley: Hoboken, NJ, 2004; pp 331–358. (c) Mayr, H.; Ofial, A. R. *Pure Appl. Chem.* **2005**, *77*, 1807–1821.



**Figure 3.** Linear correlation of the observed *pseudo*-first-order rate constants  $k_{\text{obs}}$  for the reaction of  $(\text{jul})_2\text{CH}^+$  ( $c_0 = 9.99 \times 10^{-6} \text{ M}$ ) with  $\text{BzO}^-$  in acetonitrile (25 °C) with the concentration of  $n\text{-Bu}_4\text{N}^+\text{BzO}^-$ .

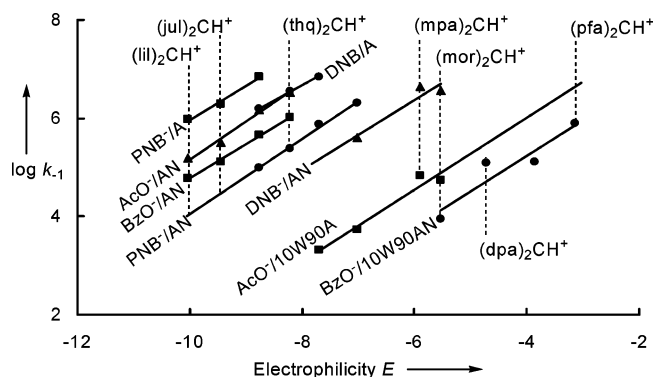
**Table 2.** Second-Order Rate Constants  $k_{-1}$  for Reactions of Benzhydryl Cations  $\text{Ar}_2\text{CH}^+$  with Carboxylates at 25 °C

$\text{RCO}_2^-^a$	solvent <sup>b</sup>	$\text{Ar}_2\text{CH}^+$	$k_{-1}, \text{M}^{-1} \text{s}^{-1}$
$\text{AcO}^-$	AN	$(\text{liI})_2\text{CH}^+$	$1.51 \times 10^5$
		$(\text{jul})_2\text{CH}^+$	$3.21 \times 10^5$
		$(\text{ind})_2\text{CH}^+$	$1.46 \times 10^6$
		$(\text{thq})_2\text{CH}^+$	$(3.42 \times 10^6)$
		$(\text{liI})_2\text{CH}^+$	$5.79 \times 10^6$
		$(\text{dpa})_2\text{CH}^+$	$1.17 \times 10^5$
		$(\text{mfa})_2\text{CH}^+$	$1.15 \times 10^5$
		$(\text{pfa})_2\text{CH}^+$	$6.87 \times 10^5$
		$(\text{pyr})_2\text{CH}^+$	$(2.06 \times 10^3)$
		$(\text{dma})_2\text{CH}^+$	$5.43 \times 10^3$
	$(\text{mpa})_2\text{CH}^+$	$6.75 \times 10^4$	
	$(\text{mor})_2\text{CH}^+$	$5.51 \times 10^4$	
	20W80A	$(\text{mpa})_2\text{CH}^+$	$9.79 \times 10^3$
		$(\text{mor})_2\text{CH}^+$	$7.59 \times 10^3$
		$(\text{dpa})_2\text{CH}^+$	$1.12 \times 10^5$
		$(\text{mfa})_2\text{CH}^+$	$9.33 \times 10^4$
		$(\text{liI})_2\text{CH}^+$	$6.07 \times 10^4$
		$(\text{jul})_2\text{CH}^+$	$1.27 \times 10^5$
		$(\text{ind})_2\text{CH}^+$	$4.48 \times 10^5$
		$(\text{thq})_2\text{CH}^+$	$3.91 \times 10^5$
$(\text{mor})_2\text{CH}^+$		$1.05 \times 10^6$	
$(\text{dpa})_2\text{CH}^+$		$(8.93 \times 10^3)$	
$\text{BzO}^-$	AN	$(\text{dpa})_2\text{CH}^+$	$1.20 \times 10^5$
		$(\text{mfa})_2\text{CH}^+$	$1.26 \times 10^5$
		$(\text{pfa})_2\text{CH}^+$	$7.79 \times 10^5$
		$(\text{ind})_2\text{CH}^+$	$9.80 \times 10^4$
		$(\text{thq})_2\text{CH}^+$	$2.46 \times 10^5$
	10W90AN	$(\text{pyr})_2\text{CH}^+$	$7.46 \times 10^5$
		$(\text{dma})_2\text{CH}^+$	$2.00 \times 10^6$
		$(\text{liI})_2\text{CH}^+$	$9.29 \times 10^5$
		$(\text{jul})_2\text{CH}^+$	$1.96 \times 10^6$
		$(\text{ind})_2\text{CH}^+$	$6.97 \times 10^6$
$\text{PNB}^-$	AN	$(\text{dma})_2\text{CH}^+$	$4.01 \times 10^5$
		$(\text{mpa})_2\text{CH}^+$	$4.39 \times 10^6$
		$(\text{mor})_2\text{CH}^+$	$3.70 \times 10^6$
		$(\text{ind})_2\text{CH}^+$	$(1.56 \times 10^6)$
		$(\text{thq})_2\text{CH}^+$	$(3.50 \times 10^6)$
	A	$(\text{pyr})_2\text{CH}^+$	$(7.06 \times 10^6)$
		$(\text{liI})_2\text{CH}^+$	$9.29 \times 10^5$
		$(\text{jul})_2\text{CH}^+$	$1.96 \times 10^6$
		$(\text{ind})_2\text{CH}^+$	$6.97 \times 10^6$
		$(\text{thq})_2\text{CH}^+$	$2.46 \times 10^5$
$\text{DNB}^-$	AN	$(\text{pyr})_2\text{CH}^+$	$7.46 \times 10^5$
		$(\text{dma})_2\text{CH}^+$	$2.00 \times 10^6$
		$(\text{liI})_2\text{CH}^+$	$9.29 \times 10^5$
		$(\text{jul})_2\text{CH}^+$	$1.96 \times 10^6$
		$(\text{ind})_2\text{CH}^+$	$6.97 \times 10^6$
	A	$(\text{thq})_2\text{CH}^+$	$2.46 \times 10^5$
		$(\text{pyr})_2\text{CH}^+$	$7.46 \times 10^5$
		$(\text{dma})_2\text{CH}^+$	$2.00 \times 10^6$
		$(\text{liI})_2\text{CH}^+$	$9.29 \times 10^5$
		$(\text{jul})_2\text{CH}^+$	$1.96 \times 10^6$

<sup>a</sup>  $\text{AcO}^-$  = acetate,  $\text{BzO}^-$  = benzoate,  $\text{PNB}^-$  = 4-nitrobenzoate,  $\text{DNB}^-$  = 3,5-dinitrobenzoate. <sup>b</sup>A = acetone, 10W90A = 10% water and 90% acetone (v/v), AN = acetonitrile. <sup>c</sup>At 20 °C.

carbocations  $\text{Ar}_2\text{CH}^+$  with carboxylate ions generally follow eq 4.

