Dissertation zur Erlangung des Doktorgrades der Fakultät für
Chemie und Pharmazie der Ludwig-Maximilians-Universität München

Changes in Solvolysis Mechanisms:
From Classical S_N1 Reactions
to Persistent Ion Conditions

Dipl. Chem. Heike Schaller

aus

Bremen

München, 2008

Erklärung

Diese Dissertation wurde im Sinne von § 13 Abs. 3 der Promotionsordnung vom 29. Januar 1998 von Herrn Prof. Dr. Herbert Mayr betreut.

Ehrenwörtliche Versicherung

Diese Dissertation wurde selbstständig und ohne unerlaubte Hilfe erarbeitet.

München, 04.09.2008

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Heike F. Schaller

Dissertation eingereicht am 04.09.2008

1. Gutachter	Prof. Dr. Herbert Mayr
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Mündliche Prüfung am 15.10.2008

Für

meine Eltern & Olli

Danksagung

Mein besonderer Dank gilt Herrn Prof. Dr. Herbert Mayr für die Überlassung des interessanten Themas, seiner Diskussionsbereitschaft und Unterstützung während der Anfertigung dieser Arbeit sowie für die Bereitstellung der hervorragenden experimentellen Bedingungen.

Allen Mitgliedern des Arbeitskreises möchte ich für das ausgezeichnete Arbeitsklima und die tolle Zusammenarbeit danken.

Mein besonderer Dank gilt meinen aktuellen und ehemaligen Kollegen Martin Breugst, Alexander Tishkov, Erik Bräuer, Florian Seeliger sowie Nicolas Streidl für die stetigen Diskussionen und Gespräche, auch abseits der Chemie.

Herrn Prof. Dr. Eberhard Riedle und besonders Uli Schmidhammer sei für die gute Zusammenarbeit bei unserem Cyanat-Projekt gedankt.

Frau Prof. Dr. Cinzia Chiappe danke ich für die Zeit, die ich in ihrer Arbeitsgruppe in Pisa forschen durfte und ihren Mitarbeitern, insbesondere Herrn Bernardo Melai, für die angenehme Arbeitsatmosphäre und die freundliche Aufnahme.

Für die schnelle und kritische Durchsicht dieser Arbeit sei Oliver Kaumanns, Martin Breugst, Patrick Kaumanns, Nicolas Streidl, Roland Appel und Dorothea Richter gedankt.

Meinen Eltern und meinem Freund danke ich vor allem für die immerwährende und bedingungslose Unterstützung.

Publikationen

Direct Observation of the Ionization Step in Solvolysis Reactions: Electrophilicity versus Electrofugality of Carbocations
H. F. Schaller, A. A. Tishkov, X. Feng, H. Mayr, *J. Am. Chem. Soc.* **2008**, *130*, 3012-3022.

"Carbokationen-Watching" bei Solvolyse-Reaktionen
"Carbocation Watching" in Solvolysis Reactions
H. F. Schaller, H. Mayr, *Angew. Chem.* **2008**, *120*, 4022-4025; *Angew. Chem. Int. Ed.* **2008**, *47*, 3958-3961.

Ambident Reactivity of the Cyanate Anion
H. F. Schaller, U. Schmidhammer, E. Riedle, H. Mayr, *Chem. Eur. J.* **2008**, *14*, 3866-3868.

Konferenzbeitrag

Direct Observation of Intermediate Carbocations in Solvolysis Reactions
Posterpräsentation auf dem European Symposium on Organic Reactivity XI, 2007

List of Abbreviations

A	acetone
abs.	absolute
AN	acetonitrile
aq.	aqueous
Bu	butyl
calc.	calculated
cf.	confer
conc.	concentrated
d	doublet
E	electrophilicity parameter
E	ethanol
EA	elementary analysis
Et	ethyl
EtOAc	ethyl acetate
eq.	equivalent(s)
exp.	experimental
h	hour(s)
i.e.	id est
i. vac.	in vacuo
k	rate constant
lit.	literature
M	mol/L
M	methanol
Me	methyl
min	minute(s)
mp	melting point
MS	mass spectrometry
N	nucleophilicity parameter
NMR	nuclear megnetic resonance
Ph	phenyl
q	quartet
Rf	retention factor
s	nucleophile specific slope parameter
s	singlet
t	triplet
UV	ultra violett
Vis	visible
vs.	versus
W	Water

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Summary

Nucleophilicity of Carboxylates

Rates and equilibria of the reactions of highly stabilized amino-substituted benzhydrylium ions (Ar_2CH^+ **1,** $-5 > E > -10$) with carboxylate ions (RCO_2^- **2**: acetate AcO^-, benzoate BzO^-, *p*-nitrobenzoate PNB^-, and 3,5-dinitrobenzoate DNB^-) have been determined photometrically in acetone and acetonitrile solutions.

Scheme 0.1. Reactions of Benzhydrylium Ions **1** with Carboxylates **2** at 25 °C.

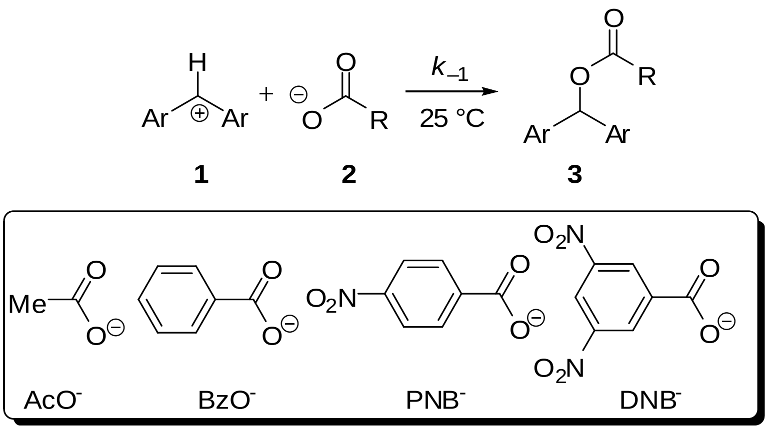


Table 0.1. Employed Benzhydrylium Ions Ar_2CH^+ and Their Electrophilicity Parameters *E*.

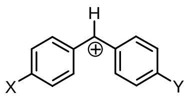
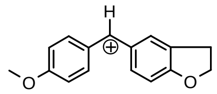
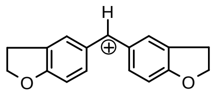
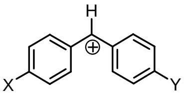
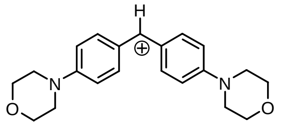
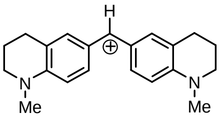
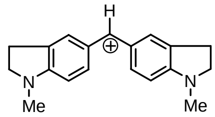
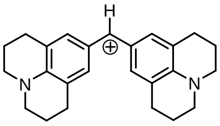
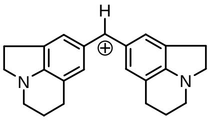
			
Ar_2CH^+	X	Y	*E*
$(ani)_2CH^+$	OCH_3	OCH_3	0.00
$(fur)(ani)CH^+$			–0.56
$(dma)(Ph)CH^+$	$N(CH_3)_2$	H	–[a]
$(fur)_2CH^+$			–1.36
$(pfa)_2CH^+$	$N(Ph)CH_2CF_3$	$N(Ph)CH_2CF_3$	–3.14

Table 0.1. *Continued.*



Ar_2CH^+	X	Y	*E*
$(mfa)_2CH^+$	$N(CH_3)CH_2CF_3$	$N(CH_3)CH_2CF_3$	–3.85
$(dpa)_2CH^+$	NPh_2	NPh_2	–4.72
$(mor)_2CH^+$			–5.53
$(mpa)_2CH^+$	$N(Ph)CH_3$	$N(Ph)CH_3$	–5.89
$(dma)_2CH^+$	$N(CH_3)_2$	$N(CH_3)_2$	–7.02
$(pyr)_2CH^+$	$N(CH_2)_4$	$N(CH_2)_4$	–7.69
$(thq)_2CH^+$			–8.22
$(ind)_2CH^+$			–8.76
$(jul)_2CH^+$			–9.45
$(lil)_2CH^+$			–10.04

[a] not determined.

Plots of the logarithmic second-order rate constants log k_{-1} of the reactions of benzhydrylium ions **1** with carboxylates **2** vs. the electrophilicity parameter *E* resulted in linear correlations (Figure 0.1).

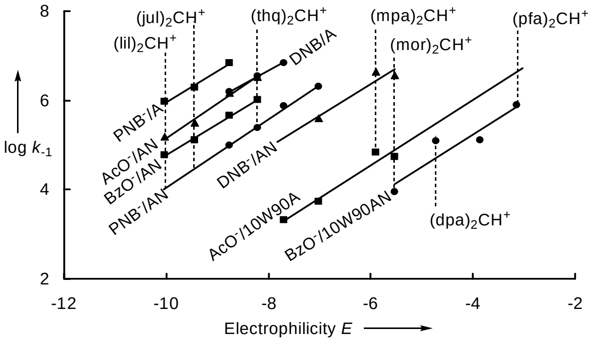


Figure 0.1. Correlations of the second-order rate constants k_{-1} (25 °C) for the combination of benzhydrylium ions **1** with carboxylate ions **2** in different solvents. A = acetone, AN = acetonitrile, W = water.

The obtained second-order rate constants k_{-1} (Scheme 0.1) have been employed to determine the nucleophilicity parameters s and N of the carboxylate ions at 25 °C, according to the linear free-energy relationship 0.1.

$$\log k = s(N + E) \qquad (0.1)$$

In this equation, the electrophiles are characterized by the electrophilicity parameter E and nucleophiles are characterized by a nucleophilicity parameter N and a nucleophile-specific slope-parameter s.

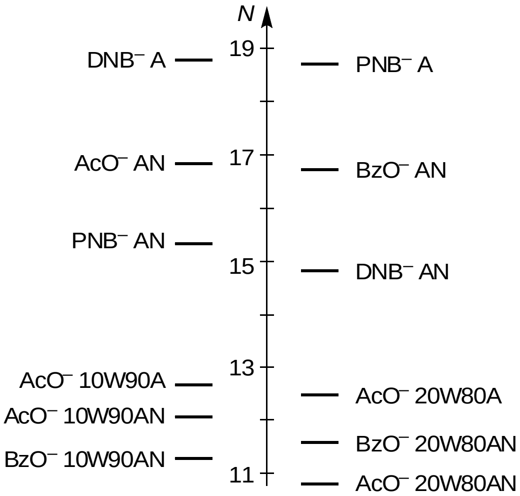


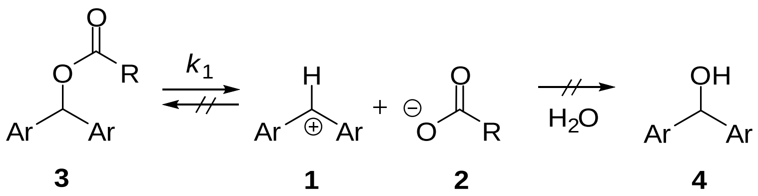
Figure 0.2. Comparison of the nucleophilicity parameters N of the carboxylates **2** in different solvents at 25 °C.

The nucleophilicity parameters N of the carboxylates are in the range of $13 > N > 10$ for aqueous solvents, and in the range of $19 > N > 14$ for pure acetone and acetonitrile.

Direct Observation of the Ionization Step in Solvolysis Reactions of Benzhydrylium Carboxylates

Kinetics of the ionization of benzhydryl carboxylates ($Ar_2CH\text{-}O_2CR$ **3**) have been studied photometrically (formation of the colored amino-substituted benzhydrylium ions Ar_2CH^+ **1** $-6 > E > -10$) by adding water to the colorless solutions of $Ar_2CH\text{-}O_2CR$ **3** in acetone or acetonitrile.

Scheme 0.2. Ionization of Benzhydrylium Carboxylates **3** in Aqueous Acetone and Acetonitrile Mixtures at 25 °C.



The resulting colored benzhydrylium ions **1** did not undergo subsequent reactions with the solvent or reactions with the carboxylate ions. One could, therefore, directly measure the first step of S_N1 reactions (exemplarily depicted in Figure 0.3 for the ionization of $(jul)_2$CH-OAc **5** in 20W80AN).

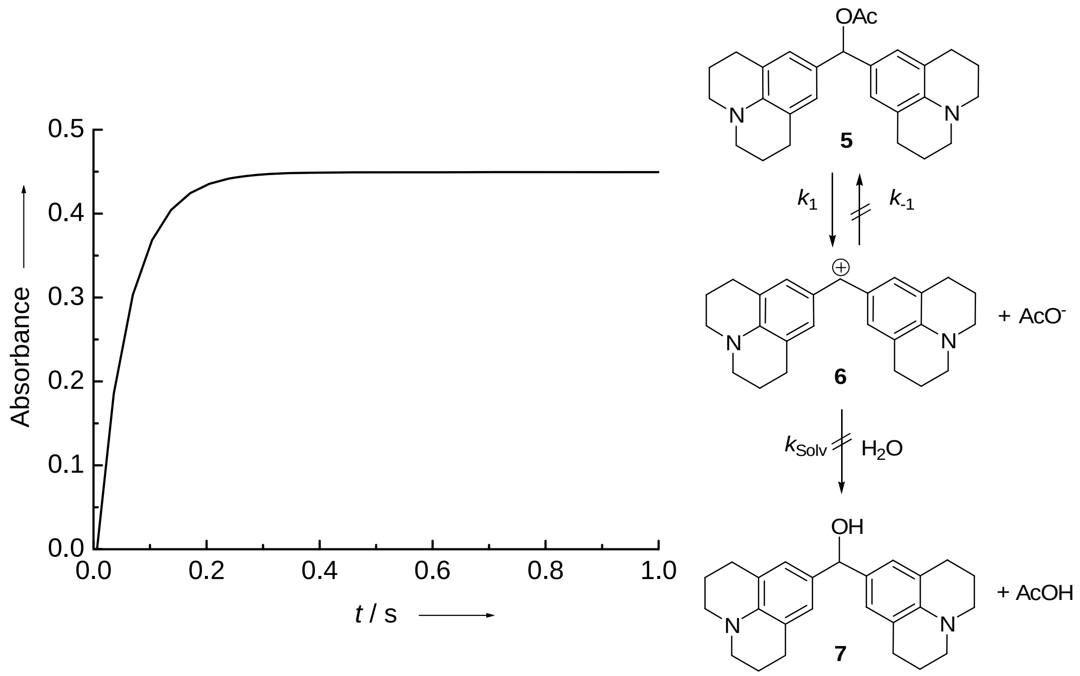


Figure 0.3. Increase of the absorbance at 632 nm (λ_{max} of $(jul)_2CH^+$ **6**) during the heterolysis of $(jul)_2$CH-OAc **5** in 80 % aqueous acetonitrile.

As shown in Figure 0.4, the logarithmic first-order rate constants log k_1 of the ionizations of benzhydryl carboxylates **3** in different solvents were linearly correlated with each other.

Complete free-energy profiles for the ionization of benzhydryl carboxylates Ar_2CH-O_2CR **3** have been constructed, which demonstrate that the transition states of the ionizations are not carbocation-like in contrast to the transition states of benzhydryl halides, which ionize with similar rate constants k_1 (Figure 0.5).

Variation of the solvent-ionizing power *Y* showed 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 S_N2 type mechanism (Figure 0.6).

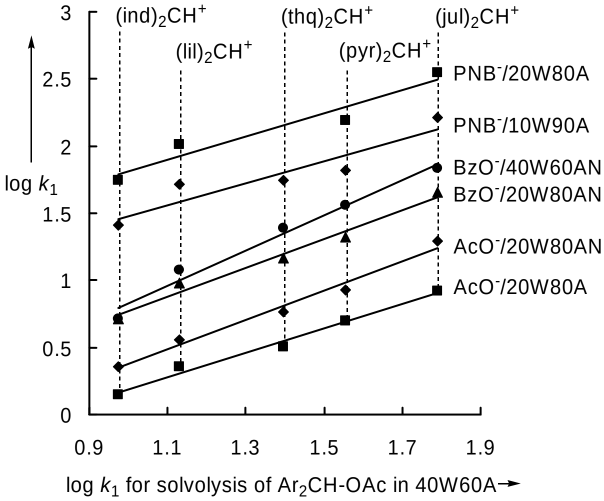


Figure 0.4. Correlation of ionization rate constants of $Ar_2CH\text{-}O_2CR$ in different solvents at 25 °C.

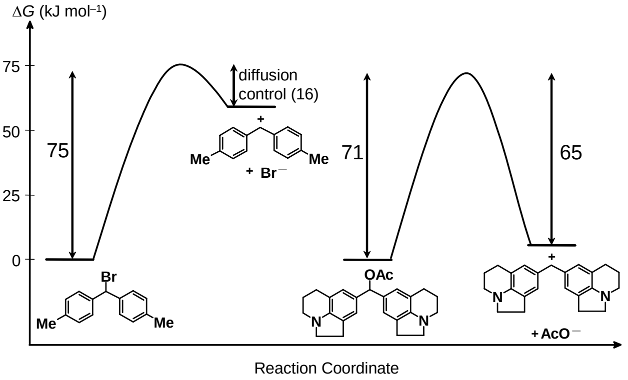


Figure 0.5. Simplified free energy profiles (25 °C) for ionizations of benzhydrylium derivatives in 80% aqueous acetone.

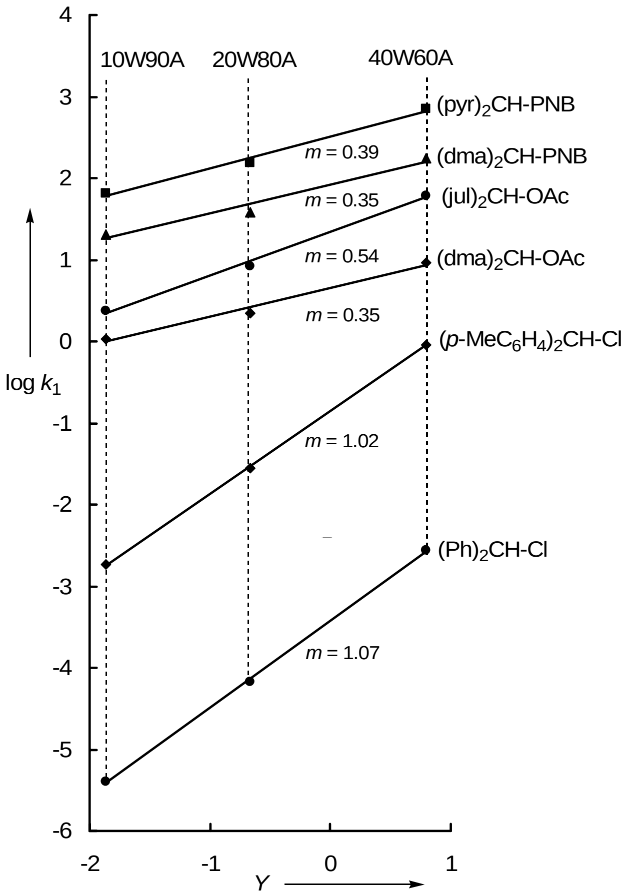


Figure 0.6. Plots of rate constants for ionization k_1 of some benzhydryl derivatives against the solvent ionizing power *Y*.

The electrofugality order, i.e., the relative ionization rates of benzhydryl esters $Ar_2CH\text{-}O_2CR$ **1** with the same anionic leaving group, is not correlated with the corresponding electrophilicity order, i.e., the relative reactivities of the corresponding benzhydrylium ions Ar_2CH^+ **2** towards a common nucleophile (exemplarily depicted in Figure 0.7 for benzhydryl benzoates). Thus, benzhydrylium ions, which are produced with equal rates by ionization of the corresponding covalent esters may differ by more than two orders of magnitude in their reactivities towards nucleophiles like carboxylate ions.

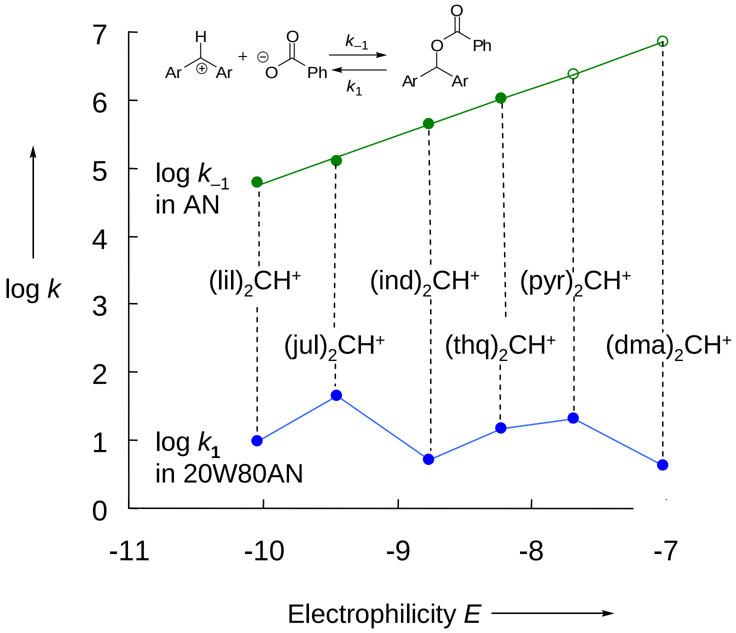
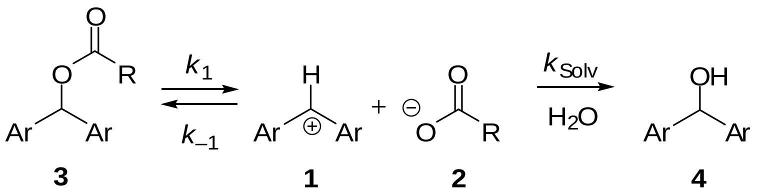


Figure 0.7. Comparison of electrophilicities (k_{-1}) and electrofugalities (k_1) of benzhydrylium ions (at 25 °C; open circles for log k_{-1} were extrapolated by equation 0.1)

“Carbocation Watching”: Ionization of Benzhydrylium Carboxylates and Subsequent Reactions of the Resulting Benzhydrylium Ions

Kinetics of the solvolyses of benzhydryl carboxylates **3** have been studied photometrically in aqueous acetone or aqueous acetonitrile. Treatment of some covalent benzhydryl acetates and benzhydryl *p*-nitrobenzoates with aqueous acetone or acetonitrile gave the colored benzhydrylium ions Ar_2CH^+ **1** ($-6 > E > -5$) in the first step, which underwent slower subsequent reactions with the solvent.

Scheme 0.3. Ionization of Benzhydrylium Carboxylates **3** in Aqueous Acetone and Acetonitrile Mixtures at 25 °C and Subsequent Reactions of the Intermediate Benzhydrylium Ion.



It was possible to derive the three rate constants involved (Scheme 0.3) from the absorbance/time correlations. The rate constants k_1, k_{-1} and k_{Solv} derived by fitting the curves (exemplarily depicted in Figure 0.8) to the mechanistic model in Scheme 0.3 are in agreement with those of discrete experiments. Therefore, in these cases it is possible to derive the three rate constants k_1, k_{-1} and k_{Solv} from only one measurement. Figure 0.8 shows the typical S_N2C^+ reaction characteristics of accumulation and consumption of the benzhydrylium ions (exemplarily depicted for the solvolysis of $(\mathrm{mor})_2\mathrm{CH}$-PNB **5** in 20W80A). One can see the increasing importance of the reverse reaction, i.e., the combination of the benzhydrylium ion with carboxylate ions, as $[\mathrm{RCO_2}^-]_0$ increases.

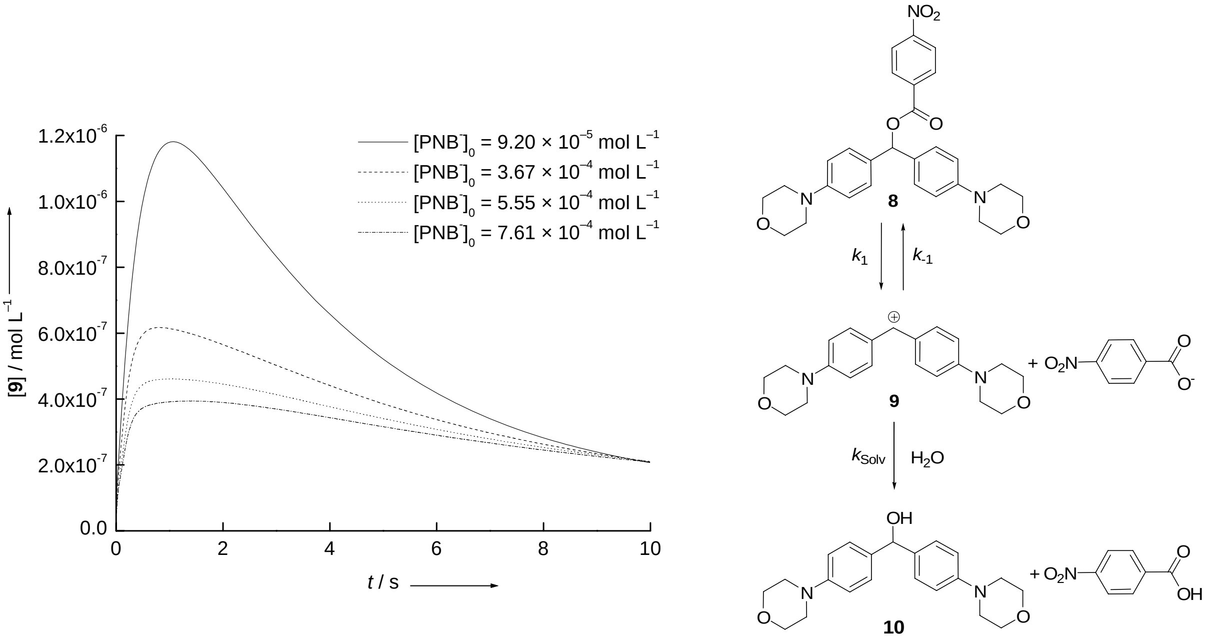


Figure 0.8. Formation and consumption of the blue $(\mathrm{mor})_2\mathrm{CH}^+$ **9** (monitored photometrically at 612 nm) during the heterolysis of $(\mathrm{mor})_2\mathrm{CH}$-PNB **8** ($1.04 \times 10^{-5}$ mol L^{-1}) in 80 % aqueous acetone in the presence of different amounts of $n\text{-}\mathrm{Bu_4N^+PNB^-}$ at 25 °C.

Electrofugality of Donor-Substituted Benzhydrylium Ions and Nucleofugality of Carboxylate Ions

Covalent benzhydryl carboxylates **3** of benzhydrylium ions ($0 > E > -5$) have been synthesized. The kinetics of the solvolysis in aqueous acetone and acetonitrile have been studied conductimetrically at 25 °C.

As shown in Figure 0.4, the logarithmic first-order rate constants log k_1 of the ionizations of benzhydryl carboxylates **3** in different solvents were linearly correlated with each other. The internal consistency of the ionization rate constants determined by different methods (log $k_1 > -1$ by UV-Vis, log $k_1 < -1$ by conductivity) is shown by the fact that the two set of data follow the same correlations (Figure 0.9)

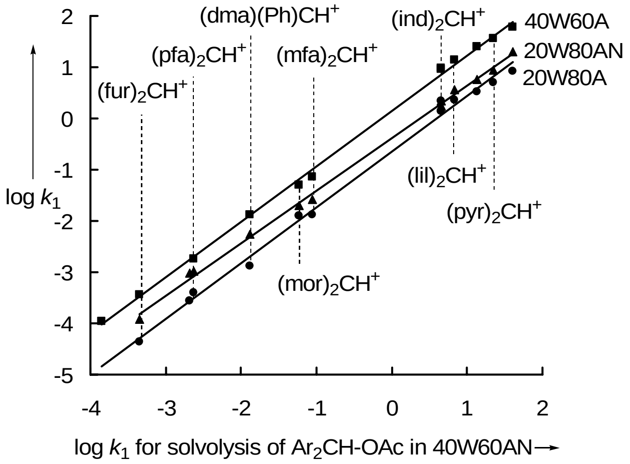


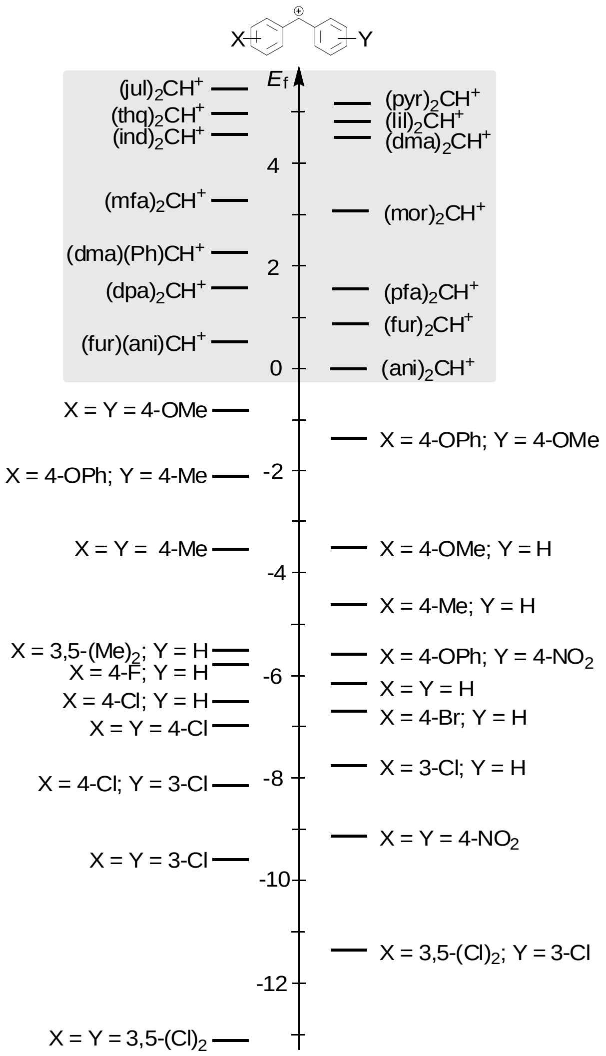
Figure 0.9. Correlation of ionization rate constants of Ar$_2$CH-OAc in different solvents.

The obtained rate constants k_1 have been used to link the different data sets and construct an electrofugality scale up to highly stabilized benzhydrylium ions according to the linear free energy relationship eq 0.2, which has recently been proposed to estimate heterolysis rate constants of benzhydryl derivatives in various solvents.

$$\log k_{(25\,°\mathrm{C})} = s_f(N_f + E_f) \qquad (0.2)$$

In these correlations, electrofuges are characterized by the electrofugality parameter E_f, whereas nucleofuges are described by a nucleofugality parameter N_f and a nucleophile-specific slope-parameter s_f.

The electrofugality parameters now cover a range of approximately 18 orders of magnitude.



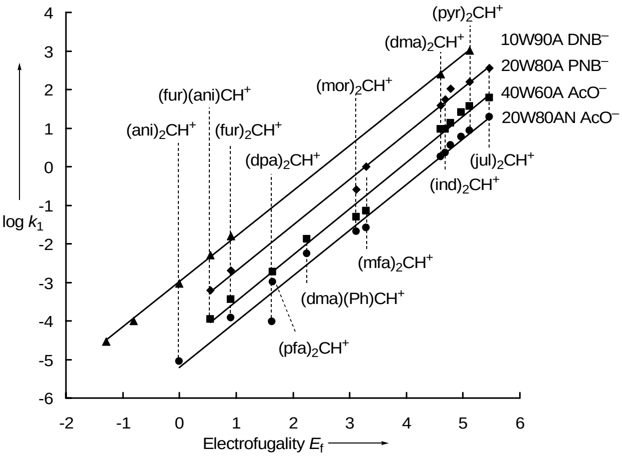


Figure 0.11. Correlation of log k_1 (25 °C) versus the new E_f parameters for donor substituted benzhydrylium ions.

Figure 0.10. Comparison of the electrofugality parameters E_f of the benzhydrylium ions **1**.

A comparison of the electrophilicity parameters E of the benzhydrylium ions (Table 0.1) with the electrofugality parameters E_f shows a tremendous aberration from the earlier assumption $E \approx -E_f$.

For $E < 0$, this assumption becomes invalid, and the electrofugalities reach a plateau at $E < -7$ (Figure 0.12). In contrast to earlier assumptions, it cannot generally be assumed that the rates of S_N1 solvolyses always reflect the carbocation stabilities.

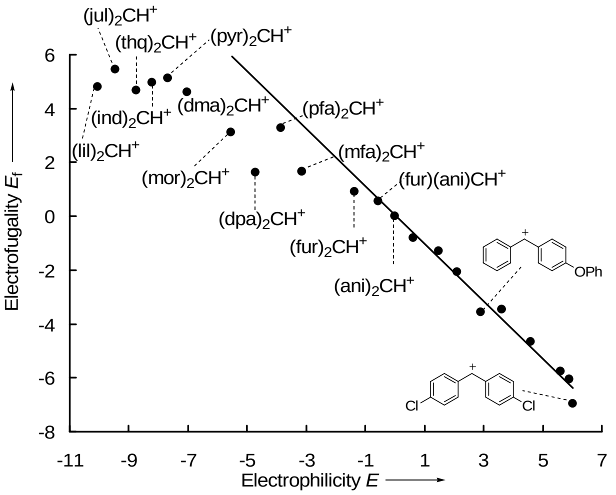


Figure 0.12. Comparison of E and E_f values of several benhzhydrylium ions.

The extended electrofugality scale was employed to fix nucleofugality parameters for carboxylates and other important leaving groups according to eq 0.2 (Figure 0.13).

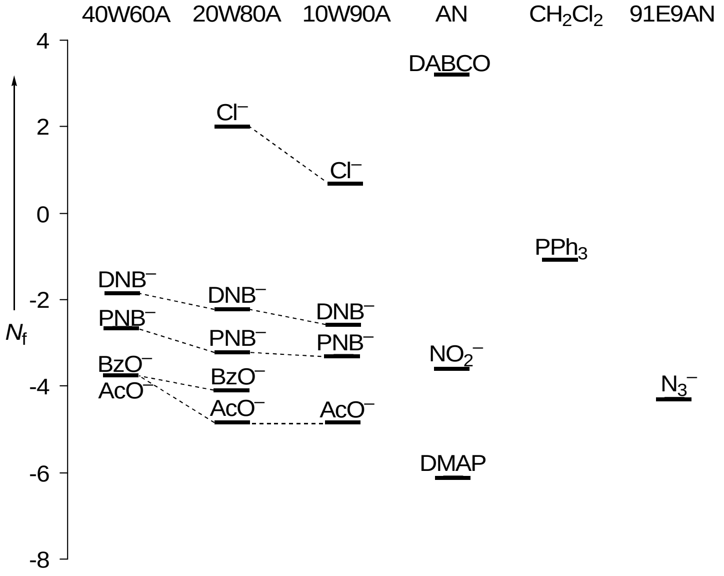


Figure 0.13. Comparison of N_f values of carboxylate ions with several common leaving groups.

Figure 0.14 summarizes the different solvolysis mechanisms observed in this work. In aqueous acetone or acetonitrile, covalent benzhydryl carboxylates derived from benzhydrylium ions with $-6 > E > -10$ ionize with formation of persistent carbocations, which do not undergo subsequent reactions with the solvent ("irreversible ionizations"). For $-5 > E > -6$, accumulation and consumption of the benzhydrylium ions is observed ("S_N2C^+ reactions"). If $E > -5$, the intermediate carbocations are not visible due to the fast subsequent reaction with the solvent ("conventional S_N1").

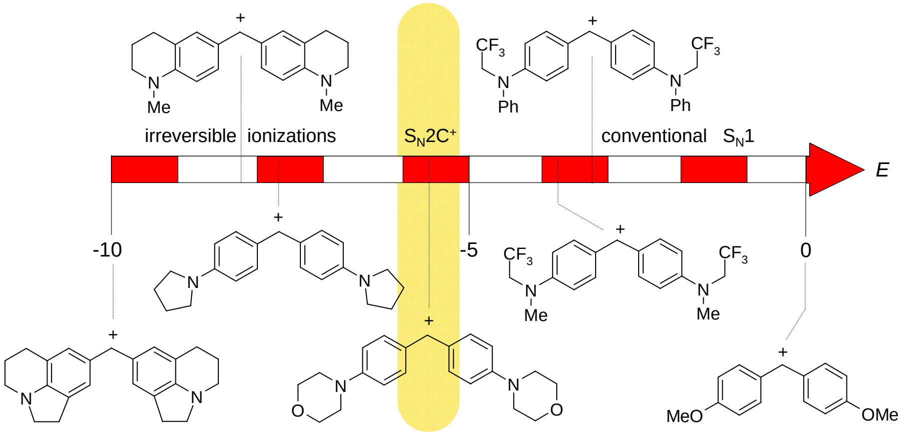
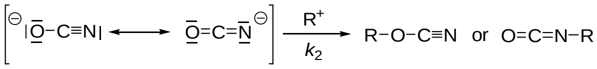


Figure 0.14. Heterolysis reactions of benzhydryl carboxylates in aqueous acetone or acetonitrile.

Ambident Reactivity of the Cyanate Ion

The kinetics of the reactions of the ambident cyanate ion with benzhydrylium ions have been studied photometrically in acetonitrile at 20 °C by stopped-flow and Laser flash technique.

Scheme 0.4. Ambident Reactions of the Cyanate Ion.



The second order rate constants log k_2 correlate linearly with the electrophilicity parameters of the benzhydrylium ions in the range of $-2 > E > -10$ and reach the diffusion limit for $E > 0$ (Figure 0.15).

The fact that the rate constants determined by the stopped-flow and the Laser flash technique are on the same correlation line shows the internal consistency of our kinetic measurements, and from the linear part of this graph we derived $N = 13.60$ and $s = 0.84$ for OCN^- in acetonitrile.