From these correlations one can derive  $N$  and  $s$  parameters (eq 4) for the carboxylate ions in different solvents (Table 3). For some benzhydrylium ions systematic dispersions are obvious. As shown in Figure 4,  $(\text{dpa})_2\text{CH}^+$  generally reacts faster than predicted by its  $E$ -parameter. The phenylmethylamino



**Figure 4.** Correlation of second-order rate constants  $k_{-1}$  (at 25 °C) for the combination of benzhydrylium ions with carboxylate ions in different solvents. A = acetone, AN = acetonitrile, W = water.

**Table 3.** Nucleophilicity Parameters (25 °C) of Carboxylate Ions in Different Solvents

$\text{RCO}_2^-$	solvent	$N_{25}^a$	$s_{25}^a$
$\text{AcO}^-$	AN	16.90	0.75
	10W90A	12.71 <sup>b</sup>	0.68 <sup>b</sup>
	20W80A	12.5 <sup>c</sup>	0.60 <sup>c</sup>
$\text{BzO}^-$	AN	16.82	0.70
	10W90AN	11.3 <sup>c</sup>	0.72 <sup>c</sup>
$\text{PNB}^-$	AN	15.30	0.76
	A	18.74	0.68
$\text{DNB}^-$	AN	14.9 <sup>c</sup>	0.71 <sup>c</sup>
	A	18.8 <sup>c</sup>	0.62 <sup>c</sup>

<sup>a</sup> Note that for the sake of compatibility with the heterolysis rate constants determined in this work (see below) all rate constants  $k_{-1}$  were measured at 25 °C (not at 20 °C as for other electrophile-nucleophile combinations), and for that reason the index “25” is added to the  $N$  and  $s$  parameters. <sup>b</sup>Additional  $k_{-1}$  values from Table 4 were used (see also Figure 6). <sup>c</sup>Values from correlations of lower quality.

substituted benzhydrylium ion  $(\text{mpa})_2\text{CH}^+$  behaves similarly, whereas  $(\text{mor})_2\text{CH}^+$  reacts more slowly than expected. We have previously observed analogous deviations of the reactions of these carbocations with a variety of nucleophiles in protic solvents.<sup>20</sup> Possibly, the phenylamino substituted benzhydrylium ions  $(\text{mpa})_2\text{CH}^+$  and  $(\text{dpa})_2\text{CH}^+$  are less efficiently solvated in protic solvents than benzhydrylium ions without phenylamino groups and, therefore, are more electrophilic in protic solvents than derived from their electrophilicity parameters which were determined in dichloromethane.

In pure acetone, acetate and benzoate react so fast with benzhydrylium ions that we were not able to determine the nucleophilicity parameters  $N$  and  $s$  of these anions in acetone. According to Table 2 the acetate ion is 2–3 times more reactive than benzoate in acetonitrile and approximately 15 times more reactive than 4-nitrobenzoate. Only one carbocation,  $(\text{dma})_2\text{CH}^+$ , could be used to derive that *p*-nitrobenzoate is 5 times more nucleophilic than 3,5-dinitrobenzoate in acetonitrile. As the slope parameters  $s$  are similar, these differences are also reflected by  $N$ , and one can deduce from Table 3 that 4-nitrobenzoate and 3,5-dinitrobenzoate are approximately 2–3 orders of magnitude more nucleophilic in acetone than in acetonitrile. In aqueous acetone (10W90A and 20W80A) the  $N$  value for acetate is 4.2 to 4.4 units smaller than that in pure acetonitrile.

**Kinetics of Ionization of Benzhydryl Carboxylates.** As described in Scheme 2, solutions of covalent benzhydryl

(20) (a) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174–5181. (b) Phan, T. B.; Mayr, H. *Can. J. Chem.* **2005**, *83*, 1554–1560.

**Table 4.** Ionization Rate Constants  $k_1$  of Benzhydryl Derivatives in Different Solvents (25 °C)

nucleofuge	solvent	Ar <sub>2</sub> CH <sup>+</sup>	$k_1$ [s <sup>-1</sup> ]	nucleofuge	solvent	Ar <sub>2</sub> CH <sup>+</sup>	$k_1$ [s <sup>-1</sup> ]
AcO <sup>-</sup>	20W80AN	(lil) <sub>2</sub> CH <sup>+</sup>	3.63	BzO <sup>-</sup>	40W60AN	(lil) <sub>2</sub> CH <sup>+</sup>	$1.19 \times 10^1$
		(jul) <sub>2</sub> CH <sup>+</sup>	$1.97 \times 10^1$			(jul) <sub>2</sub> CH <sup>+</sup>	$6.79 \times 10^1$
		(ind) <sub>2</sub> CH <sup>+</sup>	2.23			(ind) <sub>2</sub> CH <sup>+</sup>	5.16
		(thq) <sub>2</sub> CH <sup>+</sup>	5.87			(thq) <sub>2</sub> CH <sup>+</sup>	$2.45 \times 10^1$
		(pyr) <sub>2</sub> CH <sup>+</sup>	8.57			(pyr) <sub>2</sub> CH <sup>+</sup>	$3.60 \times 10^1$
		(dma) <sub>2</sub> CH <sup>+</sup>	1.77			(dma) <sub>2</sub> CH <sup>+</sup>	7.62
	40W60AN	(lil) <sub>2</sub> CH <sup>+</sup>	6.90		20W80A	(lil) <sub>2</sub> CH <sup>+</sup>	4.97
		(jul) <sub>2</sub> CH <sup>+</sup>	$3.99 \times 10^1$			(jul) <sub>2</sub> CH <sup>+</sup>	$1.97 \times 10^1$
		(ind) <sub>2</sub> CH <sup>+</sup>	4.52			(ind) <sub>2</sub> CH <sup>+</sup>	2.89
		(thq) <sub>2</sub> CH <sup>+</sup>	$1.34 \times 10^1$			(thq) <sub>2</sub> CH <sup>+</sup>	7.14
		(pyr) <sub>2</sub> CH <sup>+</sup>	$2.20 \times 10^1$			(pyr) <sub>2</sub> CH <sup>+</sup>	9.83
		(dma) <sub>2</sub> CH <sup>+</sup>	4.54			(dma) <sub>2</sub> CH <sup>+</sup>	3.49
	10W90A	(jul) <sub>2</sub> CH <sup>+</sup>	2.34 <sup>a</sup>		40W60A	(lil) <sub>2</sub> CH <sup>+</sup>	$1.93 \times 10^1$
		(ind) <sub>2</sub> CH <sup>+</sup>	0.49 <sup>b</sup>			(jul) <sub>2</sub> CH <sup>+</sup>	$9.50 \times 10^1$
		(thq) <sub>2</sub> CH <sup>+</sup>	1.09 <sup>c</sup>			(ind) <sub>2</sub> CH <sup>+</sup>	$1.38 \times 10^1$
		(pyr) <sub>2</sub> CH <sup>+</sup>	1.85 <sup>d</sup>			(thq) <sub>2</sub> CH <sup>+</sup>	$3.63 \times 10^1$
		(dma) <sub>2</sub> CH <sup>+</sup>	1.08			(pyr) <sub>2</sub> CH <sup>+</sup>	$5.05 \times 10^1$
		(lil) <sub>2</sub> CH <sup>+</sup>	2.24			(dma) <sub>2</sub> CH <sup>+</sup>	$1.27 \times 10^1$
	20W80A	(jul) <sub>2</sub> CH <sup>+</sup>	8.37		PNB <sup>-</sup>	(lil) <sub>2</sub> CH <sup>+</sup>	$5.22 \times 10^1$
		(ind) <sub>2</sub> CH <sup>+</sup>	1.40			(jul) <sub>2</sub> CH <sup>+</sup>	$1.63 \times 10^2$
		(thq) <sub>2</sub> CH <sup>+</sup>	3.36			(ind) <sub>2</sub> CH <sup>+</sup>	$2.59 \times 10^1$
		(pyr) <sub>2</sub> CH <sup>+</sup>	4.95			(thq) <sub>2</sub> CH <sup>+</sup>	$5.59 \times 10^1$
		(dma) <sub>2</sub> CH <sup>+</sup>	2.22			(pyr) <sub>2</sub> CH <sup>+</sup>	$6.59 \times 10^1$
		(lil) <sub>2</sub> CH <sup>+</sup>	$1.36 \times 10^1$			(dma) <sub>2</sub> CH <sup>+</sup>	$2.06 \times 10^1$
40W60A	(jul) <sub>2</sub> CH <sup>+</sup>	$6.15 \times 10^1$	20W80A	(lil) <sub>2</sub> CH <sup>+</sup>	$1.03 \times 10^2$		
	(ind) <sub>2</sub> CH <sup>+</sup>	9.41		(jul) <sub>2</sub> CH <sup>+</sup>	$3.53 \times 10^2$		
	(thq) <sub>2</sub> CH <sup>+</sup>	$2.49 \times 10^1$		(ind) <sub>2</sub> CH <sup>+</sup>	$5.58 \times 10^1$		
	(pyr) <sub>2</sub> CH <sup>+</sup>	$3.59 \times 10^1$		(pyr) <sub>2</sub> CH <sup>+</sup>	$1.56 \times 10^2$		
	(dma) <sub>2</sub> CH <sup>+</sup>	9.30		(dma) <sub>2</sub> CH <sup>+</sup>	$3.82 \times 10^1$		
	(lil) <sub>2</sub> CH <sup>+</sup>	9.58		(pyr) <sub>2</sub> CH <sup>+</sup>	$7.02 \times 10^2$		
BzO <sup>-</sup>	20W80AN	(jul) <sub>2</sub> CH <sup>+</sup>	$4.49 \times 10^1$	40W60A	(dma) <sub>2</sub> CH <sup>+</sup>	$1.76 \times 10^2$	
		(ind) <sub>2</sub> CH <sup>+</sup>	5.16		(pyr) <sub>2</sub> CH <sup>+</sup>	$1.06 \times 10^3$	
		(thq) <sub>2</sub> CH <sup>+</sup>	$1.47 \times 10^1$		(dma) <sub>2</sub> CH <sup>+</sup>	$2.53 \times 10^2$	
		(pyr) <sub>2</sub> CH <sup>+</sup>	$2.11 \times 10^1$		(dma) <sub>2</sub> CH <sup>+</sup>	$4.80 \times 10^2$	
		(dma) <sub>2</sub> CH <sup>+</sup>	4.28				

<sup>a</sup>  $k_{-1} = 1.85 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>b</sup>  $k_{-1} = 4.50 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>c</sup>  $k_{-1} = 9.41 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>d</sup>  $k_{-1} = 2.73 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

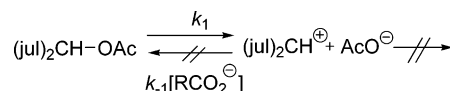
carboxylates and tetrabutylammonium carboxylates in acetone or acetonitrile were produced in the first mixing step of a stopped-flow double-mixing experiment. When these solutions were combined with aqueous acetone or aqueous acetonitrile (second mixer in Scheme 2) the regeneration of the colored benzhydrylium ions was observed photometrically. The appearance of the benzhydrylium absorbances generally followed single exponentials (eq 5) from which the rate constants  $k_{\text{obs}}$  were derived. A typical example is shown on page S34 of the Supporting Information.

$$[\text{Ar}_2\text{CH}^+] = [\text{Ar}_2\text{CH}^+]_{\text{eq}}(1 - e^{-k_{\text{obs}}t}) \quad (5)$$

Thus, unlike typical solvolyses of R–X substrates, where ionization rates are determined indirectly, in this work the appearance of the carbocations Ar<sub>2</sub>CH<sup>+</sup> is directly observed.

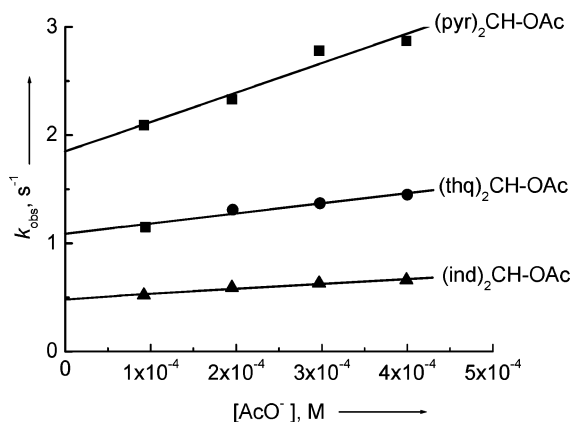
As all ionization experiments of this investigation had to be performed in the presence of variable concentrations of the carboxylate ions ( $[\textit{n}\text{-Bu}_4\text{N}^+\text{RCO}_2^-] < 6 \times 10^{-4} \text{ M}^{-1}$ ), the effect of the ionic strength on the ionization rates was studied systematically. As shown on pages S48 to S50 of the Supporting Information, the salt concentrations relevant for these studies ( $< 6 \times 10^{-4} \text{ M}^{-1}$ ) did not affect the ionization rates by more than 12%.

For most heterolysis reactions described in Table 4, constant end absorbances  $A_{\text{end}}$  which are independent of  $[\text{RCO}_2^-]$ , as well as ionization rate constants  $k_1$  which are independent of  $[\text{RCO}_2^-]$ , were observed. One can, therefore, conclude that the heterolyses described in Table 4 proceed with quantitative

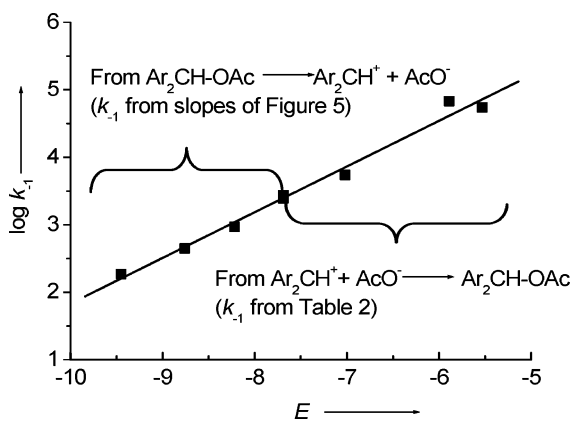
**Scheme 5.** Heterolysis of (jul)<sub>2</sub>CH–OAc in 20W80A

formation of the carbocations which do not undergo subsequent reactions with the solvent (Scheme 5).