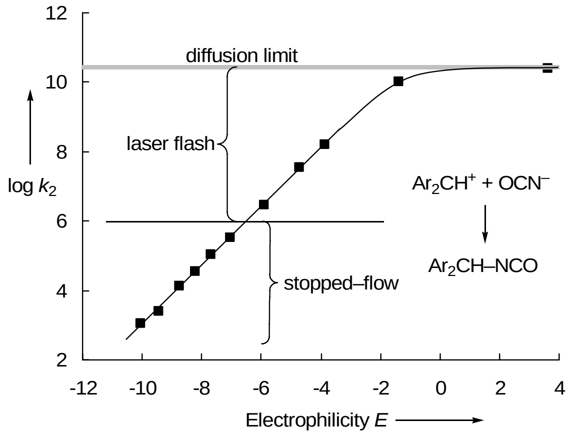


Figure 0.15. Plot of log k_2 for the reactions of the cyanate ion with several benzhydrylium ions in acetonitrile at 20 °C versus their electrophilicity parameters E.

Product studies showed that benzhydryl isocyanates are exclusively formed by N-attack at the cyanates. The continous correlation line shown in Figure 0.15 indicates that the rate-determining step does not change throughout this reaction series. Because only single exponential decays were monitored, a potential accompanying fast and reversible O-attack can only give low concentrations of the intermediate benzhydryl cyanates, which are kinetically irrelevant.

Introduction

For categorizing polar organic species and their reactions,[1] Ingold introduced the terms "electrophiles" and "nucleophiles" (greek: *philos* = friend), standing for electron-deficient and electron-rich species, respectively.

Trying to quantify these terms, many attempts have been made to establish general concepts of electrophilicity and nucleophilicity. In 1953, Swain and Scott[2] found a constant order of reactivity for different nucleophilic reagents towards different substrates in S_N2 reactions. However, the spread in relative rates varied widely from one substrate to another. Later, Ritchie reported that for the reactions of carbocations and diazonium ions with nucleophiles, the relative rate constants of two nucleophiles do not depend on the absolut reactivities of the electrophiles. He constructed a reactivity scale for nucleophiles, which covered a large range of reactivity and made it possible to calculate rate constants from only two parameters – one for the electrophile and one for the nucleophile.[3] Later it was shown that different classes of electrophiles show substantial variations in relative reactivities towards the nucleophiles and are better treated separately.[4]

In 1994, Mayr and Patz established a linear-free-energy relationship (eq 1.1) on the basis of a comprehensive correlation analysis.[5] Eq 1.1 allows the prediction of reactions of carbocations with π-, σ- and n-nucleophiles with only three parameters.

$$\log k_{(20\,^\circ\mathrm{C})} = s(N + E) \qquad (1.1)$$

E and N are the electrophilicity and the nucleophilicity parameters, respectively, and s is the nucleophile-specific slope parameter. Hundreds of nucleophiles and about 100 electrophiles have been characterized so far by applying eq 1.1.

For solvolysis reactions, which follow an S_N1 mechanism, one usually expects a slow rate determining ionization step, that is followed by a fast subsequent trapping of the intermediate carbocations by the solvent (Scheme 1.1). According to IUPAC, the leaving group that takes along the binding ion pair is called “nucleofuge” (X^-, Scheme 1.1), and the “electrofuge” is defined as the leaving group, which does not take along the ion pair (R^+, Scheme 1.1).[6]

Scheme 1.1.

$$\mathrm{R{-}X} \rightleftharpoons \mathrm{R^+} + \mathrm{X^-} \xrightarrow{\mathrm{HOSolv}} \mathrm{R{-}OSolv} + \mathrm{HX}$$

In 2002, Minegishi and Mayr showed that it can be possible to directly observe the two steps of a solvolysis reaction.[7] Afterwards, they reported that S_N1 solvolyses with inverted rate profiles, i.e., a fast ionization step and a slow subsequent reaction with the solvent (so-called S_N2C^+ solvolyses[8]), can occur when derivatives of better stabilized carbocations are investigated.[9]

For a comprehensive description of the ionization step of S_N1 solvolyses, a linear-free-energy relationship (eq 1.2), similar to eq 1.1, has been proposed in 2004.[9]

$$\log k_{(25\ °\mathrm{C})} = s_f(N_f + E_f) \qquad (1.2)$$

Nucleofuge-specific parameters s_f and N_f refer to combinations of the anionic leaving group and the solvent, whereas the electrofugality of the carbocation is characterized by E_f.

The goal of this thesis was the characterization of the electrofugalities of amino-substituted benzhydrylium ions and the search for so-called S_N2C^+ solvolyses, where the benzhydrylium ions have a significant lifetime in the solvent and can be observed directly by photometrical methods. Another objective was the investigation of the ambident reactivity of the cyanate ion.

As major parts of this thesis have already been published, individual introductions will be given at the beginning of each chapter. Unpublished investigations are reported in chapter 4.

References

(1) a) Ingold, C. K. *Recl. Trav. Pays-Bas* **1929**, *42*, 797-812. b) Ingold, C. K. *J. Chem. Soc.* **1933**, 1120-1127. c) Ingold, C. K. *Chem. Rev.* **1934**, *15*, 225-274.

(2) Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141-147.

(3) a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348-354. b) Ritchie, C. D.; van Verth, J. E.; Virtanene, P. O. I. *J. Am. Chem. Soc.* **1982**, *104*, 3491-3497. c) Ritchie, C. D. *J. Am. Chem. Soc.* **1984**, *106*, 7187-7194.

(4) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239-2250.

(5) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990-1010; *Angew Chem. Int. Ed.* **1994**, *33*, 938-955.

(6) McNaught, A. D.; Wilkinson, A. *IUPAC Compendium of Chemical Terminology*, *2 ed*, Blackwell Science, New York, **1997**.

(7) Mayr, H.; Minegishi, S. *Angew. Chem.* **2002**, *114*, 4674-4676; *Angew. Chem. Int. Ed.* **2002**, *41*, 4493-4495.

(8) Gelles, E.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1954**, 2918-2929.

(9) Denegri, B.; Minegishi, S.; Kronja, O.; Mayr, H. *Angew. Chem.* **2004**, *116*, 2353-2356; *Angew. Chem. Int. Ed.* **2004**, *43*, 2302-2305.

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

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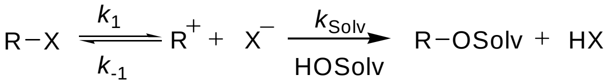
Introduction

Kinetic investigations of solvolysis reactions have been a major source for the development of electronic theory of Organic Chemistry.[1] In typical S_N1 solvolysis reactions (Scheme 1), the carbocation 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 RX or of the products ROSolv or HX as a function of time.

Scheme 2.1.

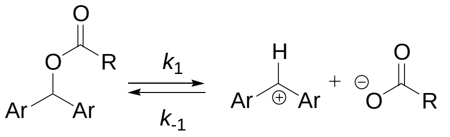


$$\mathrm{R{-}X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R^+ + X^-} \xrightarrow[\mathrm{HOSolv}]{k_{\mathrm{Solv}}} \mathrm{R{-}OSolv + HX}$$

However, as initially pointed out by Winstein,[2] the observed gross rate constant k_{obs} often is a complex quantity. Since the S_N1 reaction (Scheme 2.1) may be affected by nucleophilic solvent participation or accompanied by S_N2 processes, there has been much controversy about the mechanism of solvolysis reactions, which is still ongoing.[3,4]

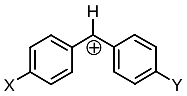
In recent work,[5] we have reported the change from the typical S_N1 mechanism (Scheme 1, $k_1 < k_{\mathrm{solv}}$) to the so-called S_N2C^+ mechanism[6] (Scheme 1, $k_1 > k_{\mathrm{solv}}$), where ionization is faster than the subsequent reaction with the solvent. In the latter case, the intermediate carbocation R^+ may accumulate. If the ionization equilibrium $k_1/(k_{-1}[X^-])$ 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 2.1) derived from the benzhydrylium ions listed in Chart 2.1.

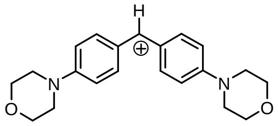
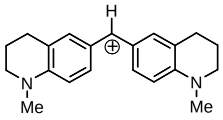
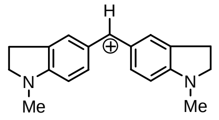
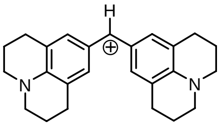
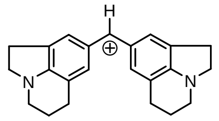
In addition, we will report on the direct determination of the rates of the reverse reactions as well as of some of the relevant equilibrium constants. By combining these pieces of information we will arrive at complete free-energy profiles for solvolysis reactions of benzhydryl carboxylates, which allow us to determine the intrinsic barriers[7,8] for ionization processes. It will be shown that, in contrast to intuition and earlier assumptions,[5] there is no significant correlation between the rates of ionization of benzhydryl carboxylates and the electrophilic reactivities of the resulting carbocations.



(2.1)

Chart 2.1. Benzhydrylium Ions Ar_2CH^+ and their Electrophilicity Parameters *E*.



Ar_2CH^+	X	Y	*E*[a]
$(pfa)_2CH^+$	$N(Ph)CH_2CF_3$	$N(Ph)CH_2CF_3$	–3.14
$(mfa)_2CH^+$	$N(CH_3)CH_2CF_3$	$N(CH_3)CH_2CF_3$	–3.85
$(dpa)_2CH^+$	NPh_2	NPh_2	–4.72
$(mor)_2CH^+$			–5.53
$(mpa)_2CH^+$	$N(Ph)CH_3$	$N(Ph)CH_3$	–5.89
$(dma)_2CH^+$	$N(CH_3)_2$	$N(CH_3)_2$	–7.02
$(pyr)_2CH^+$	$N(CH_2)_4$	$N(CH_2)_4$	–7.69
$(thq)_2CH^+$			–8.22
$(ind)_2CH^+$			–8.76
$(jul)_2CH^+$			–9.45
$(lil)_2CH^+$			–10.04

[a] Electrophilicity parameter as defined by eq 2.4 (from reference 9).

Materials. Acetone and acetonitrile were distilled over $CaSO_4$ 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.[10] The tetrafluoroborate salts of the benzhydrylium ions listed in Chart 2.1 were synthesized as reported in ref. 9.

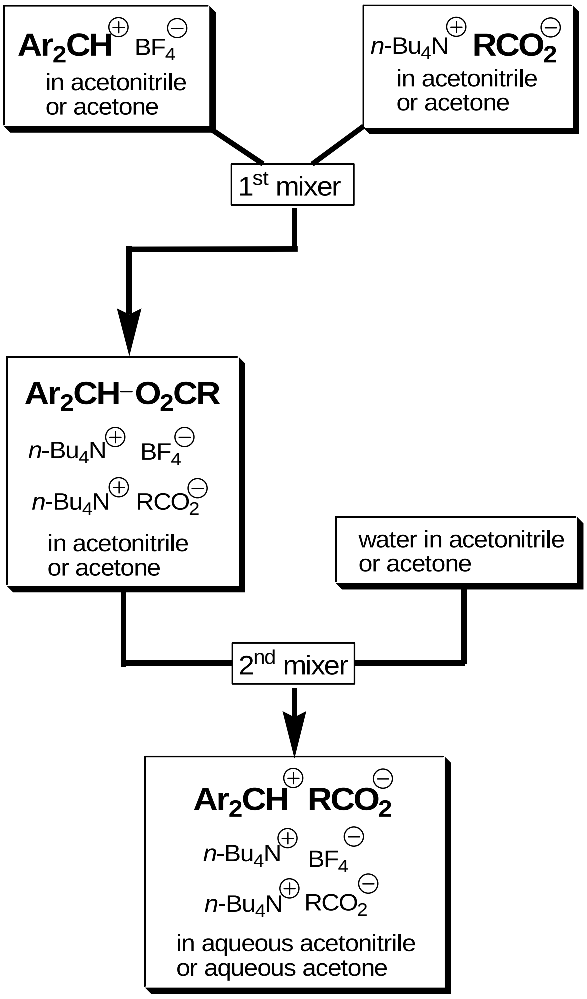
Determination of Equilibrium Constants. Equilibrium constants were measured by UV-Vis spectroscopy in acetonitrile as follows: To solutions of the benzhydrylium tetrafluoroborates in acetonitrile, whose UV-Vis maxima are reported in the Experimental Section, small volumes of stock solutions of tetra-*n*-butylammonium 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 2.1). Reactions of carboxylate ions with the colored benzhydrylium ions gave colorless products. The reactions were followed photometrically at the absorption maxima of Ar_2CH^+ by UV-Vis spectrometry using a stopped-flow instrument (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software) in single- or double-mixing mode as described previously.[9,11] All experiments were performed under pseudo-first-order conditions (excess of $n\text{-}Bu_4N^+RCO_2^-$) at 25 °C in acetonitrile, acetone, or mixtures of these solvents with water. First-order rate constants k_{obs} were obtained by least-squares fitting of the absorbance to the mono-exponential function $A_t = A_0 \exp(-k_{obs}t) + C$.

Determination of Ionization Rates (k_1 in eq 2.1). Because benzhydrylium carboxylates $Ar_2CH\text{-}O_2CR$, which are derived from highly stabilized benzhydrylium ions, cannot be isolated, the double mixing technique illustrated in Scheme 2.2 was employed. In the first mixer, a solution of Ar_2CH^+ 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

$n\mathrm{Bu_4N^+RCO_2^-}$ 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 $\mathrm{Ar_2CH\text{-}O_2CR}$. The ionizations are followed photometrically at the absorption maxima of $\mathrm{Ar_2CH^+}$.

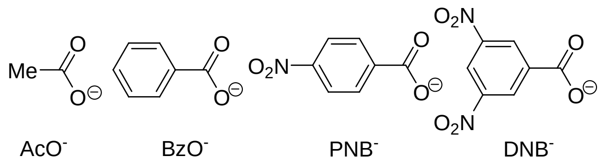
Scheme 2.2. Generation and Subsequent Ionization of Benzhydryl Carboxylates in a Double-Mixing Stopped Flow Spectrometer.



By this protocol we have rapidly collected a large number of rate constants at different concentrations of $n\text{-}\mathrm{Bu_4N^+RCO_2^-}$ 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 carboxylates (anions used: AcO^-, BzO^-, PNB^- and DNB^-) in pure acetonitrile (Scheme 2.3).



Scheme 2.3.

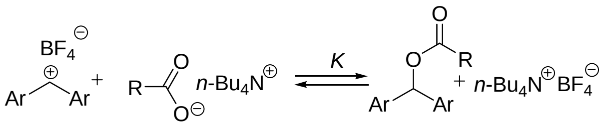


Figure 2.1 shows that the benzhydrylium ion absorbance at 632 nm decreases when increasing amounts of tetra-*n*-butylammonium benzoate ($n\text{-}Bu_4N^+BzO^-$) are added to a solution of $(lil)_2CH^+BF_4^-$ in acetonitrile.

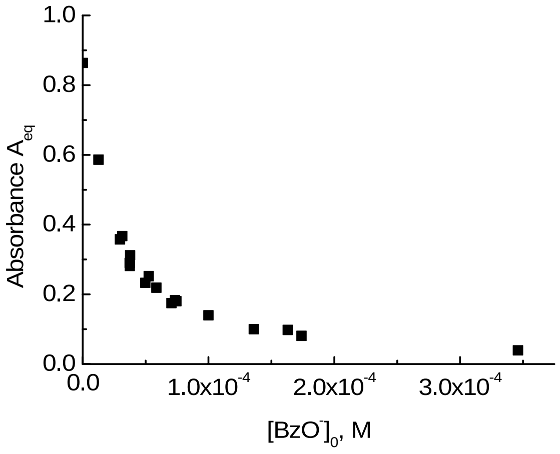


Figure 2.1. Determination of the equilibrium constant for the reaction of $n\text{-}Bu_4N^+BzO^-$ with $(lil)_2CH^+$ BF_4^- [(1.43–1.46) × 10^{-5} M] in acetonitrile at 25 °C. – $A_{eq} = \varepsilon \times [Ar_2CH^+] \times d$

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 2.2 provides a satisfactory description of the equilibria in acetonitrile at the low concentrations used (ionic strengths from 2.82×10^{-5} to 1.96×10^{-3}). The drifts of K with increasing carboxylate concentration, which were observed in some cases (see Experimental Section), were so small that an explicit treatment of these effects was not attempted.

$$K = \frac{[\mathrm{Ar_2CH\text{-}O_2CR}]_{\mathrm{eq}}}{[\mathrm{Ar_2CH^+}]_{\mathrm{eq}}[\mathrm{RCO_2^-}]_{\mathrm{eq}}} \tag{2.2}$$

$$= \frac{[\mathrm{Ar_2CH^+}]_0 - [\mathrm{Ar_2CH^+}]_{\mathrm{eq}}}{[\mathrm{Ar_2CH^+}]_{\mathrm{eq}}([\mathrm{RCO_2^-}]_0 - [\mathrm{Ar_2CH^+}]_0 + [\mathrm{Ar_2CH^+}]_{\mathrm{eq}})}$$

From the initial concentrations, $[\mathrm{Ar_2CH^+}]_0$ and $[\mathrm{RCO_2^-}]_0$, and the absorbance of $\mathrm{Ar_2CH^+BF_4^-}$ ($A = \varepsilon \times [\mathrm{Ar_2CH^+}] \times d$), the equilibrium concentrations $[\mathrm{Ar_2CH^+}]_{\mathrm{eq}}$, $[\mathrm{RCO_2^-}]_{\mathrm{eq}}$ and $[\mathrm{Ar_2CH\text{-}O_2CR}]_{\mathrm{eq}}$ were calculated. Substitution into eq 2.2 yielded the equilibrium constants K listed in Table 2.1.

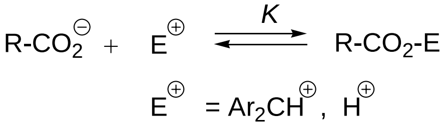
Table 2.1. Equilibrium Constants K (M^{-1}) for Reactions of Benzhydrylium Ions with Carboxylate Ions in Acetonitrile at 25 °C.

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

[a] $\mathrm{BzO^-}$ = benzoate [b] $\mathrm{PNB^-}$ = 4-nitrobenzoate [c] $\mathrm{DNB^-}$ = 3,5-dinitrobenzoate

As the equilibrium constants K defined by eq 2.2 reflect the relative Lewis basicities of these carboxylate ions toward benzhydrylium ions in acetonitirile, while pK_a values reflect the relative basicities of these anions toward the proton (Scheme 2.4), a comparison between these two quantities is appropriate (Figure 2.2).

Scheme 2.4.



The vertical ordering of the correlation lines provides a direct comparison of the affinities of the benzoate ions BzO^-, PNB^-, 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 $(dma)_2CH^+$ 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 2.1 one can derive that at high carboxylate concentration in acetonitrile, the equilibrium lies far on the side of 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.