The formation of persistent solutions of carbocations is in accordance with the estimated rate constants for the reactions of these carbocations with the leaving group and the solvent. For the ionization of (jul)<sub>2</sub>CH–OAc in 20W80A a rate constant of  $k_1 = 8.37 \text{ s}^{-1}$  was determined (Table 4). With  $N_{25}$  and  $s_{25}$  values for the acetate ion in 20W80A (12.5 and 0.60, Table 3) and the electrophilicity parameter for (jul)<sub>2</sub>CH<sup>+</sup> ( $E = -9.45$ , Chart 1), one calculates  $k_{-1} = 67 \text{ M}^{-1} \text{ s}^{-1}$  by using eq 4. For the highest concentration of tetra-*n*-butylammonium acetate present in the ionization experiments ( $[\text{AcO}^-] = 3.88 \times 10^{-4} \text{ M}$ ) one obtains  $k_{-1}[\text{AcO}^-] = 2.6 \times 10^{-2} \text{ s}^{-1}$ , i.e.,  $k_1 \gg k_{-1}[\text{AcO}^-]$  corresponding to a quantitative ionization process. From the nucleophilicity parameters of the solvent mixture 20W80A ( $N = 5.77$ ,  $s = 0.87$ )<sup>5</sup> and  $E$  ((jul)<sub>2</sub>CH<sup>+</sup>) =  $-9.45$ ) one calculates (eq 4) a rate constant of  $6.29 \times 10^{-4} \text{ s}^{-1}$  for the reaction of (jul)<sub>2</sub>CH<sup>+</sup> with the solvent. This is in line with the observation that the benzhydrylium ion (jul)<sub>2</sub>CH<sup>+</sup> does not undergo fast subsequent reactions with the solvent. Analogous calculations can be performed to rationalize why none of the carbocations generated under the conditions described in Table 4 is rapidly intercepted by the solvent.



**Figure 5.** Correlation of the observed rate constants for the ionization of  $(\text{pyr})_2\text{CH-OAc}$  ( $1.00 \times 10^{-5}$  M),  $(\text{thq})_2\text{CH-OAc}$  ( $8.70 \times 10^{-6}$  M), and  $(\text{ind})_2\text{CH-OAc}$  ( $1.00 \times 10^{-5}$  M) in 10W90A with the concentration of  $n\text{-Bu}_4\text{N}^+\text{AcO}^-$  (at 25 °C).



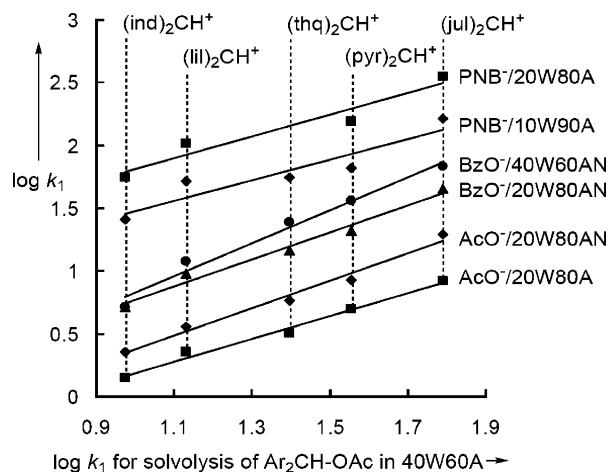
**Figure 6.** Correlation of the combination rate constants for the reactions of  $\text{Ar}_2\text{CH}^+\text{BF}_4^-$  with  $n\text{-Bu}_4\text{N}^+\text{AcO}^-$  in 10W90A ( $\log k_{-1} = 8.60 + 0.68E$ ).

A different situation is encountered when the heterolysis reactions of the benzhydryl acetates are studied in 10W90A. Now, the final absorbances decrease with increasing acetate ion concentration and the observed first-order rate constants  $k_{\text{obs}}$  increase with increasing acetate ion concentration as depicted in Figure 5, indicating the reversibility of the ionization processes.

Because the observed first-order rate constants  $k_{\text{obs}}$  of reversible processes reflect the sum of the forward and the backward reactions (eq 3),<sup>18</sup> the ionization rate constants  $k_1$  were obtained as the intercepts of the plots of  $k_{\text{obs}}$  versus the concentration of  $n\text{-Bu}_4\text{N}^+\text{AcO}^-$  (Figure 5). The slopes of these plots yield  $k_{-1}$ , i.e., the second-order rate constants for the combination reactions of the carbocations with the acetate ions.

The consistency of this evaluation is shown by Figure 6, where the rate constants  $k_{-1}$  obtained from ion combination reactions (Table 2) and from the ionization reactions are directly compared with each other. While  $k_{-1}$  for  $(\text{pyr})_2\text{CH-OAc}$  has been determined by both methods, for the other systems only one method could be employed. As required by eq 4, all rate constants for the ion combinations are on the same correlation line.

A slight increase of  $k_{\text{obs}}$  with increasing concentration of carboxylate ions was also observed for some heterolyses of benzhydryl acetates and benzoates in 20W80A (see Supporting Information). Since, in these cases, the ionizations were much



**Figure 7.** Correlation of ionization rate constants of  $\text{Ar}_2\text{CH-O}_2\text{CR}$  in different solvents (given as v/v; W = water, A = acetone, AN = acetonitrile) at 25 °C.

faster than the ion recombinations ( $k_1 \gg k_{-1}[\text{RCO}_2^-]$ ), only the ionization constants  $k_1$  were derived from these experiments.

The ionization rate constants of different benzhydryl carboxylates are compared in Figure 7. Though some of the correlations of Figure 7 are only of moderate quality, the positions of the different correlation lines clearly show a decrease of the leaving group abilities in the series  $\text{PNB}^- > \text{BzO}^- > \text{AcO}^-$  as well as an increase of the ionization rates with higher water content in the solvent mixtures.

**Transition States of the Ionizations.** In 1948 Winstein and Grunwald reported that rates of the  $\text{S}_{\text{N}}1$  solvolyses of neutral RX substrates in different solvents can be described by the linear free energy relationship (eq 6).<sup>21</sup>

$$\log(k/k_0) = mY \quad (6)$$

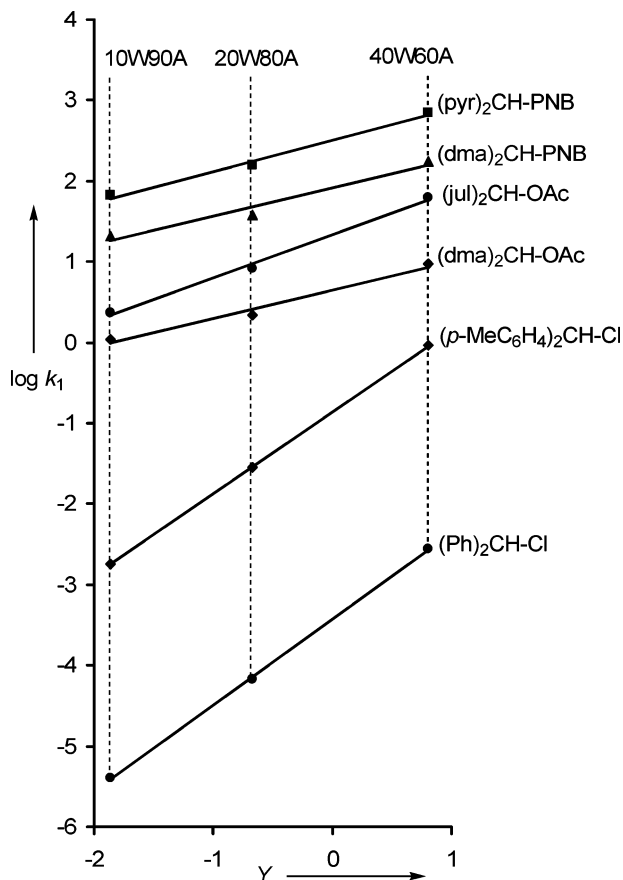
In this relationship,  $k$  and  $k_0$  are rate constants for solvolysis of RX in a given solvent and in 80% aqueous ethanol, respectively. Winstein and Grunwald selected the solvolysis of *tert*-butyl chloride as a reference reaction ( $m = 1$ ) for establishing  $Y$  as a measure of the ionizing power of a solvent (relative to 80% aqueous ethanol). The slope  $m$  of a plot of  $\log(k/k_0)$  against  $Y$  thus measures the sensitivity of a reaction to the ionizing power of the solvent. Values of  $m$  close to 1.0 were found for numerous  $\text{S}_{\text{N}}1$  solvolysis reactions,<sup>21,22</sup> and  $m$  values below 0.5 were considered as evidence for  $\text{S}_{\text{N}}2$  reactions. The value of  $m$  therefore was suggested as a criterion for distinguishing the two mechanisms.

Figure 8 compares plots of  $\log(k/k_0)$  against  $Y$  for typical  $\text{S}_{\text{N}}1$  solvolyses of the parent benzhydryl chloride and its *p,p*-dimethyl derivative<sup>23,24</sup> with the corresponding plots for the amino-substituted benzhydryl carboxylates studied in this work.

While the slopes for benzhydryl chloride ( $m = 1.07$ ) and *p,p*-dimethylbenzhydryl chloride ( $m = 1.02$ ) are those expected for rate-limiting ionization processes, much smaller slopes are found

- (21) (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846–854. (b) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770–2777.  
 (22) Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121–158.  
 (23) Denegri, B.; Streiter, A.; Juric, S.; Ofial, A. R.; Kronja, O.; Mayr, H. *Chem.–Eur. J.* **2006**, *12*, 1648–1656; *Chem.–Eur. J.* **2006**, *12*, 5415.  
 (24) (a) Double determination of  $k_1$  for  $(p\text{-MeC}_6\text{H}_4)_2\text{CH-Cl}$  in 40W60A in this work:  $k_1(25\text{ °C}) = 0.916\text{ s}^{-1}$ . (b) Solvolysis rate constant  $k_1(25\text{ °C})$  for  $(\text{Ph})_2\text{CH-Cl}$  in 40W60A from: Liu, K.-T.; Lin, Y.-S.; Tsao, M.-L. *J. Phys. Org. Chem.* **1998**, *11*, 223–229.





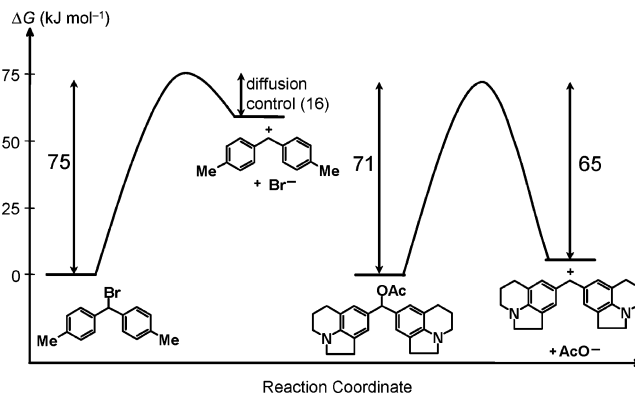
**Figure 8.** Correlation of rate constants for ionization of some benzhydryl derivatives with solvent ionizing power  $Y$  ( $k_1$  for  $\text{Ar}_2\text{CH}-\text{Cl}$  in 10W90A and 20W80A from ref 23;  $k_1$  for  $\text{Ar}_2\text{CH}-\text{Cl}$  in 40W60A from ref 24. Slopes:  $(\text{pyr})_2\text{CH}-\text{DNB} = 0.39$ ,  $(\text{dma})_2\text{CH}-\text{DNB} = 0.35$ ,  $(\text{lil})_2\text{CH}-\text{OAc} = 0.54$ ,  $(\text{dma})_2\text{CH}-\text{OAc} = 0.35$ ,  $(p\text{-MeC}_6\text{H}_4)_2\text{CH}-\text{Cl} = 1.02$ ,  $(\text{Ph})_2\text{CH}-\text{Cl} = 1.07$ ).

for the benzhydryl carboxylates ( $m = 0.35\text{--}0.54$ ) despite the fact that these rate constants also refer to rate-limiting ionization processes.

How can one explain that reactions with rate-limiting ionization have  $m$  values similar to those of  $\text{S}_{\text{N}}2$  reactions? In previous work,<sup>25</sup> we have demonstrated that the rates of the reactions of  $(\text{Ph})_2\text{CH}^+$  and  $(p\text{-MeC}_6\text{H}_4)_2\text{CH}^+$  with chloride and bromide ions in 20W80AN are diffusion limited. Consequently the combination rates of these ions must also be diffusion controlled in the less polar solvents 20W80A and 10W90A. The principle of microscopic reversibility requires transition states for the reverse reactions which correspond to the carbocations (Figure 9, left).

With this information, we can now construct the free energy diagrams for the ionization of  $(p\text{-MeC}_6\text{H}_4)_2\text{CH}-\text{Br}$  and  $(\text{lil})_2\text{CH}-\text{OAc}$  in 80% aqueous acetone. The Eyring equation allows one to calculate  $\Delta G^\ddagger = RT \ln(k_{\text{B}}T/hk) = 74.9 \text{ kJ mol}^{-1}$  (25 °C) from the solvolysis rate constant of  $(p\text{-MeC}_6\text{H}_4)_2\text{CH}-\text{Br}$  in 80% aqueous acetone ( $4.65 \times 10^{-1} \text{ s}^{-1}$ , from ref 23). As the reverse reaction is diffusion controlled, we substituted  $k_{-1} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  into the Eyring equation and arrived at a formal barrier of  $16 \text{ kJ mol}^{-1}$  for the reverse reaction (Figure 9).