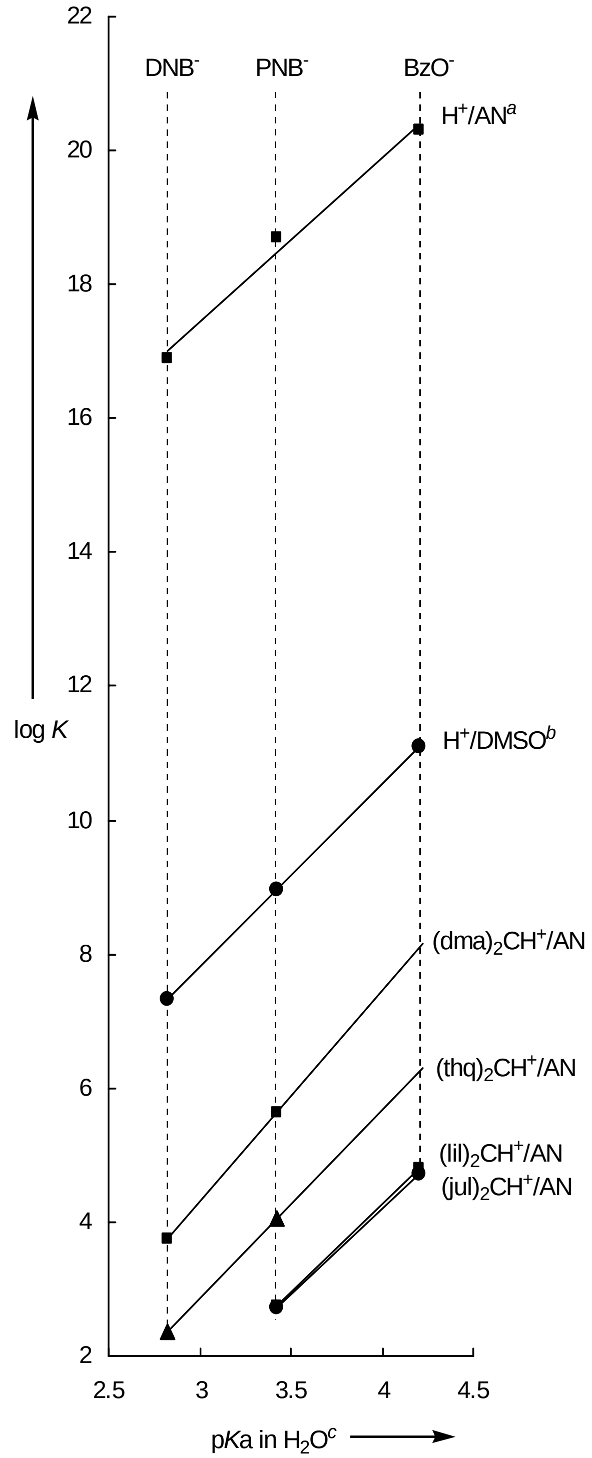


Figure 2.2. Comparison of the equilibrium constants (25 °C) for reactions of benzhydrylium ions with benzoate (BzO$^-$), 4-nitrobenzoate (PNB$^-$) and 3,5-dinitrobenzoate (DNB$^-$) ions with the pK_a values of the corresponding carboxylic acids in different solvents (AN: acetonitrile). – ^{a} pK_a(in 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). ^{b} 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). ^{c} 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).

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 six equivalents of tetrabutylammonium carboxylates, followed single exponentials from which the concentration-dependent first-order rate constants k_{obs} were derived. As illustrated in Figure 2.3, k_{obs} increases linearly with the concentration of n-Bu$_4$N$^+$ RCO$_2^-$

, indicating that only a small percentage of Ar_2CH^+ can be paired with RCO_2^-. Since 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^-.

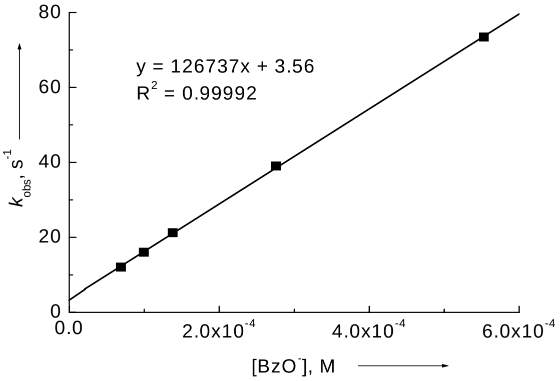


Figure 2.3. Linear correlation of the observed *pseudo*-first-order rate constants k_{obs} for the reaction of $(jul)_2CH^+$ ($c_0 = 9.99 \times 10^{-6}$ M) with BzO^- in acetonitrile (25 °C) with the concentration of n-$Bu_4N^+BzO^-$.

Some plots of k_{obs} against the carboxylate concentrations show considerable intercepts on the ordinate as illustrated on pages 70–71 (Experimental Section). 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 2.3.[18]

$$k_{obs} = k_1 + k_{-1}[RCO_2^-] \qquad (2.3)$$

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 Experimental Section). 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 mono-exponential 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 mono-exponential decays of the carbocation absorbances were observed, rate constants for the combinations of benzhydrylium ions with carboxylate ions could be determined (Table 2.2). In Table 2.2 values of rate constants given in parentheses are approximate, with typical errors of 8 – 10 %.

Table 2.2. Second-Order Rate Constants k_{-1} for Reactions of Benzhydryl Cations Ar_2CH^+ with Carboxylates at 25 °C.

RCO_2^{-} [a]	Solvent [b]	Ar_2CH^+	k_{-1}, M^{-1} s^{-1}
AcO^-	AN	$(lil)_2CH^+$	1.51×10^5
		$(jul)_2CH^+$	3.21×10^5
		$(ind)_2CH^+$	1.46×10^6
		$(thq)_2CH^+$	(3.42×10^6)
	A	$(lil)_2CH^+$	5.79×10^6
	10W90AN	$(dpa)_2CH^+$	1.17×10^5
		$(mfa)_2CH^+$	1.15×10^5
		$(pfa)_2CH^+$	6.87×10^5
	20W80AN	$(pfa)_2CH^+$	(8.67×10^4)
	10W90A	$(pyr)_2CH^+$	(2.06×10^3)
		$(dma)_2CH^+$	5.43×10^3
		$(mpa)_2CH^+$	6.75×10^4
		$(mor)_2CH^+$	5.51×10^4

Table 2.2. *Continued.*

RCO_2^- [a]	Solvent [b]	Ar_2CH^+	k_{-1}, M^{-1} s^{-1}
	20W80A	$(mpa)_2CH^+$	9.79×10^3
		$(mor)_2CH^+$	7.59×10^3
		$(dpa)_2CH^+$	1.12×10^5
		$(mfa)_2CH^+$	9.33×10^4
BzO^-	AN	$(lil)_2CH^+$	6.07×10^4
		$(jul)_2CH^+$	1.27×10^5
		$(ind)_2CH^+$	4.48×10^5
			3.91×10^5 [c]
		$(thq)_2CH^+$	1.05×10^6
	10W90AN	$(mor)_2CH^+$	(8.93×10^3)
		$(dpa)_2CH^+$	1.20×10^5
		$(mfa)_2CH^+$	1.26×10^5
		$(pfa)_2CH^+$	7.79×10^5
PNB^-	AN	$(ind)_2CH^+$	9.80×10^4
		$(thq)_2CH^+$	2.46×10^5
		$(pyr)_2CH^+$	7.46×10^5
		$(dma)_2CH^+$	2.00×10^6
	A	$(lil)_2CH^+$	9.29×10^5
		$(jul)_2CH^+$	1.96×10^6
		$(ind)_2CH^+$	6.97×10^6
DNB^-	AN	$(dma)_2CH^+$	4.01×10^5
		$(mpa)_2CH^+$	4.39×10^6
		$(mor)_2CH^+$	3.70×10^6
	A	$(ind)_2CH^+$	(1.56×10^6)
		$(thq)_2CH^+$	(3.50×10^6)
		$(pyr)_2CH^+$	(7.06×10^6)

[a] AcO^- = acetate, BzO^- = benzoate, PNB^- = 4-nitrobenzoate, DNB^- = 3,5-dinitrobenzoate. [b] A = acetone, 10W90A = 10% water and 90% acetone (v/v), AN = acetonitrile. [c] At 20 °C.

In previous work,[9,11,19] we have shown that reactions of carbocations with nucleophiles can be described by eq 2.4,

$$\log k = s(N + E) \qquad (2.4)$$

where k is the second-order rate constant, E is a nucleophile-independent electrophilicity parameter, and N and s are electrophile-independent nucleophilicity parameters. Figure 2.4 correlates some of the second-order rate constants listed in Table 2.2 with the previously reported electrophilicity parameters of benzhydrylium ions[9,11] and shows that the reactions of the carbocations Ar_2CH^+ with carboxylate ions generally follow eq 2.4.

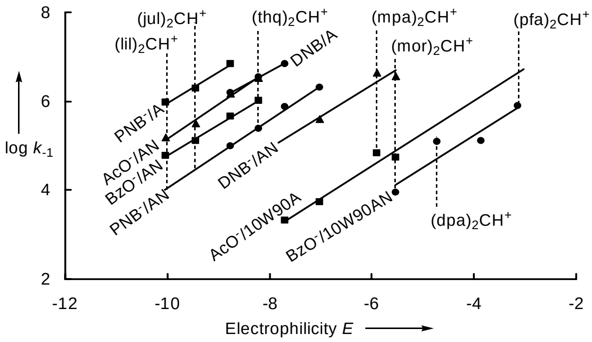


Figure 2.4. Correlation of second-order rate constants k_{-1} (at 25 °C) for the combination of benzhydrylium ions with carboxylate ions in different solvents. – A = acetone, AN = acetonitrile, W = water

From these correlations one can derive N and s parameters (eq 2.4) for the carboxylate ions in different solvents (Table 2.3). For some benzhydrylium ions systematic dispersions are obvious. As shown in Figure 2.4, (dpa)$_2$CH$^+$ generally reacts faster than predicted by its E-parameter. The phenylmethylamino substituted benzhydrylium ion (mpa)$_2$CH$^+$ behaves similarly, whereas (mor)$_2$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.[20] Possibly, the N-phenyl substituted benzhydrylium ions (mpa)$_2$CH$^+$ and (dpa)$_2$CH$^+$ are less efficiently solvated in protic solvents than benzhydrylium ions without *N*-phenyl groups and, therefore, are more electrophilic in protic solvents than implied by their electrophilicity parameters which were determined in dichloromethane.

Table 2.3. Nucleophilicity Parameters (25 °C) of Carboxylate Ions in Different Solvents.

RCO_2^-	Solvent	N_{25} [a]	s_{25} [a]
AcO^-	AN	16.90	0.75
	10W90A	12.71 [b]	0.68 [b]
	20W80A	12.5 [c]	0.60 [c]
BzO^-	AN	16.82	0.70
	10W90AN	11.3 [c]	0.72 [c]
PNB^-	AN	15.30	0.76
	A	18.74	0.68
DNB^-	AN	14.9 [c]	0.71 [c]
	A	18.8 [c]	0.62 [c]

[a] 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. [b] Additional k_{-1} values from Table 2.4 were used. [c] Values from correlations of lower quality.

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 2.2 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, $(dma)_2CH^+$, 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 2.3 that 4-nitrobenzoate and 3,5-dinitrobenzoate are approximately three 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 in pure acetonitrile.

Kinetics of Ionization of Benzhydryl Carboxylates. As described in Scheme 2.2, solutions of covalent benzhydryl 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 2.2) the regeneration of the colored benzhydrylium ions was observed photometrically. The appearance of the benzhydrylium absorbances generally followed single exponentials (eq 2.5) from which the rate constants k_{obs} were derived.

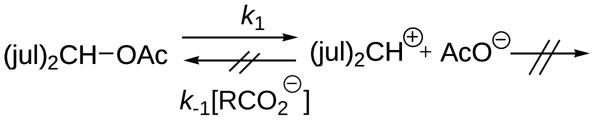
$$[Ar_2CH^+] = [Ar_2CH^+]_{eq}(1 - e^{-k_{obs}t}) \qquad (2.5)$$

Thus, unlike typical solvolyses of R-X substrates, where ionization rates are determined indirectly, in this work the appearance of the carbocations Ar_2CH^+ is directly observed.

As all ionization experiments of this investigation had to be performed in the presence of variable concentrations of the carboxylate ions ($[n\text{-}Bu_4N^+RCO_2^-] < 6 \times 10^{-4}$ M^{-1}), the effect of the ionic strength on the ionization rates was studied systematically. As shown on pages 93 to 95 (Experimental Section), the salt concentrations relevant for these studies ($< 6 \times 10^{-4}$ M^{-1}) did not affect the ionization rates by more than 12 %.

For most heterolysis reactions described in Table 2.4, constant end absorbances A_{end} which are independent of $[RCO_2^-]$, as well as ionization rate constants k_1 which are independent of $[RCO_2^-]$, were observed. One can, therefore, conclude that the heterolyses described in Table 2.4 proceed with quantitative formation of the carbocations which do not undergo subsequent reactions with the solvent (Scheme 2.5).

Scheme 2.5. Heterolysis of $(jul)_2CH$-OAc in 20W80A.



$$(jul)_2CH{-}OAc \underset{k_{-1}[RCO_2^{\ominus}]}{\overset{k_1}{\rightleftarrows}} (jul)_2CH^{\oplus} + AcO^{\ominus} \nrightarrow$$

The formation of persistent solutions of carbocations is in accordance with the estimated rate constants for the reactions of these carbocations with leaving group and solvent. For the ionization of $(jul)_2CH$-OAc in 20W80A a rate constant of $k_1 = 8.37$ s^{-1} was determined (Table 2.4). With N_{25} and s_{25} values for the acetate ion in 20W80A (12.5 and 0.60, Table 2.3) and the electrophilicity parameter for $(jul)_2CH^+$ ($E = -9.45$, Chart 2.1) one calculates $k_{-1} = 67$ M^{-1} s^{-1} by using eq 2.4. For the highest concentration of tetra-*n*-butylammonium acetate present in the ionization experiments ($[AcO^-] = 3.88 \times 10^{-4}$ M) one obtains $k_{-1}[AcO^-] = 2.6 \times 10^{-2}$ s^{-1}, i.e., $k_1 >> k_{-1}[AcO^-]$ corresponding to a quantitative ionization process. From the nucleophilicity parameters of the solvent mixture 20W80A ($N = 5.77$, $s = 0.87$)[5] and E ($(jul)_2CH^+$) = –9.45) one calculates (eq 2.4) a rate constant of 6.29×10^{-4} s^{-1} for the reaction of $(jul)_2CH^+$ with the solvent. This is in line with the observation that the benzhydrylium ion $(jul)_2CH^+$ 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 2.4 is rapidly intercepted by the solvent.

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_{obs} increase with increasing acetate ion concentration as depicted in Figure 2.5, indicating the reversibility of the ionization processes.

Because the observed first-order rate constants k_{obs} of reversible processes reflect the sum of the forward and the backward reactions (eq 2.3),[18] the ionization rate constants k_1 were obtained as the intercepts of the plots of k_{obs} versus the concentration of n-$Bu_4N^+AcO^-$ (Figure 2.5). 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.

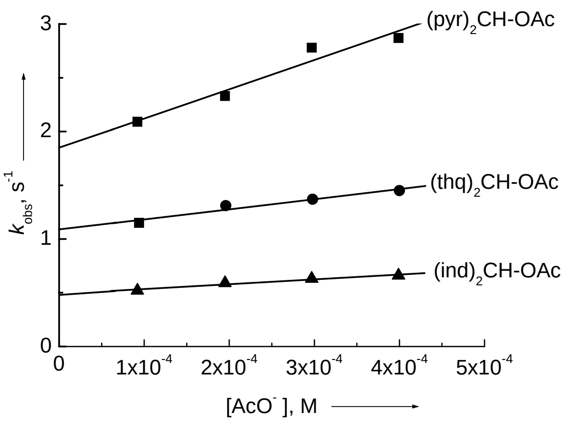


Figure 2.5. Correlation of the observed rate constants for the ionization of $(pyr)_2CH\text{-}OAc$ (1.00 × 10^{-5} M), $(thq)_2CH\text{-}OAc$ (8.70 × 10^{-6} M), and $(ind)_2CH\text{-}OAc$ (1.00 × 10^{-5} M) in 10W90A with the concentration of $n\text{-}Bu_4N^+AcO^-$ (at 25 °C).

The consistency of this evaluation is shown by Figure 2.6, where the rate constants k_{-1} obtained from ion combination reactions (Table 2.2) and from the ionization reactions are directly compared with each other. While k_{-1} for $(pyr)_2CH\text{-}OAc$ has been determined by both methods, for the other systems only one method could be employed. As required by eq 2.4, all rate constants for the ion combinations are on the same correlation line.

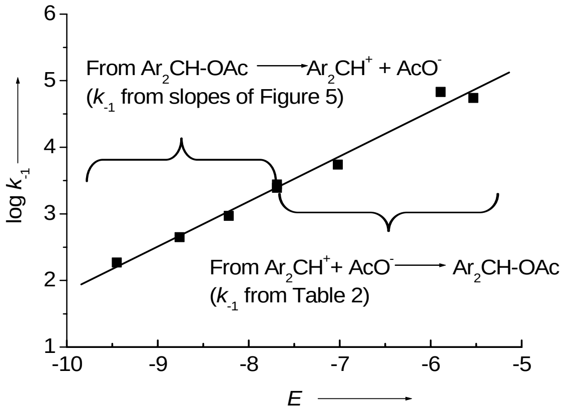


Figure 2.6. Correlation of the combination rate constants for the reaction of $Ar_2CH^+BF_4^-$ with $n\text{-}Bu_4N^+AcO^-$ in 10W90A ($\log k_{-1} = 8.60 + 0.68E$).

A slight increase of k_{obs} with increasing concentration of carboxylate ions was also observed for some heterolyses of benzhydryl acetates and benzoates in 20W80A (see Experimental Section). Since in these cases the ionizations were much faster than the ion recombinations ($k_1 >> k_{-1}[RCO_2^-]$), only the ionization constants k_1 were derived from these experiments.

Table 2.4. Ionization Rate Constants k_1 of Benzhydryl Derivatives in Different Solvents (25 °C).