For the ionization of  $(\text{lil})_2\text{CH}-\text{OAc}$  in 80% aqueous acetone,  $\Delta G^\ddagger = 71.0 \text{ kJ mol}^{-1}$  can be calculated from the ionization



**Figure 9.** Simplified free energy profiles (25 °C) for ionizations of benzhydrylium derivatives in 80% aqueous acetone (encounter complexes not specified).

constant at 25 °C listed in Table 4. Even though the  $N_{25}$  and  $s_{25}$  values given for acetate in 80% aqueous acetone in Table 3 are not very precise, the calculated rate constant of  $29.5 \text{ M}^{-1} \text{ s}^{-1}$  (for  $(\text{lil})_2\text{CH}^+ + \text{OAc}^-$ , 20W80A) can be expected to be reliable within a factor of 1.5 because application of eq 4 requires only a short extrapolation beyond the experimental range studied in Table 2 ( $\text{Ar}_2\text{CH}^+ + \text{OAc}^-$ , 20W80A). Substitution of this rate constant into the Eyring equation yields  $\Delta G^\ddagger = 64.6 \text{ kJ mol}^{-1}$  (25 °C). Though the standard free energy  $\Delta G^\circ$  of the ionic  $(\text{lil})_2\text{CH}^+ \text{OAc}^-$  is thus calculated slightly above that of the covalent compound (Figure 9), the ionization equilibrium is fully on the side of the ions at low concentrations of acetate anions, as observed during the experiments described in Table 4. The right part of Figure 9 thus describes an ionization process with a transition state which is in between a covalent ester and ionic products. As the transition state is not carbocation-like, a small value of  $m$  results (Figure 8). One implication of this result is that  $m$  cannot generally be employed to differentiate  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  processes.

**Philicity–Fugality Relationships: The Role of Intrinsic Barriers.** A further consequence of the non-carbocation-like transition states of these ionization processes are the dramatically different orders of electrofugalities (Figure 7) and electrophilicities (Chart 1, Table 2).

Table 5 compares electrophilicities and electrofugalities of different benzhydrylium ions. Because it was not possible to identify a single carboxylate ion, for which rate constants for the reactions with all benzhydrylium ions could be measured, the relative reactivities toward  $p$ -nitrobenzoate and benzoate ions were considered and the reactivity of  $(\text{thq})_2\text{CH}^+$  ( $k_{\text{rel}} = 12.3$ ) was employed to link the two series of data. It is found that the electrophilic reactivities of benzhydrylium ions toward  $\text{ArCO}_2^-$  decrease by more than 2 orders of magnitude in the series from  $(\text{dma})_2\text{CH}^+$  to  $(\text{lil})_2\text{CH}^+$ . The same order of electrophilicities has previously been observed in reactions of these carbocations with more than 100 other nucleophiles.

The relative electrofugalities of benzhydrylium ions follow a completely different order. The  $(\text{dma})_2\text{CH}^+$  cation which reacts 130 times faster with carboxylate ions than  $(\text{lil})_2\text{CH}^+$  (Table 5, top) is formed with exactly the same rate as that of the latter carbocation by heterolysis of the corresponding benzhydrylium acetate in 80% aqueous acetone (Table 5, bottom). Figure 7 shows that the electrofugality order of benzhydrylium ions shown in Table 5 is consistently found for ionizations of various

(25) Minegishi, S.; Loos, R.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2005**, *127*, 2641–2649.

**Table 5.** Comparison of Relative Electrophilicities and Relative Electrofugalities of Benzhydrylium Ions

Reaction	Relative electrophilic reactivities in acetonitrile <sup>a</sup>					
	(dma) <sub>2</sub> CH <sup>+</sup>	(pyr) <sub>2</sub> CH <sup>+</sup>	(thq) <sub>2</sub> CH <sup>+</sup>	(ind) <sub>2</sub> CH <sup>+</sup>	(jul) <sub>2</sub> CH <sup>+</sup>	(lil) <sub>2</sub> CH <sup>+</sup>
(Ar) <sub>2</sub> CH <sup>+</sup> + PNB <sup>-</sup> ↓ <i>k</i> <sub>-1</sub> (Ar) <sub>2</sub> CH-PNB	= 100	37.3	12.3	4.90		
(Ar) <sub>2</sub> CH <sup>+</sup> + BzO <sup>-</sup> ↓ <i>k</i> <sub>-1</sub> (Ar) <sub>2</sub> CH-OBz			= 12.3	5.25	1.49	0.71
	Relative electrofugalities in 20W80A <sup>b</sup>					
	(dma) <sub>2</sub> CH <sup>+</sup>	(pyr) <sub>2</sub> CH <sup>+</sup>	(thq) <sub>2</sub> CH <sup>+</sup>	(ind) <sub>2</sub> CH <sup>+</sup>	(jul) <sub>2</sub> CH <sup>+</sup>	(lil) <sub>2</sub> CH <sup>+</sup>
(Ar) <sub>2</sub> CH-OAc ↓ <i>k</i> <sub>1</sub> (Ar) <sub>2</sub> CH <sup>+</sup> + AcO <sup>-</sup>	= 100	223	151	63.1	377	101

<sup>a</sup> From Table 2. <sup>b</sup> From Table 4.

covalent benzhydryl acetates and benzoates in a variety of solvents.

The fact that *m*- and *p*-substituents in the amino-substituted benzhydrylium ions exert completely different effects on the rates of formation and consumption of these carbocations implies that forward and backward reactions cannot be described by the same Hammett substituent parameters. The  $\sigma^+$  values for the different amino groups, which have previously been derived from nucleophilic additions to these benzhydrylium ions, should therefore be considered with caution.<sup>9</sup>

It is generally assumed that stabilized carbocations, which are rapidly formed in heterolysis reactions, show low reactivities toward nucleophiles. On the other hand, less stabilized carbocations are supposed to form slowly in S<sub>N</sub>1 processes and react rapidly with nucleophiles. Extensive work by Richard on trifluoromethyl substituted carbocations had already shown that this simple relationship does not hold universally, which was attributed to differences in intrinsic barriers.<sup>7,8,26,27</sup> While, in Richard's systems, structural variations were made in direct vicinity to the reaction center, we now find that changes in intrinsic barriers may also be caused by substituent variation at positions more remote from the reaction center.

How can we explain the fact that the order of electrophilicity, as reflected by the second-order rate constants for the combination of benzhydrylium ions with carboxylate ions (Table 2), does not correlate at all with the order of electrofugality which is reflected by first-order rate constants of ionization of benzhydryl carboxylates (Table 4). Why is (lil)<sub>2</sub>CH<sup>+</sup>, the least electrophilic benzhydrylium ion of the series, not generated rapidly by the heterolytic process but is formed relatively slowly?

The Marcus equation<sup>28</sup> expresses the activation free energy of a reaction by a combination of the reaction free energy  $\Delta G^\circ$

**Table 6.**  $\Delta G^\ddagger$ ,  $\Delta G^\circ$ , and  $\Delta G_0^\ddagger$  (in kJ mol<sup>-1</sup>) for the Ionization of Ar<sub>2</sub>CH-O<sub>2</sub>CR at 25 °C<sup>a</sup>

Ar <sub>2</sub> CH <sup>+</sup>		AcO in 10W90A	AcO in 20W80A	BzO in AN	PNB in AN	DNB in AN
(lil) <sub>2</sub> CH <sup>+</sup>	$\Delta G^\ddagger$		71.0	73.1 <sup>d</sup>	66.0 <sup>e</sup>	
	$\Delta G^\circ$		6.4 <sup>c</sup>	27.4	15.8	
	$\Delta G_0^\ddagger$		67.8	58.6	57.8	
(jul) <sub>2</sub> CH <sup>+</sup>	$\Delta G^\ddagger$	70.9	67.7	70.9 <sup>d</sup>	63.1 <sup>e</sup>	
	$\Delta G^\circ$	10.8 <sup>b</sup>	5.1 <sup>c</sup>	27.0	15.5	
	$\Delta G_0^\ddagger$	65.4	65.1	56.6	55.1	
(ind) <sub>2</sub> CH <sup>+</sup>	$\Delta G^\ddagger$	74.8	72.2		67.5 <sup>d</sup>	61.1 <sup>e</sup>
	$\Delta G^\circ$	16.9 <sup>b</sup>	11.9 <sup>c</sup>		23.0	13.1
	$\Delta G_0^\ddagger$	66.0	66.1		55.4	54.4
(thq) <sub>2</sub> CH <sup>+</sup>	$\Delta G^\ddagger$	72.8	70.1		65.4 <sup>d</sup>	59.3 <sup>e</sup>
	$\Delta G^\circ$	16.8 <sup>b</sup>	11.8 <sup>c</sup>		23.1	13.5
	$\Delta G_0^\ddagger$	64.1	64.1		53.2	52.4
(pyr) <sub>2</sub> CH <sup>+</sup>	$\Delta G^\ddagger$	71.5	69.0		65.2 <sup>d</sup>	59.3 <sup>e</sup>
	$\Delta G^\circ$	17.4 <sup>b</sup>	12.5 <sup>c</sup>		25.7	15.6
	$\Delta G_0^\ddagger$	62.5	62.6		51.5	51.2
(dma) <sub>2</sub> CH <sup>+</sup>	$\Delta G^\ddagger$	72.8	71.0		69.2 <sup>d</sup>	62.4 <sup>e</sup>
	$\Delta G^\circ$	21.1 <sup>b</sup>	16.8 <sup>c</sup>		32.2	21.3
	$\Delta G_0^\ddagger$	61.8	62.4		51.9	51.1

<sup>a</sup> Note that *K* defined by Scheme 3 and eq 2 refers to the ion combination, i.e., the reverse of ionization reaction. For that reason,  $\Delta G^\circ$  for the ionization process is given by  $+RT \ln K$ . <sup>b</sup> *K* derived from experimental *k*<sub>1</sub> and *k*<sub>-1</sub>. <sup>c</sup> *K* derived from experimental *k*<sub>1</sub> and calculated (eq 4) *k*<sub>-1</sub>. <sup>d</sup> *k*<sub>1</sub> derived from experimental *K* and *k*<sub>-1</sub>. <sup>e</sup> *k*<sub>1</sub> derived from experimental *K* and calculated (eq 4) *k*<sub>-1</sub>.

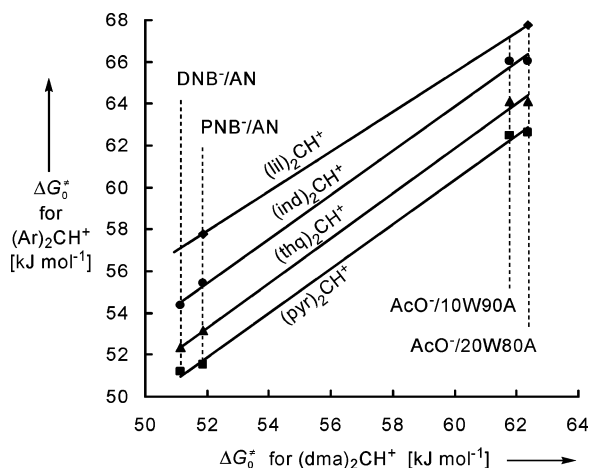
and the intrinsic barrier  $\Delta G_0^\ddagger$ , which is defined as the activation free energy of a process with  $\Delta G^\circ = 0$ . If the work term in the Marcus equation is omitted, eq 7 can be used to calculate  $\Delta G^\ddagger$  from the reaction free energy  $\Delta G^\circ$  and the intrinsic barrier  $\Delta G_0^\ddagger$ .

$$\Delta G^\ddagger = \Delta G_0^\ddagger + 0.5\Delta G^\circ + ((\Delta G^\circ)^2/16\Delta G_0^\ddagger) \quad (7)$$

For about half of the combinations of electrophiles and nucleophiles given in Table 6, rate and equilibrium constants are available from Tables 1, 2, and 4, which are converted into  $\Delta G^\circ$  and  $\Delta G^\ddagger$  values and are listed in Table 6. Substitution of

- (26) (a) Richard, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 1455–1465. (b) Amyes, T. L.; Stevens, I. W.; Richard, J. P. *J. Org. Chem.* **1993**, *58*, 6057–6066. (c) Richard, J. P.; Williams, K. B.; Amyes, T. L. *J. Am. Chem. Soc.* **1999**, *121*, 8403–8404.  
(27) Richard, J. P.; Toteva, M. M.; Crugeiras, J. *J. Am. Chem. Soc.* **2000**, *122*, 1664–1674.

- (28) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891–899. (b) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227–263.



**Figure 10.** Correlation of intrinsic barriers for the ionization of benzhydryl carboxylates in different solvents. The corresponding lines for  $(\text{jul})_2\text{CH}^+$  and  $(\text{dma})_2\text{CH}^+$  coincide with those of  $(\text{ind})_2\text{CH}^+$  and  $(\text{pyr})_2\text{CH}^+$ , respectively, and have not been drawn.

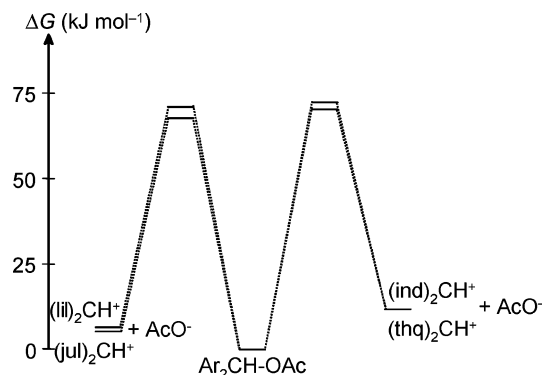
these values into the Marcus eq 7 yields the intrinsic barriers  $\Delta G_0^\ddagger$ , which are also listed in Table 6.