Nucleofuge	Solvent	Ar_2CH^+	k_1 [s^{-1}]
AcO^-	20W80AN	$(lil)_2CH^+$	3.63
		$(jul)_2CH^+$	1.97×10^1
		$(ind)_2CH^+$	2.23
		$(thq)_2CH^+$	5.87
		$(pyr)_2CH^+$	8.57
		$(dma)_2CH^+$	1.77
	40W60AN	$(lil)_2CH^+$	6.90
		$(jul)_2CH^+$	3.99×10^1
		$(ind)_2CH^+$	4.52
		$(thq)_2CH^+$	1.34×10^1
		$(pyr)_2CH^+$	2.20×10^1
		$(dma)_2CH^+$	4.54
	10W90A	$(jul)_2CH^+$	2.34 [a]
		$(ind)_2CH^+$	0.49 [b]
		$(thq)_2CH^+$	1.09 [c]
		$(pyr)_2CH^+$	1.85 [d]
		$(dma)_2CH^+$	1.08
	20W80A	$(lil)_2CH^+$	2.24
		$(jul)_2CH^+$	8.37
		$(ind)_2CH^+$	1.40
		$(thq)_2CH^+$	3.36

Table 2.4. *Continued.*

Nucleofuge	Solvent	Ar$_2$CH$^+$	k_1 [s^{-1}]
		(pyr)$_2$CH$^+$	4.95
		(dma)$_2$CH$^+$	2.22
	40W60A	(lil)$_2$CH$^+$	1.36×10^1
		(jul)$_2$CH$^+$	6.15×10^1
		(ind)$_2$CH$^+$	9.41
		(thq)$_2$CH$^+$	2.49×10^1
		(pyr)$_2$CH$^+$	3.59×10^1
		(dma)$_2$CH$^+$	9.30
BzO$^-$	20W80AN	(lil)$_2$CH$^+$	9.58
		(jul)$_2$CH$^+$	4.49×10^1
		(ind)$_2$CH$^+$	5.16
		(thq)$_2$CH$^+$	1.47×10^1
		(pyr)$_2$CH$^+$	2.11×10^1
		(dma)$_2$CH$^+$	4.28
	40W60AN	(lil)$_2$CH$^+$	1.19×10^1
		(jul)$_2$CH$^+$	6.79×10^1
		(ind)$_2$CH$^+$	5.16
		(thq)$_2$CH$^+$	2.45×10^1
		(pyr)$_2$CH$^+$	3.60×10^1
		(dma)$_2$CH$^+$	7.62
	20W80A	(lil)$_2$CH$^+$	4.97
		(jul)$_2$CH$^+$	1.97×10^1
		(ind)$_2$CH$^+$	2.89
		(thq)$_2$CH$^+$	7.14
		(pyr)$_2$CH$^+$	9.83
		(dma)$_2$CH$^+$	3.49
	40W60A	(lil)$_2$CH$^+$	1.93×10^1

Table 2.4. *Continued.*

Nucleofuge	Solvent	Ar_2CH^+	k_1 [s^{-1}]
		$(jul)_2CH^+$	9.50×10^1
		$(ind)_2CH^+$	1.38×10^1
		$(thq)_2CH^+$	3.63×10^1
		$(pyr)_2CH^+$	5.05×10^1
		$(dma)_2CH^+$	1.27×10^1
PNB^-	10W90A	$(lil)_2CH^+$	5.22×10^1
		$(jul)_2CH^+$	1.63×10^2
		$(ind)_2CH^+$	2.59×10^1
		$(thq)_2CH^+$	5.59×10^1
		$(pyr)_2CH^+$	6.59×10^1
		$(dma)_2CH^+$	2.06×10^1
	20W80A	$(lil)_2CH^+$	1.03×10^2
		$(jul)_2CH^+$	3.53×10^2
		$(ind)_2CH^+$	5.58×10^1
		$(pyr)_2CH^+$	1.56×10^2
		$(dma)_2CH^+$	3.82×10^1
	40W60A	$(pyr)_2CH^+$	7.02×10^2
		$(dma)_2CH^+$	1.76×10^2
DNB^-	10W90A	$(pyr)_2CH^+$	1.06×10^3
		$(dma)_2CH^+$	2.53×10^2
	20W80A	$(dma)_2CH^+$	4.80×10^2

[a] $k_{-1} = 1.85 \times 10^2$ M^{-1} s^{-1}. [b] $k_{-1} = 4.50 \times 10^2$ M^{-1} s^{-1}. [c] $k_{-1} = 9.41 \times 10^2$ M^{-1} s^{-1}. [d] $k_{-1} = 2.73 \times 10^3$ M^{-1} s^{-1}.

The ionization rate constants of different benzhydrylium carboxylates are compared in Figure 2.7. Though some of the correlations of Figure 2.7 are only of moderate quality, the positions of the different correlation lines clearly show a decrease of the leaving group abilities in the series PNB^- >

BzO^- > AcO^- as well as an increase of the ionization rates with higher water content in the solvent mixtures.

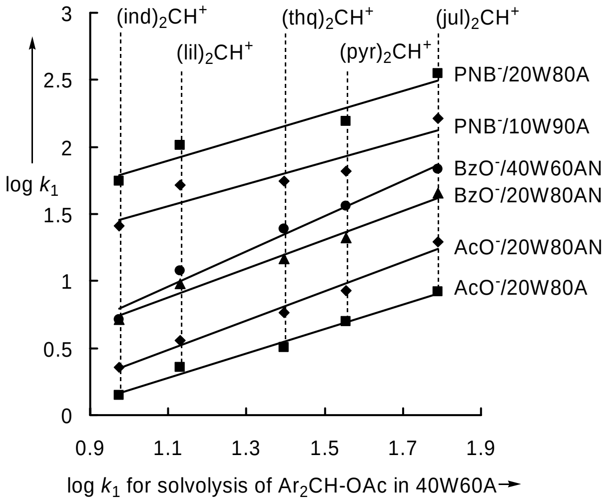


Figure 2.7. Correlation of ionization rate constants of $Ar_2CH\text{-}O_2CR$ in different solvents (given as (v/v); W = water, A = acetone, AN = acetonitrile) at 25 °C.

Transition States of the Ionizations. In 1948 Winstein and Grunwald reported that rates of the S_N1 solvolyses of neutral RX substrates in different solvents can be described by the linear free energy relationship (eq 2.6).[21]

$$\log (k/k_0) = mY \qquad (2.6)$$

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 S_N1 solvolysis reactions,[21,22] and m values below 0.5 were considered as evidence for S_N2 reactions. The value of m therefore was suggested as a criterion for distinguishing the two mechanisms.

Figure 2.8 compares plots of log (k/k_0) against Y for typical S_N1 solvolyses of the parent benzhydryl chloride and its *p,p*-dimethyl derivative[23,24] with the corresponding plots for the amino-substituted benzhydryl carboxylates studied in this work.

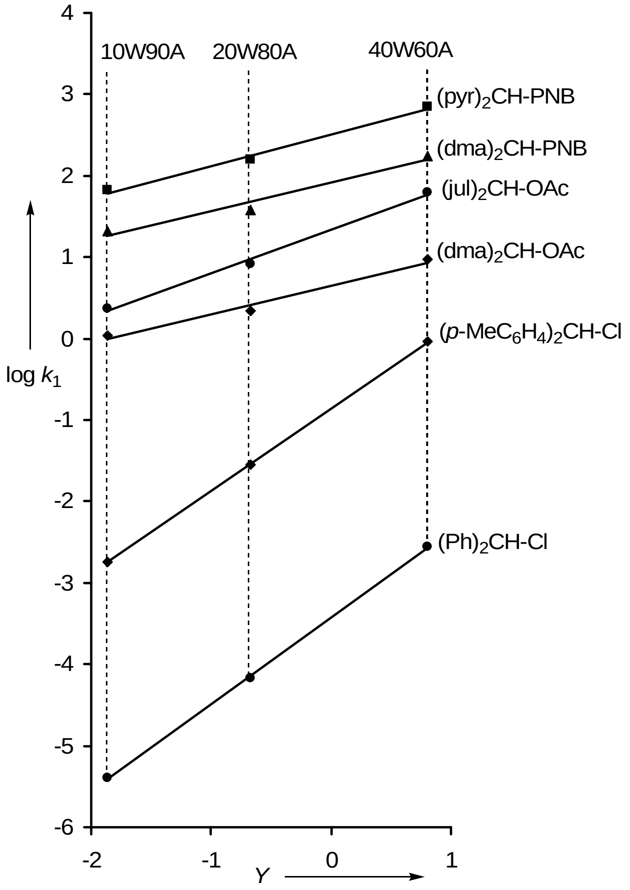


Figure 2.8. Correlation of rate constants for ionization of some benzhydryl derivatives with solvent ionizing power *Y* (k_1 for Ar_2CH-Cl in 10W90A and 20W80A from ref. 23; k_1 for Ar_2CH-Cl in 40W60A from ref. 24. Slopes: $(pyr)_2CH$-PNB = 0.39, $(dma)_2CH$-PNB = 0.35, $(jul)_2CH$-OAc = 0.54, $(dma)_2CH$-OAc = 0.35, (p-$MeC_6H_4)_2CH$-Cl = 1.02, $(Ph)_2CH$-Cl = 1.07).

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 for the benzhydryl carboxylates (m = 0.35 – 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 S_N2 reactions? In previous work,[25] we have demonstrated that the rates of the reactions of $(Ph)_2CH^+$ and (p-$MeC_6H_4)_2CH^+$ 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 2.9, left).

With this information, we can now construct the free energy diagrams for the ionization of (p-$MeC_6H_4)_2$CH-Br and (lil)$_2$CH-OAc in 80% aqueous acetone. The Eyring equation allows one to calculate $\Delta G^{\neq} = RT\ln(k_BT/hk) = 74.9$ kJ mol^{-1} (25 °C) from the solvolysis rate constant of (p-$MeC_6H_4)_2$CH-Br in 80% aqueous acetone (4.65×10^{-1} s^{-1}, from ref 23). As the reverse reaction is diffusion controlled, we substituted $k_{-1} = 10^{10}$ M^{-1}s^{-1} into the Eyring equation and arrived at a formal barrier of 16 kJ mol^{-1} for the reverse reaction (Figure 2.9).

For the ionization of (lil)$_2$CH-OAc in 80% aqueous acetone, $\Delta G^{\neq} = 71.0$ kJ mol^{-1} can be calculated from the ionization constant at 25 °C listed in Table 4. Even though the N and s values given for acetate in 80% aqueous acetone in Table 2.3 are not very precise, the calculated rate constant of 29.5 M^{-1}s^{-1} (for (lil)$_2$CH$^+$ + OAc$^-$, 20W80A) can be expected to be reliable within a factor of 1.5 because application of eq 2.4 requires only a short extrapolation beyond the experimental range studied in Table 2 (Ar_2CH^+ + OAc$^-$, 20W80A). Substitution of this rate constant into the Eyring equation yields $\Delta G^{\neq} = 64.6$ kJ mol^{-1} (25 °C). Though the standard free energy ΔG^0 of the ionic (lil)$_2$CH$^+$ OAc$^-$ is thus calculated slightly above that of the covalent compound (Figure 2.9), 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 2.4. The right part of Figure 2.9 thus describes an ionization process with a transition state which is in between covalent ester and ionic products. As the transition state is not carbocation-like, a small value of m results (Figure 2.8). One implication of this result is that m cannot generally be employed to differentiate S_N1 and S_N2 processes.

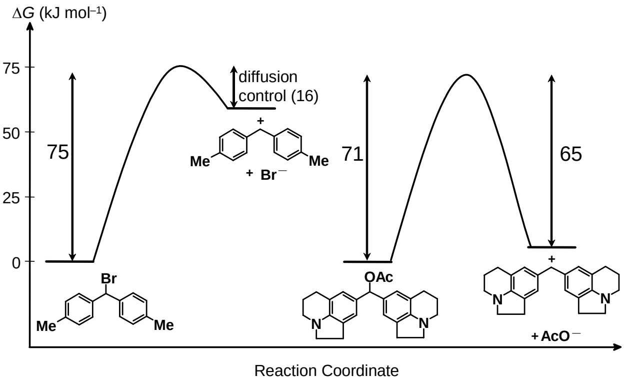


Figure 2.9. Simplified free energy profiles (25 °C) for ionizations of benzhydrylium derivatives in 80% aqueous acetone (encounter complexes not specified).

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 2.7) and electrophilicities (Chart 2.1, Table 2.2).

Table 2.5 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 $(thq)_2CH^+$ (k_{rel} = 12.3) was employed to link the two series of data. It is found that the electrophilic reactivities of benzhydrylium ions toward $ArCO_2^-$ decrease by more than two orders of magnitude in the series from $(dma)_2CH^+$ to $(lil)_2CH^+$. The same order of electrophilicities has previously been observed in reactions of these carbocations with more than hundred other nucleophiles.

Table 2.5. Comparison of Relative Electrophilicities and Relative Electrofugalities of Benzhydrylium Ions.

Reaction	Relative electrophilic reactivities in acetonitrile[a]					
	$(dma)_2CH^+$	$(pyr)_2CH^+$	$(thq)_2CH^+$	$(ind)_2CH^+$	$(jul)_2CH^+$	$(lil)_2CH^+$
$(Ar)_2CH^+ + PNB^- \xrightarrow{k_{-1}} (Ar)_2CH\text{-}PNB$	= 100	37.3	12.3	4.90		
$(Ar)_2CH^+ + BzO^- \xrightarrow{k_{-1}} (Ar)_2CH\text{-}OBz$			= 12.3	5.25	1.49	0.71
	Relative electrofugalities in 20W80A[b]					
	$(dma)_2CH^+$	$(pyr)_2CH^+$	$(thq)_2CH^+$	$(ind)_2CH^+$	$(jul)_2CH^+$	$(lil)_2CH^+$
$(Ar)_2CH\text{-}OAc \xrightarrow{k_1} (Ar)_2CH^+ + AcO^-$	= 100	223	151	63.1	377	101

[a] From Table 2.2. [b] From Table 2.4.

The relative electrofugalities of benzhydrylium ions follow a completely different order. The $(dma)_2CH^+$ cation which reacts 130 times faster with carboxylate ions than $(lil)_2CH^+$ (Table 2.5, top) is formed with exactly the same rate as the latter carbocation by heterolysis of the corresponding benzhydrylium acetate in 80% aqueous acetone (Table 2.5, bottom). Figure 2.7 shows that the electrofugality order of benzhydrylium ions shown in Table 2.5 is consistently found for ionizations of various 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 σ^+ values for the different amino groups, which have previously been derived from nucleophilic additions to these benzhydrylium ions, should therefore be considered with caution.[9]

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_N1 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.[7,8,26,27] 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 far 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 2.2), does not correlate at all with the order of electrofugality which is reflected by first-order rate constants of ionization of benzhydryl carboxylates (Table 2.4). Why is $(\text{lil})_2\text{CH}^+$, the least electrophilic benzhydrylium ion of the series, not generated rapidly by the heterolytic process, but is formed relatively slowly?

The Marcus equation[28] expresses the activation free energy of a reaction by a combination of the reaction free energy ΔG^0 and the intrinsic barrier $\Delta G_0^{\neq}$, which is defined as the activation free energy of a process with $\Delta G^0 = 0$. If the work term in the Marcus equation is omitted, eq 2.7 can be used to calculate $\Delta G^{\neq}$ from the reaction free energy ΔG^0 and the intrinsic barrier $\Delta G_0^{\neq}$.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + 0.5\Delta_r G^0 + ((\Delta_r G^{\circ})^2/16\Delta G_0^{\ddagger}) \qquad (2.7)$$

For about half of the combinations of electrophiles and nucleophiles given in Table 6, rate and equilibrium constants are available from Tables 2.1, 2.2 and 2.4, which are converted into ΔG^0 and $\Delta G^{\neq}$ values and are listed in Table 2.6. Substitution of these values into the Marcus equation (7) yields the intrinsic barriers $\Delta G_0^{\neq}$, which are also listed in Table 2.6.

The high reliability of eq 2.4 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 2.3.

Table 2.6. $\Delta G^{\neq}$, ΔG^0 and $\Delta G_0^{\neq}$ (in kJ mol^{-1}) for the Ionization of Ar_2CH-O_2CR at 25°C.[a]

Ar_2CH^+		AcO in 10W90A	AcO in 20W80A	BzO in AN	PNB in AN	DNB in AN
$(lil)_2CH^+$	$\Delta G^{\neq}$		71.0	73.1[d]	66.0[e]	
	ΔG^0		6.4[c]	27.4	15.8	
	$\Delta G_0^{\neq}$		67.8	58.6	57.8	
$(jul)_2CH^+$	$\Delta G^{\neq}$	70.9	67.7	70.9[d]	63.1[e]	
	ΔG^0	10.8[b]	5.1[c]	27.0	15.5	
	$\Delta G_0^{\neq}$	65.4	65.1	56.6	55.1	
$(ind)_2CH^+$	$\Delta G^{\neq}$	74.8	72.2		67.5[d]	61.1[e]
	ΔG^0	16.9[b]	11.9[c]		23.0	13.1
	$\Delta G_0^{\neq}$	66.0	66.1		55.4	54.4
$(thq)_2CH^+$	$\Delta G^{\neq}$	72.8	70.1		65.4[d]	59.3[e]
	ΔG^0	16.8[b]	11.8[c]		23.1	13.5
	$\Delta G_0^{\neq}$	64.1	64.1		53.2	52.4
$(pyr)_2CH^+$	$\Delta G^{\neq}$	71.5	69.0		65.2[d]	59.3[e]
	ΔG^0	17.4[b]	12.5[c]		25.7	15.6
	$\Delta G_0^{\neq}$	62.5	62.6		51.5	51.2
$(dma)_2CH^+$	$\Delta G^{\neq}$	72.8	71.0		69.2[d]	62.4[e]
	ΔG^0	21.1[b]	16.8[c]		32.2	21.3
	$\Delta G_0^{\neq}$	61.8	62.4		51.9	51.1

[a] Note that K defined by Scheme 2.3 and eq 2.2 refers to the ion combination, i.e., the reverse of ionization reaction. For that reason, ΔG^0 for the ionization process is given by $+RT \ln K$. [b] K derived from experimental k_1 and k_{-1}. [c] K derived from experimental k_1 and calculated (eq 2.4) k_{-1}. [d] k_1 derived from experimental K and k_{-1}. [e] k_1 derived from experimental K and calculated (eq 2.4) k_{-1}.

A graphical comparison of the intrinsic barriers is shown in Figure 2.10. As the intrinsic barriers for the ionizations of $(ind)_2CH$-O_2CR and $(jul)_2CH$-O_2CR as well as those for $(pyr)_2CH$-O_2CR and

$(dma)_2CH\text{-}O_2CR$ are very similar, Figure 2.10 presents only data for the first compound of these pairs.

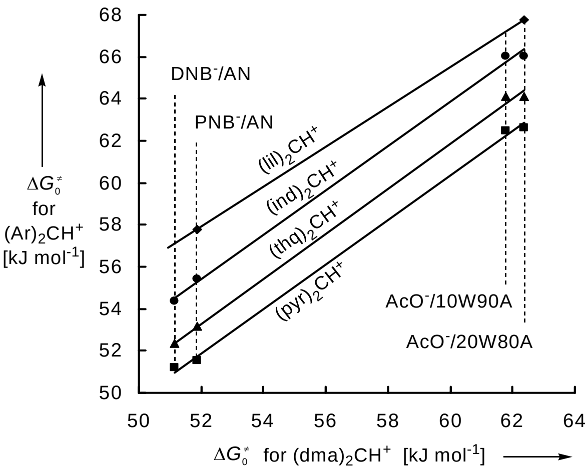


Figure 2.10. Correlation of intrinsic barriers for the ionization of benzhydryl carboxylates in different solvents. The corresponding lines for $(jul)_2CH^+$ and $(dma)_2CH^+$ coincide with those of $(ind)_2CH^+$ and $(pyr)_2CH^+$, respectively, and have not been drawn.

One can see that for all benzhydrylium derivatives, the intrinsic barriers increase by approximately 9-10 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 CH_3CN are relatively small ($\approx$ 1 kJ mol^{-1}, Table 2.6), 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.[8,29] In line with these numbers, Richard reported an intrinsic barrier of 61 kJ mol^{-1} for the reactions of the acetate anion with the tritylium ion in water.[27]

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 $(lil)_2CH^+ > (ind)_2CH^+ \approx (jul)_2CH^+ > (thq)_2CH^+ > (pyr)_2CH^+ \approx (dma)_2CH^+$ (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 $\Delta G_0^{\neq}$ would be 1 kJ mol^{-1}. The equal ranking of the different compounds in Figure 2.10 indicates that the relative magnitudes of the intrinsic barriers $\Delta G_0^{\neq}$ are even more accurate. An error limit of < 1 kJ mol^{-1} for the *relative magnitudes* of $\Delta G_0^{\neq}$ obviously holds also for intrinsic barriers which are derived from calculated rate constants (eq 2.4), because intrinsic barriers derived from experimental and calculated rate constants show exactly the same regularity in Figure 2.10.

It is evident that compounds with benzo-annulated five-membered rings, i.e. (lil)$_2$CH$^+$ and (ind)$_2$CH$^+$ have higher intrinsic barriers than their six-membered ring analogs (jul)$_2$CH$^+$ and (thq)$_2$CH$^+$, respectively (see structures in Chart 2.1). 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 2.6 and illustrated in Figure 2.11, the ionizations of (lil)$_2$CH-OAc and (jul)$_2$CH-OAc have similar reaction free energies ΔG^0. Because (jul)$_2$CH-OAc has a lower intrinsic barrier than (lil)$_2$CH-OAc, (jul)$_2$CH-OAc ionizes 3.7 times faster and at the same time (jul)$_2$CH$^+$ reacts 2.3 faster with nucleophiles than (lil)$_2$CH$^+$ in 20W80A (Figure 2.11). Similar rate ratios are found for other carboxylates. Analogously the ionizations of (ind)$_2$CH-OAc and (thq)$_2$CH-OAc have similar values of ΔG^0, and the higher electrophilic reactivity of (thq)$_2$CH$^+$ (Figures 2.4 and 2.6) as well as the higher ionization rates of the (thq)$_2$CH-esters compared with the (ind)$_2$CH-esters (Figure 2.7) are again caused by different intrinsic barriers (Figure 2.11).

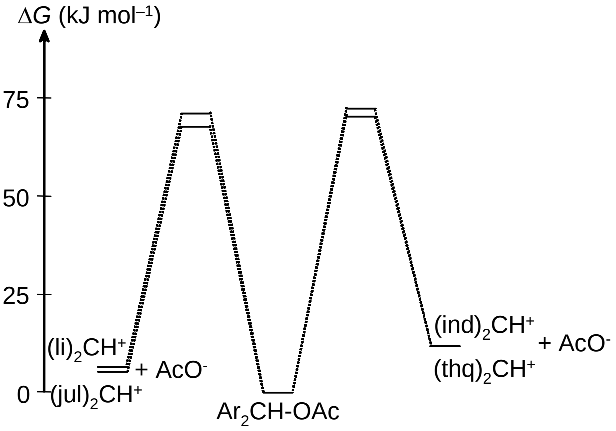


Figure 2.11. Gibbs free energy profiles (25 °C) for the reactions of the acetate ion with benzhydrylium ions in 20W80A.

Accidentally, the ionizations of (ind)$_2$CH-O$_2$CR and (jul)$_2$CH-O$_2$CR have almost the same intrinsic barriers (Table 2.6). The higher ionization rate of (jul)$_2$CH-O$_2$CR as well as the lower electrophilic reactivity of (jul)$_2$CH$^+$ are, therefore, a consequence of the better stabilization of the (jul)$_2$CH$^+$ ion compared with (ind)$_2$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.[5,23,30]

This opinion has now to be revised. 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.

References

(1) a) Streitwieser, A. Jr. in *Solvolytic Displacement Reactions*, McGraw-Hill, New York, **1962**. b) *Carbonium Ions,* Vol. 1–5 (Eds.: Olah, G. A.; Schleyer, P. v. R.), Wiley-Interscience, New York, **1968-1976**. c) Ingold, C. K. *Structure and Mechanism in Organic Chemistry, 2nd ed*, Cornell Univ. Press, Ithaca, NY, **1969**. d) Vogel, P. *Carbocation Chemistry*, Elsevier, Amsterdam, **1985**. e) *Advances in Carbocation Chemistry,* Vol. 1 (Ed.: Creary, X.), JAI, Greenwich, **1989**. f) *Advances in Carbocation Chemistry,* Vol. 2 (Ed.: Coxon, J.), JAI, Greenwich, **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) Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46–53. b) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. *Ions and Ion Pairs in Organic Reactions*, Vol. 2, Szwarc, M. Ed.; Wiley: New York, **1974**. 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.

(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. *Acc. Chem. Res.* **1987**, *20*, 301–308. c) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119–238. d) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9–16. e) Guthrie, J. P. *ChemPhysChem* **2003**, *4*, 809–816. f) 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.

(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.

(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.

(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.

(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-MeC$_6$H$_4$)$_2$CH-Cl in 40W60A in this work: k_1(25 °C) = 0.916 s^{-1}. b) Solvolysis rate constant k_1(25 °C) for (Ph)$_2$CH-Cl in 40W60A from: Liu, K.-T.; Lin, Y.-S.; Tsao, M.-L. *J. Phys. Org. Chem.* **1998**, *11*, 223–229.

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

(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.

(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.

–Experimental Section–

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

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X. Feng's contributions are stated in *italics*.

1 Determination of Equilibrium Constants. Equilibrium constants were measured by UV/Vis spectroscopy in acetonitrile as follows: To solutions of the benzhydrylium tetrafluoroborates in acetonitrile small volumes of stock solutions of tetrabutylammonium carboxylates were added and the decay of the absorptions was monitored. When the absorbance was constant (typically after 5-15 seconds), another portion of stock solution was added. This procedure was repeated four to five times for each benzhydrylium salt solution.

1.1 Equilibrium Constants for the Reactions of Benzhydrylium Ions with the Benzoate Anion

Equilibrium constant for the Reaction of the Benzoate Anion with (lil)$_2$CH$^+$ BF$_4^-$ in Acetonitrile at 25 °C (λ = 632 nm)

No.	[(lil)$_2$CH$^+$]$_0$, M	[BzO]$_0$, M	A_{eq}	[(lil)$_2$CH$^+$]$_{eq}$, M	[BzO]$_{eq}$, M	[(lil)$_2$CH-OBz]$_{eq}$, M	K, M^{-1}
0	1.44×10^{-5}	0	0.864	0	0	0	-
1	1.44×10^{-5}	3.74×10^{-5}	0.290	4.86×10^{-6}	2.78×10^{-5}	9.59×10^{-6}	7.11×10^{4}
2	1.44×10^{-5}	4.98×10^{-5}	0.233	3.90×10^{-6}	3.93×10^{-5}	1.05×10^{-5}	6.87×10^{4}
3	1.44×10^{-5}	7.06×10^{-5}	0.175	2.93×10^{-6}	5.91×10^{-5}	1.15×10^{-5}	6.65×10^{4}
4	1.44×10^{-5}	1.74×10^{-4}	0.081	1.36×10^{-6}	1.61×10^{-4}	1.30×10^{-5}	5.98×10^{4}
5	1.46×10^{-5}	1.26×10^{-5}	0.586	9.81×10^{-6}	7.82×10^{-6}	4.75×10^{-6}	6.19×10^{4}
6	1.46×10^{-5}	3.77×10^{-5}	0.312	5.22×10^{-6}	2.84×10^{-5}	9.33×10^{-6}	6.30×10^{4}
7	1.46×10^{-5}	5.86×10^{-5}	0.219	3.67×10^{-6}	4.77×10^{-5}	1.09×10^{-5}	6.22×10^{4}
8	1.45×10^{-5}	1.00×10^{-4}	0.140	2.34×10^{-6}	8.82×10^{-5}	1.22×10^{-5}	5.90×10^{4}
9	1.45×10^{-5}	1.63×10^{-4}	0.098	1.64×10^{-6}	1.50×10^{-4}	1.29×10^{-5}	5.23×10^{4}

No.	$[(lil)_2CH^+]_0$, M	$[BzO]_0$, M	A_{eq}	$[(lil)_2CH^+]_{eq}$, M	$[BzO]_{eq}$, M	$[(lil)_2CH\text{-}OBz]_{eq}$, M	K, M^{-1}
10	1.46×10^{-5}	3.15×10^{-5}	0.367	6.14×10^{-6}	2.30×10^{-5}	8.45×10^{-6}	5.97×10^{4}
11	1.46×10^{-5}	5.25×10^{-5}	0.252	4.22×10^{-6}	4.21×10^{-5}	1.04×10^{-5}	5.84×10^{4}
12	1.46×10^{-5}	7.34×10^{-5}	0.183	3.06×10^{-6}	6.19×10^{-5}	1.15×10^{-5}	6.08×10^{4}
13	1.46×10^{-5}	1.36×10^{-4}	0.100	1.67×10^{-6}	1.23×10^{-4}	1.29×10^{-5}	6.25×10^{4}
14	1.43×10^{-5}	2.49×10^{-5}	0.413	6.91×10^{-6}	1.75×10^{-5}	7.39×10^{-6}	6.11×10^{4}
15	1.43×10^{-5}	2.96×10^{-5}	0.358	5.99×10^{-6}	2.13×10^{-5}	8.32×10^{-6}	6.52×10^{4}
16	1.43×10^{-5}	3.75×10^{-5}	0.282	4.71×10^{-6}	3.28×10^{-5}	9.59×10^{-6}	6.44×10^{4}
17	1.43×10^{-5}	7.45×10^{-5}	0.180	3.02×10^{-6}	6.32×10^{-5}	1.13×10^{-5}	5.91×10^{4}
18	1.43×10^{-5}	2.69×10^{-4}	0.127	2.12×10^{-6}	2.30×10^{-4}	3.91×10^{-5}	6.36×10^{4}
19	1.43×10^{-5}	2.09×10^{-4}	0.066	1.11×10^{-6}	1.96×10^{-4}	1.32×10^{-5}	6.07×10^{4}
20	1.43×10^{-5}	3.46×10^{-5}	0.040	6.62×10^{-7}	3.32×10^{-4}	1.36×10^{-5}	6.18×10^{4}

$K = (6.20 \pm 0.40) \times 10^{4}\ M^{-1}$

Equilibrium constant for the Reactions of the Benzoate Anion with $(jul)_2CH^+\ BF_4^-$ in Acetonitrile at 25 °C (λ = 635 nm)

No.	$[(jul)_2CH^+]_0$, M	$[BzO]_0$, M	A_{eq}	$[(jul)_2CH^+]_{eq}$, M	$[BzO]_{eq}$, M	$[(jul)_2CH\text{-}OBz]_{eq}$, M	K, M^{-1}
0	1.98×10^{-5}	0	1.250	0	0	0	-
1	1.98×10^{-5}	6.42×10^{-6}	1.094	1.73×10^{-5}	3.90×10^{-6}	2.52×10^{-6}	3.73×10^{4}
2	1.98×10^{-5}	1.28×10^{-5}	0.943	1.49×10^{-5}	7.97×10^{-6}	4.88×10^{-6}	4.10×10^{4}
3	1.98×10^{-5}	1.93×10^{-5}	0.808	1.28×10^{-5}	1.23×10^{-5}	6.97×10^{-6}	4.44×10^{4}
4	1.97×10^{-5}	2.57×10^{-5}	0.695	1.10×10^{-5}	1.70×10^{-5}	8.70×10^{-6}	4.66×10^{4}
5	1.96×10^{-5}	3.63×10^{-5}	0.512	8.11×10^{-6}	2.48×10^{-5}	1.15×10^{-5}	5.70×10^{4}
6	1.95×10^{-5}	4.69×10^{-5}	0.389	6.16×10^{-6}	3.36×10^{-5}	1.33×10^{-5}	6.43×10^{4}
7	1.92×10^{-5}	7.90×10^{-5}	0.254	4.02×10^{-6}	6.38×10^{-5}	1.52×10^{-5}	5.95×10^{4}
8	1.90×10^{-5}	1.11×10^{-4}	0.180	2.85×10^{-6}	9.50×10^{-5}	1.61×10^{-5}	5.93×10^{4}
9	1.85×10^{-5}	1.54×10^{-4}	0.113	1.78×10^{-6}	1.37×10^{-4}	1.67×10^{-5}	6.86×10^{4}
10	1.72×10^{-5}	2.18×10^{-4}	0.083	1.31×10^{-6}	2.02×10^{-4}	1.59×10^{-5}	6.02×10^{4}

$K = (5.38 \pm 1.06) \times 10^{4}\ M^{-1}$

1.2 Equilibrium Constants for the reactions of Benzhydrylium Ions with the 4-Nitrobenzoate Anion

Equilibrium constant for the reactions of the 4-Nitrobenzoate Anion with $(lil)_2CH^+\ BF_4^-$ in Acetonitrile at 25 °C (λ = 632 nm)

No.	$[(lil)_2CH^+]_0$, M	$[PNB]_0$, M	A_{eq}	$[(lil)_2CH^+]_{eq}$, M	$[PNB]_{eq}$, M	$[(lil)_2CH–PNB]_{eq}$, M	K, M^{-1}
0	1.69×10^{-5}	0	1.009	0	0	0	-
1	1.69×10^{-5}	4.62×10^{-4}	0.790	1.32×10^{-5}	4.59×10^{-4}	3.69×10^{-6}	6.08×10^{2}
2	1.68×10^{-5}	8.39×10^{-4}	0.675	1.13×10^{-5}	8.34×10^{-4}	5.45×10^{-6}	5.79×10^{2}
3	1.66×10^{-5}	1.21×10^{-3}	0.585	9.79×10^{-6}	1.20×10^{-3}	6.79×10^{-6}	5.77×10^{2}
4	1.69×10^{-5}	3.07×10^{-4}	0.86	1.44×10^{-5}	3.05×10^{-4}	2.47×10^{-6}	5.63×10^{2}
5	1.67×10^{-5}	6.85×10^{-4}	0.72	1.21×10^{-5}	6.80×10^{-4}	4.65×10^{-6}	5.67×10^{2}

$K = (5.79 \pm 0.16) \times 10^{2}\ M^{-1}$

Equilibrium constant for the reactions of the 4-Nitrobenzoate Anion with $(\text{jul})_2\text{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 635 nm)

No.	$[(\text{jul})_2\text{CH}^+]_0$, M	$[\text{PNB}]_0$, M	A_{eq}	$[(\text{jul})_2\text{CH}^+]_{\text{eq}}$, M	$[\text{PNB}]_{\text{eq}}$, M	$[(\text{jul})_2\text{CH–PNB}]_{\text{eq}}$, M	K, M^{-1}
0	1.67×10^{-5}	0	1.054	0	0	0	-
1	1.67×10^{-5}	2.31×10^{-4}	0.940	1.49×10^{-5}	2.30×10^{-4}	1.78×10^{-6}	5.19×10^{2}
2	1.66×10^{-5}	3.84×10^{-4}	0.880	1.39×10^{-5}	3.81×10^{-4}	2.67×10^{-6}	5.01×10^{2}
3	1.65×10^{-5}	5.36×10^{-4}	0.819	1.30×10^{-5}	5.32×10^{-4}	3.56×10^{-6}	5.16×10^{2}
4	1.64×10^{-5}	9.09×10^{-4}	0.705	1.12×10^{-5}	9.04×10^{-4}	5.21×10^{-6}	5.16×10^{2}
5	1.49×10^{-5}	6.84×10^{-4}	0.691	1.09×10^{-5}	6.80×10^{-4}	3.99×10^{-6}	5.36×10^{2}

$K = (5.18 \pm 0.11) \times 10^{2}\ \text{M}^{-1}$

Equilibrium constant for the reactions of the 4-Nitrobenzoate Anion with $(\text{ind})_2\text{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 616 nm)

No.	$[(\text{ind})_2\text{CH}^+]_0$, M	$[\text{PNB}]_0$, M	A_{eq}	$[(\text{ind})_2\text{CH}^+]_{\text{eq}}$, M	$[\text{PNB}]_{\text{eq}}$, M	$[(\text{ind})_2\text{CH-PNB}]_{\text{eq}}$, M	K, M^{-1}
0	1.98×10^{-5}	0	1.362	0	0	0	-
1	1.98×10^{-5}	3.16×10^{-5}	1.027	1.49×10^{-5}	2.67×10^{-5}	4.89×10^{-6}	1.23×10^{4}
2	1.98×10^{-5}	1.10×10^{-4}	0.642	9.33×10^{-6}	1.00×10^{-5}	1.05×10^{-5}	1.12×10^{4}
3	1.97×10^{-5}	1.89×10^{-4}	0.464	6.74×10^{-6}	1.76×10^{-4}	1.30×10^{-5}	1.10×10^{4}
4	1.97×10^{-5}	3.45×10^{-4}	0.291	4.23×10^{-6}	3.29×10^{-4}	1.54×10^{-5}	1.11×10^{4}
5	1.96×10^{-5}	5.00×10^{-4}	0.209	3.04×10^{-6}	4.83×10^{-4}	1.65×10^{-5}	1.13×10^{4}
6	1.98×10^{-5}	1.58×10^{-4}	0.546	7.94×10^{-6}	1.46×10^{-4}	1.18×10^{-5}	1.02×10^{4}
7	1.97×10^{-5}	3.14×10^{-4}	0.340	4.94×10^{-6}	2.99×10^{-4}	1.48×10^{-5}	9.97×10^{3}
8	1.96×10^{-5}	4.69×10^{-4}	0.246	3.58×10^{-6}	4.53×10^{-4}	1.60×10^{-5}	9.90×10^{3}
9	1.96×10^{-5}	6.23×10^{-4}	0.190	2.76×10^{-6}	6.07×10^{-4}	1.68×10^{-5}	1.00×10^{4}

$K = (1.08 \pm 0.08) \times 10^{4}$ M

Equilibrium constant for the reactions of the 4-Nitrobenzoate Anion with $(\text{thq})_2\text{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 620 nm)

No.	$[(\text{thq})_2\text{CH}^+]_0$, M	$[\text{PNB}]_0$, M	A_{eq}	$[(\text{thq})_2\text{CH}^+]_{\text{eq}}$, M	$[\text{PNB}]_{\text{eq}}$, M	$[(\text{thq})_2\text{CH-PNB}]_{\text{eq}}$, M	K, M^{-1}
0	1.96×10^{-5}	0	0.869	0	0	0	-
1	1.96×10^{-5}	1.56×10^{-5}	0.737	1.66×10^{-5}	1.26×10^{-5}	3.01×10^{-6}	1.44×10^{4}
2	1.96×10^{-5}	6.24×10^{-5}	0.526	1.19×10^{-5}	5.46×10^{-5}	7.74×10^{-6}	1.19×10^{4}
3	1.96×10^{-5}	1.09×10^{-4}	0.402	9.07×10^{-6}	9.85×10^{-5}	1.05×10^{-5}	1.18×10^{4}
4	1.96×10^{-5}	1.56×10^{-4}	0.312	7.04×10^{-6}	1.43×10^{-4}	1.25×10^{-5}	1.24×10^{4}
5	1.95×10^{-5}	2.33×10^{-4}	0.223	5.03×10^{-6}	2.18×10^{-4}	1.45×10^{-5}	1.32×10^{4}
6	2.19×10^{-5}	6.26×10^{-5}	0.650	1.47×10^{-5}	5.54×10^{-5}	7.20×10^{-6}	8.87×10^{3}
7	2.18×10^{-5}	1.09×10^{-4}	0.499	1.13×10^{-5}	9.88×10^{-5}	1.06×10^{-5}	9.51×10^{3}
8	2.18×10^{-5}	1.73×10^{-4}	0.374	8.44×10^{-6}	1.58×10^{-4}	1.34×10^{-5}	1.00×10^{4}
9	2.18×10^{-5}	2.49×10^{-4}	0.284	6.41×10^{-6}	2.34×10^{-4}	1.53×10^{-5}	1.03×10^{4}
10	2.17×10^{-5}	3.26×10^{-4}	0.227	5.12×10^{-6}	3.10×10^{-4}	1.66×10^{-5}	1.05×10^{4}