The high reliability of eq 4 to calculate rate constants for the reactions of benzhydrylium ions with nucleophiles also allows us to derive rate constants for the combinations of benzhydrylium ions with carboxylate ions in different solvents, which cannot directly be measured, from the  $N$  and  $s$  parameters in Table 3.

A graphical comparison of the intrinsic barriers is shown in Figure 10. As the intrinsic barriers for the ionizations of  $(\text{ind})_2\text{CH}-\text{O}_2\text{CR}$  and  $(\text{jul})_2\text{CH}-\text{O}_2\text{CR}$  as well as those for  $(\text{pyr})_2\text{CH}-\text{O}_2\text{CR}$  and  $(\text{dma})_2\text{CH}-\text{O}_2\text{CR}$  are very similar, Figure 10 presents only data for the first compound of these pairs.

One can see that, for all benzhydrylium derivatives, the intrinsic barriers increase by approximately 9–10  $\text{kJ mol}^{-1}$  when changing from dinitrobenzoates and *p*-nitrobenzoates in acetonitrile to acetates in aqueous acetone. Since the differences between intrinsic barriers for benzoates, *p*-nitrobenzoates, and 3,5-dinitrobenzoates of each of the benzhydrylium systems in  $\text{CH}_3\text{CN}$  are relatively small ( $\sim 1 \text{ kJ mol}^{-1}$ , Table 6), one has to assume that the higher barriers for the reactions of acetates in aqueous acetone are predominantly due to the change of solvents. Most likely, the increase of the intrinsic barriers in aqueous solvents reflects the higher energy of reorganization of the water molecules to solvate the ions.<sup>8,29</sup> In line with these numbers, Richard reported an intrinsic barrier of 61  $\text{kJ mol}^{-1}$  for the reactions of the acetate anion with the tritylium ion in water.<sup>27</sup>

Most intriguing is the order of intrinsic barriers for the different benzhydrylium systems. In all cases (different solvents and different nucleofuges) we find the ordering  $(\text{lil})_2\text{CH}^+ > (\text{ind})_2\text{CH}^+ \approx (\text{jul})_2\text{CH}^+ > (\text{thq})_2\text{CH}^+ > (\text{pyr})_2\text{CH}^+ \approx (\text{dma})_2\text{CH}^+$  (Figure 10). If one assumes a 10% error in the experimentally determined rate and equilibrium constants and an accumulation of the errors, the maximum absolute error of  $\Delta G_0^\ddagger$  would be 1  $\text{kJ mol}^{-1}$ . The equal ranking of the different compounds in Figure 10 indicates that the relative magnitudes of the intrinsic barriers  $\Delta G_0^\ddagger$  are even more accurate. An error limit of  $< 1 \text{ kJ mol}^{-1}$  for the relative magnitudes of  $\Delta G_0^\ddagger$



**Figure 11.** Gibbs free energy profiles (25 °C) for the reactions of the acetate ion with benzhydrylium ions in 20W80A.

obviously holds also for intrinsic barriers which are derived from calculated rate constants (eq 4), because intrinsic barriers derived from experimental and calculated rate constants show exactly the same regularity in Figure 10.

It is evident that compounds with benzo-annulated five-membered rings, i.e.,  $(\text{lil})_2\text{CH}^+$  and  $(\text{ind})_2\text{CH}^+$  have higher intrinsic barriers than their six-membered ring analogues  $(\text{jul})_2\text{CH}^+$  and  $(\text{thq})_2\text{CH}^+$ , respectively (see structures in Chart 1). While we presently do not understand the reason for the different intrinsic barriers for the different ring sizes, it is obvious that these differences are responsible for the breakdown of the rate–equilibrium relationships.

As reported in Table 6 and illustrated in Figure 11, the ionizations of  $(\text{lil})_2\text{CH}-\text{OAc}$  and  $(\text{jul})_2\text{CH}-\text{OAc}$  have similar reaction free energies  $\Delta G^\circ$ . Because  $(\text{jul})_2\text{CH}-\text{OAc}$  has a lower intrinsic barrier than  $(\text{lil})_2\text{CH}-\text{OAc}$ ,  $(\text{jul})_2\text{CH}-\text{OAc}$  ionizes 3.7 times faster and at the same time  $(\text{jul})_2\text{CH}^+$  reacts 2.3 faster with nucleophiles than  $(\text{lil})_2\text{CH}^+$  in 20W80A (Figure 11). Similar rate ratios are found for other carboxylates. Analogously the ionizations of  $(\text{ind})_2\text{CH}-\text{OAc}$  and  $(\text{thq})_2\text{CH}-\text{OAc}$  have similar values of  $\Delta G^\circ$ , and the higher electrophilic reactivity of  $(\text{thq})_2\text{CH}^+$  (Figures 4 and 6) as well as the higher ionization rates of the  $(\text{thq})_2\text{CH}$ -esters compared with the  $(\text{ind})_2\text{CH}$ -esters (Figure 7) are again caused by different intrinsic barriers (Figure 11).

Accidentally, the ionizations of  $(\text{ind})_2\text{CH}-\text{O}_2\text{CR}$  and  $(\text{jul})_2\text{CH}-\text{O}_2\text{CR}$  have almost the same intrinsic barriers (Table 6). The higher ionization rate of  $(\text{jul})_2\text{CH}-\text{O}_2\text{CR}$  as well as the lower electrophilic reactivity of  $(\text{jul})_2\text{CH}^+$  are, therefore, a consequence of the better stabilization of the  $(\text{jul})_2\text{CH}^+$  ion compared with  $(\text{ind})_2\text{CH}^+$ . As we are presently unable to predict the relative magnitudes of the intrinsic barriers, we cannot generally derive information about relative carbocation stabilities from kinetic data, unless the reverse reaction (ion recombination) occurs without a barrier.

## Conclusion

From the excellent correlation between the averaged electrophilic reactivities of the carbocations toward a large variety of nucleophiles and the ethanolysis rate constants of the corresponding alkyl chlorides we had previously concluded that carbocation electrophilicity is inversely related to electrofugality.<sup>5,23,30</sup>

(29) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 3219–3234.

(30) Mayr, H.; Patz, M.; Gotta, M. F.; Ofial, A. R. *Pure Appl. Chem.* **1998**, *70*, 1993–2000.

This opinion now requires revision. Obviously, the inverse relationship between electrophilicity and electrofugality holds only for carbocations which are less stabilized than 4,4'-dimethoxy benzhydrylium ions though even in this range some exceptions have been reported. If better stabilized carbocations are considered (in this work amino-substituted benzhydrylium ions), ionization rates are largely controlled by differences in intrinsic barriers, and simple rate-equilibrium relationships break down. Further work must focus on the origin of the intrinsic barriers.

**Acknowledgment.** Dedicated to Professor Sema L. Ioffe on the occasion of his 70th birthday. We thank Prof. T. W. Bentley and Dr. A. R. Ofial for discussions and the Deutsche Forschungsgemeinschaft (Ma 673-20) and the Fonds der Chemischen Industrie for financial support.

**Supporting Information Available:** Details of kinetic experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0765464