$K = (1.13 \pm 0.17) \times 10^{4}\ \text{M}^{-1}$

Equilibrium constant for the reactions of the 4-Nitrobenzoate Anion with $(\text{pyr})_2\text{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 612 nm)

No.	$[(\text{pyr})_2\text{CH}^+]_0$, M	$[\text{PNB}]_0$, M	A_{eq}	$[(\text{pyr})_2\text{CH}^+]_{\text{eq}}$, M	$[\text{PNB}]_{\text{eq}}$, M	$[(\text{pyr})_2\text{CH-PNB}]_{\text{eq}}$, M	K, M^{-1}
0	1.64×10^{-5}	0	1.559	0	0	0	-
1	1.64×10^{-5}	3.16×10^{-5}	0.892	9.38×10^{-6}	2.47×10^{-5}	6.99×10^{-6}	3.02×10^{4}
2	1.64×10^{-5}	4.74×10^{-5}	0.702	7.39×10^{-6}	3.85×10^{-5}	8.98×10^{-6}	3.16×10^{4}
3	1.64×10^{-5}	6.32×10^{-5}	0.573	6.03×10^{-6}	5.29×10^{-5}	1.03×10^{-5}	3.24×10^{4}
4	1.63×10^{-5}	9.48×10^{-5}	0.418	4.40×10^{-6}	8.28×10^{-5}	1.19×10^{-5}	3.28×10^{4}
5	1.63×10^{-5}	1.42×10^{-4}	0.295	3.10×10^{-6}	1.29×10^{-4}	1.32×10^{-5}	3.31×10^{4}

$K = (3.20 \pm 0.10) \times 10^4\ \text{M}^{-1}$

Equilibrium constant for the reactions of the 4-Nitrobenzoate Anion with $(\text{dma})_2\text{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 606 nm)

No.	$[(\text{dma})_2\text{CH}^+]_0$, M	$[\text{PNB}]_0$, M	A_{eq}	$[(\text{dma})_2\text{CH}^+]_{\text{eq}}$, M	$[\text{PNB}]_{\text{eq}}$, M	$[(\text{dma})_2\text{CH-PNB}]_{\text{eq}}$, M	K, M^{-1}
0	1.86×10^{-5}	0	1.500	0	0	0	-
1	1.86×10^{-5}	2.53×10^{-5}	0.284	3.48×10^{-6}	1.02×10^{-5}	1.51×10^{-5}	4.26×10^{5}
2	1.86×10^{-5}	3.47×10^{-5}	0.162	2.01×10^{-6}	1.82×10^{-5}	1.66×10^{-5}	4.52×10^{5}
3	1.86×10^{-5}	5.05×10^{-5}	0.092	1.14×10^{-6}	3.31×10^{-5}	1.74×10^{-5}	4.63×10^{5}
4	1.87×10^{-5}	2.54×10^{-5}	0.298	3.71×10^{-6}	1.04×10^{-5}	1.50×10^{-5}	3.87×10^{5}
5	1.87×10^{-5}	4.12×10^{-5}	0.129	1.60×10^{-6}	2.42×10^{-5}	1.71×10^{-5}	4.40×10^{5}
6	1.87×10^{-5}	4.76×10^{-5}	0.102	1.27×10^{-6}	3.02×10^{-5}	1.74×10^{-5}	4.54×10^{5}
7	1.87×10^{-5}	1.59×10^{-5}	0.581	7.22×10^{-6}	4.43×10^{-5}	1.14×10^{-5}	3.57×10^{5}
8	1.86×10^{-5}	3.17×10^{-5}	0.186	2.31×10^{-6}	1.54×10^{-5}	1.63×10^{-5}	4.60×10^{5}
9	1.86×10^{-5}	4.75×10^{-5}	0.102	1.27×10^{-6}	3.02×10^{-5}	1.74×10^{-5}	4.54×10^{5}
10	1.86×10^{-5}	6.34×10^{-5}	0.073	9.11×10^{-6}	4.56×10^{-5}	1.77×10^{-5}	4.26×10^{5}

$K = (4.32 \pm 0.33) \times 10^5\ \text{M}^{-1}$

1.3 Equilibrium Constants for the reactions of Benzhydrylium Ions with the 3,5-Dinitrobenzoate Anion

Equilibrium constant for the reactions of the 3,5-Dinitrobenzoate Anion with $(\text{ind})_2\text{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 616 nm)

No.	$[(\text{ind})_2\text{CH}^+]_0$, M	$[\text{DNB}]_0$, M	A_{eq}	$[(\text{ind})_2\text{CH}^+]_{\text{eq}}$, M	$[\text{DNB}]_{\text{eq}}$, M	$[(\text{ind})_2\text{CH-DNB}]_{\text{eq}}$, M	K, M^{-1}
0	1.91×10^{-5}	0	1.314	0	0	0	-
1	1.91×10^{-5}	3.80×10^{-5}	1.202	1.75×10^{-5}	3.78×10^{-4}	1.59×10^{-6}	2.41×10^{2}
2	1.89×10^{-5}	8.46×10^{-4}	1.116	1.62×10^{-5}	8.44×10^{-4}	2.65×10^{-6}	1.94×10^{2}
3	1.85×10^{-5}	1.75×10^{-3}	0.981	1.43×10^{-5}	1.75×10^{-3}	4.24×10^{-6}	1.70×10^{2}
4	1.89×10^{-5}	4.71×10^{-4}	1.179	1.71×10^{-5}	4.69×10^{-4}	1.77×10^{-6}	2.20×10^{2}
5	1.87×10^{-5}	9.32×10^{-4}	1.092	1.59×10^{-5}	9.30×10^{-4}	2.84×10^{-6}	1.93×10^{2}
6	1.84×10^{-5}	1.83×10^{-3}	0.956	1.39×10^{-5}	1.82×10^{-3}	4.46×10^{-6}	1.76×10^{2}

$K = (1.99 \pm 0.25) \times 10^2\ \text{M}^{-1}$

Equilibrium constant for the reactions of the 3,5-Dinitrobenzoate Anion with $(\mathrm{thq})_2\mathrm{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 620 nm)

No.	$[(\mathrm{thq})_2\mathrm{CH}^+]_0$, M	$[\mathrm{DNB}]_0$, M	A_eq	$[(\mathrm{thq})_2\mathrm{CH}^+]_\mathrm{eq}$, M	$[\mathrm{DNB}]_\mathrm{eq}$, M	$[(\mathrm{thq})_2\mathrm{CH\text{-}DNB}]_\mathrm{eq}$, M	K, M^{-1}
0	1.87×10^{-5}	0	0.829	0	0	0	-
1	1.87×10^{-5}	5.60×10^{-4}	0.725	1.64×10^{-5}	5.58×10^{-4}	2.36×10^{-6}	2.59×10^{2}
2	1.85×10^{-5}	1.02×10^{-3}	0.675	1.52×10^{-5}	1.01×10^{-3}	3.30×10^{-6}	2.14×10^{2}
3	1.82×10^{-5}	1.90×10^{-3}	0.586	1.32×10^{-5}	1.90×10^{-3}	4.95×10^{-6}	1.97×10^{2}
4	2.15×10^{-5}	4.70×10^{-4}	0.845	1.91×10^{-5}	4.67×10^{-4}	2.46×10^{-6}	2.76×10^{2}
5	2.13×10^{-5}	9.30×10^{-4}	0.774	1.75×10^{-5}	9.26×10^{-4}	3.84×10^{-6}	2.38×10^{2}
6	2.09×10^{-5}	1.82×10^{-3}	0.667	1.51×10^{-5}	1.82×10^{-3}	5.85×10^{-6}	2.14×10^{2}

$K = (2.33 \pm 0.28) \times 10^{2}$ M^{-1}

Equilibrium constant for the reactions of the 3,5-Dinitrobenzoate Anion with $(\mathrm{pyr})_2\mathrm{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 612 nm)

No.	$[(\mathrm{pyr})_2\mathrm{CH}^+]_0$, M	$[\mathrm{DNB}]_0$, M	A_eq	$[(\mathrm{pyr})_2\mathrm{CH}^+]_\mathrm{eq}$, M	$[\mathrm{DNB}]_\mathrm{eq}$, M	$[(\mathrm{pyr})_2\mathrm{CH\text{-}DNB}]_\mathrm{eq}$, M	K, M^{-1}
0	1.29×10^{-5}	0	1.226	0	0	0	-
1	1.29×10^{-5}	1.88×10^{-4}	1.112	1.17×10^{-5}	1.87×10^{-4}	1.21×10^{-6}	5.54×10^{2}
2	1.29×10^{-5}	3.75×10^{-4}	1.013	1.07×10^{-5}	3.73×10^{-4}	2.20×10^{-6}	5.54×10^{2}
3	1.29×10^{-5}	5.61×10^{-4}	0.937	9.86×10^{-6}	5.58×10^{-4}	2.95×10^{-6}	5.37×10^{2}
4	1.28×10^{-5}	7.45×10^{-4}	0.865	9.10×10^{-6}	7.41×10^{-4}	3.66×10^{-6}	5.43×10^{2}
5	1.15×10^{-5}	1.70×10^{-4}	1.005	1.06×10^{-5}	1.69×10^{-4}	9.28×10^{-7}	5.21×10^{2}
6	1.15×10^{-5}	3.38×10^{-4}	0.926	9.74×10^{-6}	3.36×10^{-4}	1.72×10^{-6}	5.25×10^{2}
7	1.13×10^{-5}	1.16×10^{-3}	0.658	6.92×10^{-6}	1.16×10^{-3}	4.34×10^{-6}	5.41×10^{2}
8	1.11×10^{-5}	1.96×10^{-3}	0.482	5.07×10^{-6}	1.95×10^{-3}	6.00×10^{-6}	6.06×10^{2}

Equilibrium constant for the reactions of the 3,5-Dinitrobenzoate Anion with $(\mathrm{dma})_2\mathrm{CH}^+$ BF_4^- in Acetonitrile at 25 °C (λ = 606 nm)

No.	$[(\mathrm{dma})_2\mathrm{CH}^+]_0$, M	$[\mathrm{DNB}]_0$, M	A_eq	$[(\mathrm{dma})_2\mathrm{CH}^+]_\mathrm{eq}$, M	$[\mathrm{DNB}]_\mathrm{eq}$, M	$[\mathrm{dma\text{-}DNB}]_\mathrm{eq}$, M	K, M^{-1}
0	1.73×10^{-5}	0	1.391	0	0	0	-
1	1.73×10^{-5}	1.46×10^{-4}	0.778	9.67×10^{-6}	1.38×10^{-4}	7.65×10^{-6}	5.73×10^{3}
2	1.73×10^{-5}	3.36×10^{-4}	0.503	6.25×10^{-6}	3.25×10^{-4}	1.10×10^{-5}	5.42×10^{3}
3	1.72×10^{-5}	5.24×10^{-4}	0.370	4.60×10^{-6}	5.12×10^{-4}	1.26×10^{-5}	5.34×10^{3}
4	1.83×10^{-5}	9.60×10^{-5}	0.970	1.21×10^{-5}	8.98×10^{-5}	6.22×10^{-6}	5.74×10^{3}
5	1.82×10^{-5}	2.87×10^{-4}	0.588	7.31×10^{-6}	2.76×10^{-4}	1.09×10^{-5}	5.40×10^{3}
6	1.81×10^{-5}	4.76×10^{-4}	0.420	5.22×10^{-6}	4.63×10^{-4}	1.29×10^{-5}	5.33×10^{3}
7	1.81×10^{-5}	6.64×10^{-4}	0.325	4.04×10^{-6}	6.50×10^{-4}	1.40×10^{-5}	5.34×10^{3}
8	1.80×10^{-5}	8.51×10^{-4}	0.265	3.30×10^{-6}	8.36×10^{-4}	1.47×10^{-5}	5.34×10^{3}

$K = (5.46 \pm 0.16) \times 10^{3}$ M^{-1}

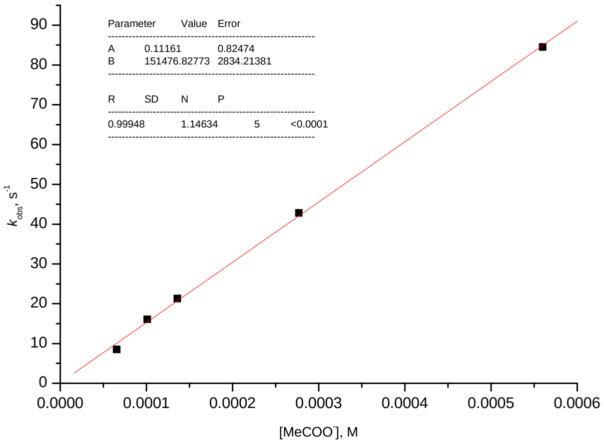
2. Determination of the Rates of the Combinations of Benzhydrylium Ions with Carboxylate Anions. Reactions of carboxylate ions with the colored benzhydryl cations gave colorless products. The reactions were followed photometrically at the absorption maxima of Ar2CH+ by UV-Vis spectometry using a stopped flow instrument (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software) in single- or double-mixing mode as described previously. All experiments were performed under pseudo-first-order conditions (excess of n-Bu4N+RCO2–) at 25 °C in acetonitrile, acetone or mixtures of these solvents with water. First order rate constants kobs were obtained by least-squares fitting of the absorbances to the mono-exponential curve At = A0 exp(-kobst) + C.

$(Ar)_2CH^+\ BF_4^-$	E	λ_{max} (nm)
$(lil)_2CH^+\ BF_4^-$	-10.04	632
$(jul)_2CH^+\ BF_4^-$	-9.45	635
$(ind)_2CH^+\ BF_4^-$	-8.76	616
$(thq)_2CH^+\ BF_4^-$	-8.22	620
$(pyr)_2CH^+\ BF_4^-$	-7.69	612
$(dma)_2CH^+\ BF_4^-$	-7.02	606

2.1 Combination of the Acetate Anion with Benzhydryl Cations in Acetonitrile

Reaction of Tetrabutylammonium Acetate with $(lil)_2CH^+\ BF_4^-$ in Acetonitrile at 25 ^{o}C

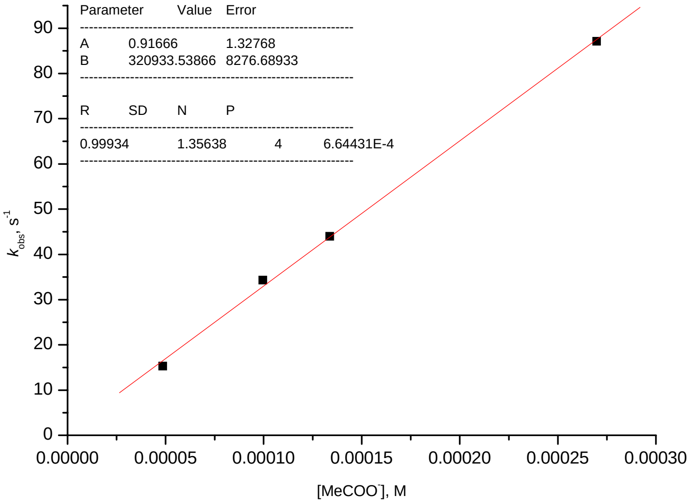
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s $^{-1}$
1	9.95×10^{-6}	7.06×10^{-5}	8.46
2	9.95×10^{-6}	1.06×10^{-4}	16.1
3	9.95×10^{-6}	1.41×10^{-4}	21.3
4	9.95×10^{-6}	2.82×10^{-4}	42.8
5	9.95×10^{-6}	5.65×10^{-4}	83.5



$\boldsymbol{k_{-1} = 1.51 \times 10^5\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium Acetate with $(jul)_2CH^+\ BF_4^-$ in Acetonitrile at 25 °C

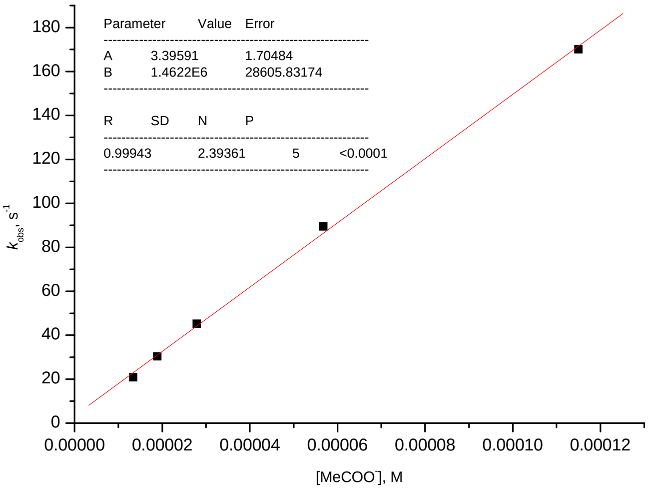
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	5.04×10^{-6}	5.11×10^{-5}	15.3
2	5.04×10^{-6}	1.02×10^{-4}	34.2
3	5.04×10^{-6}	1.36×10^{-4}	44.0
4	5.04×10^{-6}	2.72×10^{-4}	87.1



$\boldsymbol{k_{-1} = 3.21 \times 10^5\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium Acetate with $(ind)_2CH^+\ BF_4^-$ in Acetonitrile at 25 °C

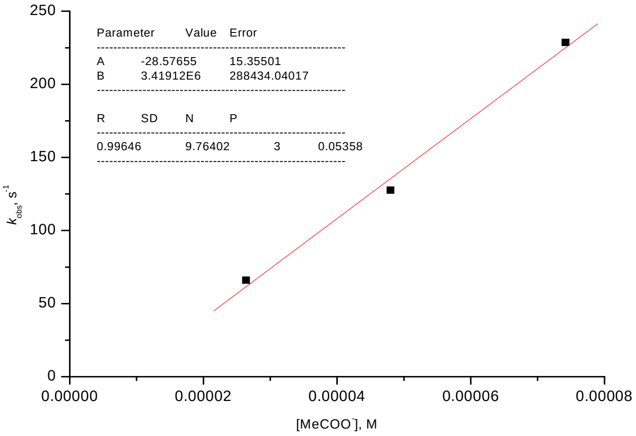
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.03×10^{-6}	1.44×10^{-5}	20.9
2	2.03×10^{-6}	1.99×10^{-5}	30.4
3	2.03×10^{-6}	2.89×10^{-5}	45.2
4	2.03×10^{-6}	5.78×10^{-5}	91.1
5	2.03×10^{-6}	1.16×10^{-4}	176



k_{-1} = 1.46 × 10^6 M^{-1} s^{-1}

Reaction of Tetrabutylammonium Acetate with $(thq)_2CH^+$ BF_4^- in Acetonitrile at 25 °C

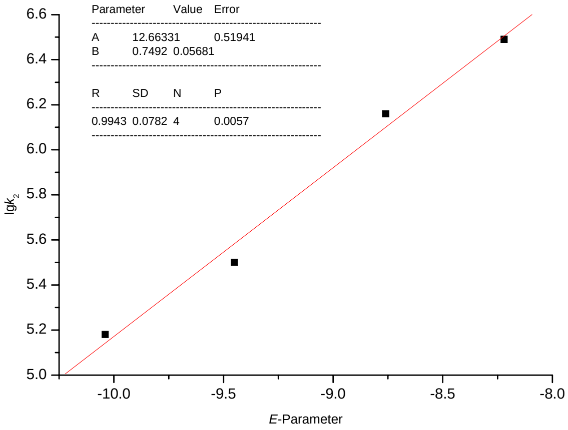
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	5.03 × 10^{-6}	2.89 × 10^{-5}	66.3
2	5.03 × 10^{-6}	5.05 × 10^{-5}	127
3	5.03 × 10^{-6}	7.67 × 10^{-5}	228
4	5.03 × 10^{-6}	1.16 × 10^{-4}	371



k_{-1} = 3.42 × 10^6 M^{-1} s^{-1}

Nucleophilicity parameter of the Acetate Anion in Acetonitrile at 25 °C

Ar_2CH^+	E	k_{-1}, M^{-1} s^{-1}	$\lg k_{-1}$
$(lil)_2CH^+$	-10.04	1.51×10^5	5.18
$(jul)_2CH^+$	-9.45	3.21×10^5	5.50
$(ind)_2CH^+$	-8.76	1.46×10^6	6.16
$(thq)_2CH^+$	-8.22	3.42×10^6	6.53

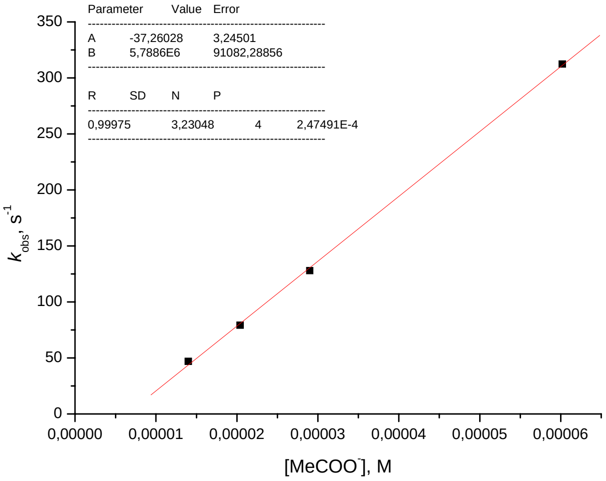


***N* = 16.90**
***s* = 0.75**

2.2 Combination of the Acetate Anion with Benzhydryl Cations in Acetone

Reaction of Tetrabutylammonium Acetate with $(lil)_2CH^+$ BF_4^- in Acetone at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.15×10^{-6}	1.51×10^{-5}	47.0
2	2.15×10^{-6}	2.15×10^{-5}	79.2
3	2.15×10^{-6}	3.01×10^{-5}	127
4	2.15×10^{-6}	6.02×10^{-5}	312

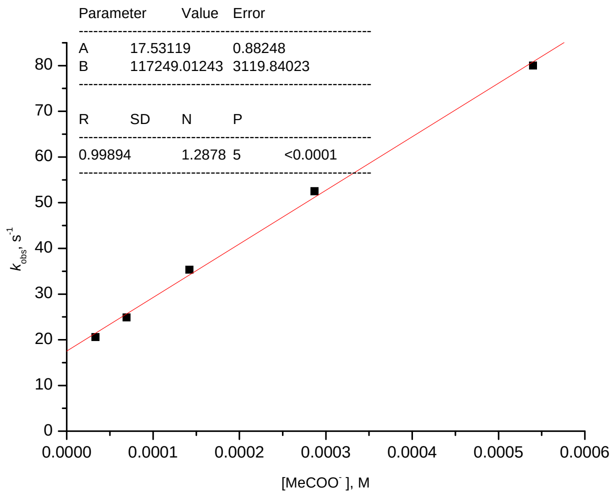


k_{-1} = 5.79 × 10^6 M^{-1} s^{-1}

2.3 Combination of the Acetate Anion with Benzhydryl Cations in 10:90 (v/v) Water Acetonitrile Mixtures (10W90AN)

Reaction of Tetrabutylammonium Acetate with $(dpa)_2CH^+ BF_4^-$ in 10W90AN at 25 °C

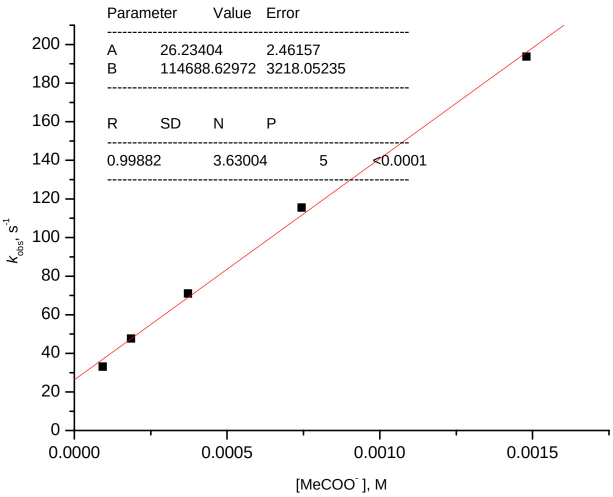
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	6.03×10^{-6}	3.32×10^{-5}	20.6
2	6.03×10^{-6}	6.94×10^{-5}	24.9
4	6.03×10^{-6}	1.42×10^{-4}	35.3
5	6.03×10^{-6}	2.87×10^{-4}	52.5
6	6.03×10^{-6}	5.40×10^{-4}	80.0



$k_{-1} = 1.17 \times 10^5\ M^{-1}\ s^{-1}$

Reaction of Tetrabutylammonium Acetate with $(mfa)_2CH^+ BF_4^-$ in 10W90AN at 25 °C

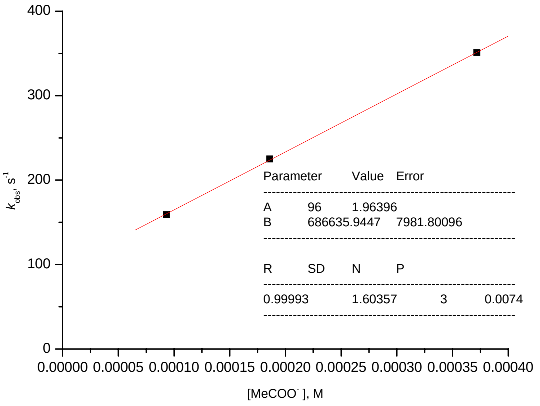
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	8.04×10^{-6}	9.30×10^{-5}	33.1
2	8.04×10^{-6}	1.86×10^{-4}	47.6
3	8.04×10^{-6}	3.72×10^{-4}	71.0
4	8.04×10^{-6}	7.44×10^{-4}	116
5	8.04×10^{-6}	1.48×10^{-3}	194



k_{-1} = 1.15 × 10^5 M^{-1} s^{-1}

Reaction of Tetrabutylammonium Acetate with $(pfa)_2CH^+$ BF_4^- in 10W90AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.72×10^{-6}	9.30×10^{-5}	155
2	2.72×10^{-6}	1.86×10^{-4}	219
3	2.72×10^{-6}	3.72×10^{-4}	378

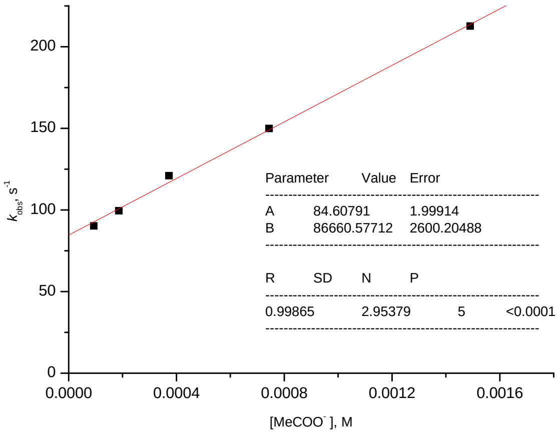


k_{-1} = 6.87 × 10^5 M^{-1} s^{-1}

2.4 Combination of the Acetate Anion with Benzhydryl Cations in 20:80 (v/v) Water Acetonitrile Mixtures (20W80AN)

Reaction of Tetrabutylammonium Acetate with $(pfa)_2CH^+$ BF_4^- in 20W80AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.72×10^{-6}	9.30×10^{-5}	90.2
2	2.72×10^{-6}	1.86×10^{-4}	99.5
3	2.72×10^{-6}	3.72×10^{-4}	121
4	2.72×10^{-6}	7.44×10^{-4}	150
5	2.72×10^{-6}	1.49×10^{-4}	212

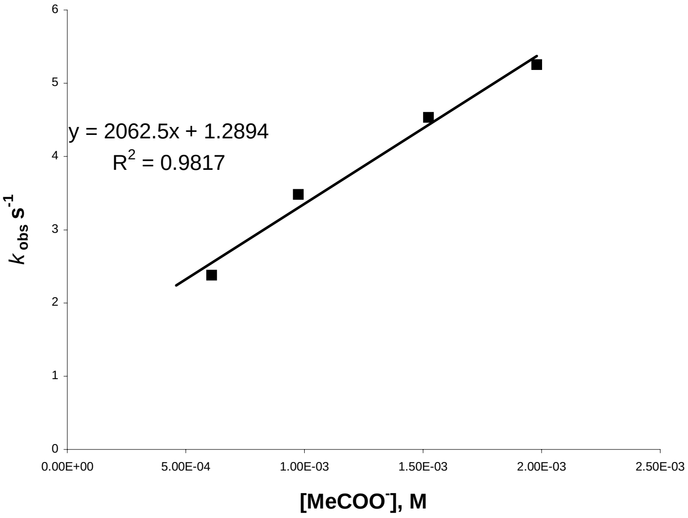


$k_{-1} = 8.67 \times 10^4$ M^{-1} s^{-1}

2.5 Combination of the Acetate Anion with Benzhydryl Cations in 10:90 (v/v) Water Acetone Mixtures (10W90A)

Reaction of Tetrabutylammonium Acetate with $(pyr)_2CH^+$ BF_4^- in 10W90A at 25 °C

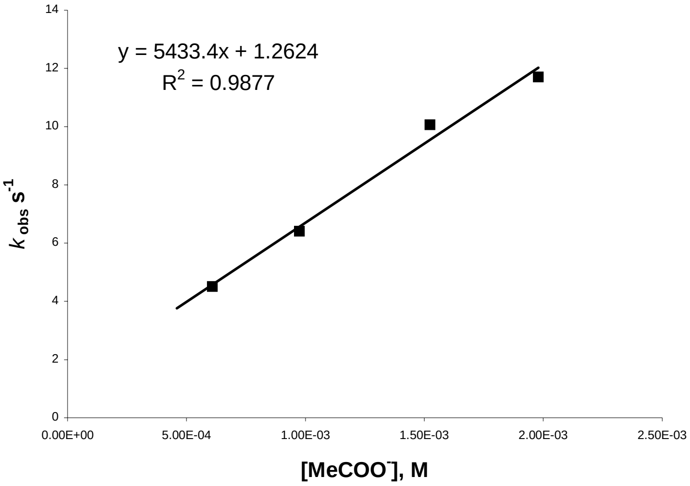
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	1.99×10^{-5}	6.09×10^{-4}	2.38
2	1.99×10^{-5}	9.75×10^{-4}	3.48
3	1.99×10^{-5}	1.53×10^{-3}	4.54
4	1.99×10^{-5}	1.98×10^{-3}	5.26



$k_{-1} = 2.06 \times 10^3$ M^{-1} s^{-1}

Reaction of Tetrabutylammonium Acetate with $(dma)_2CH^+$ BF_4^- in 10W90A at 25 °C

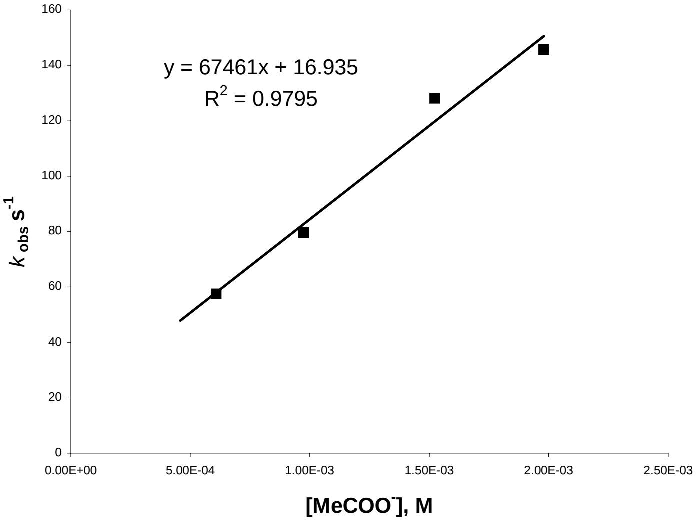
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.00×10^{-5}	6.09×10^{-4}	4.51
2	2.00×10^{-5}	9.75×10^{-4}	6.41
3	2.00×10^{-5}	1.53×10^{-3}	10.07
4	2.00×10^{-5}	1.98×10^{-3}	11.71



$\boldsymbol{k_{-1} = 5.43 \times 10^3\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium Acetate with $(mpa)_2CH^+$ BF_4^- in 10W90A at 25 °C

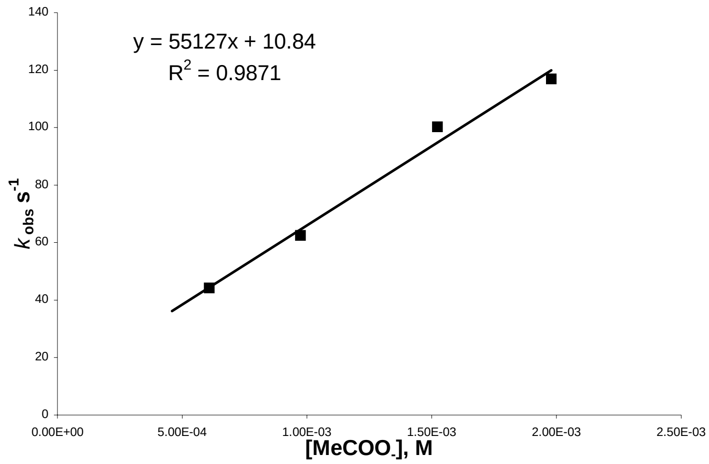
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.00×10^{-5}	6.09×10^{-4}	57.49
2	2.00×10^{-5}	9.75×10^{-4}	79.62
3	2.00×10^{-5}	1.53×10^{-3}	128.14
4	2.00×10^{-5}	1.98×10^{-3}	145.70



$\boldsymbol{k_{-1} = 6.75\times 10^4\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium Acetate Anion with $(mor)_2CH^+$ BF_4^- in 10W90A at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.00×10^{-5}	6.09×10^{-4}	44.17
2	2.00×10^{-5}	9.75×10^{-4}	62.47
3	2.00×10^{-5}	1.53×10^{-3}	100.25
4	2.00×10^{-5}	1.98×10^{-3}	116.93

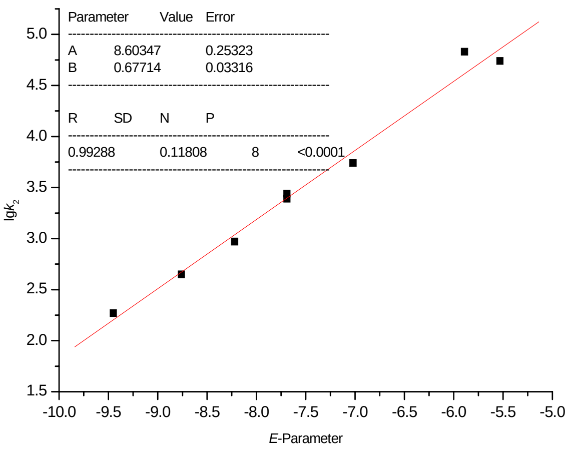


$$\boldsymbol{k_{-1} = 5.51\times 10^4\ M^{-1}\ s^{-1}}$$

Nucleophilicity parameter of the Acetate Anion in 10W90A at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	lgk_{-1}
$(jul)_2CH^{+a}$	-9.45	1.85×10^2	2.27
$(ind)_2CH^{+a}$	-8.76	4.50×10^2	2.65
$(thq)_2CH^{+a}$	-8.22	9.41×10^2	2.97
$(pyr)_2CH^{+a}$	-7.69	2.73×10^3	3.44
$(pyr)_2CH^+$	-7.69	2.06×10^3	3.39
$(dma)_2CH^+$	-7.02	5.43×10^3	3.74
$(mpa)_2CH^+$	-5.89	6.75×10^4	4.83
$(mor)_2CH^+$	-5.53	5.51×10^4	4.74

[a] data taken from reversible ionization experiments of $(Ar)_2CH$-OAc in 10W 90A.



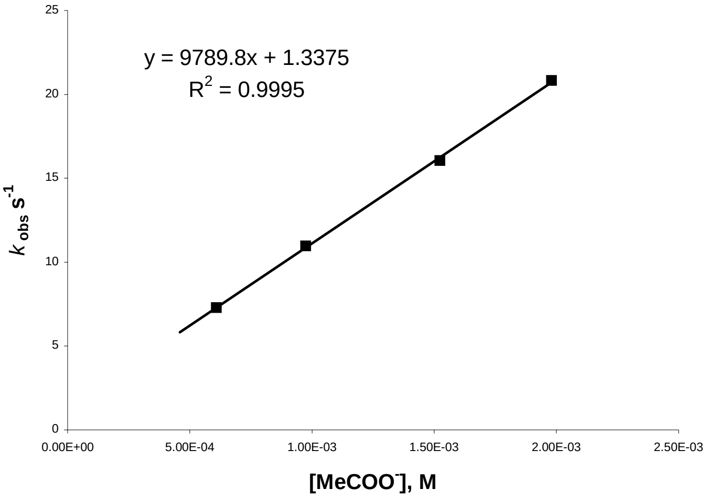
```
Parameter      Value    Error
------------------------------------------------------------
A       8.60347       0.25323
B       0.67714       0.03316
------------------------------------------------------------

R       SD       N       P
------------------------------------------------------------
0.99288       0.11808       8       <0.0001
------------------------------------------------------------
```

***N* = 12.71**
***s* = 0.68**

2.6 Combination of the Acetate Anion with Benzhydryl Cations in 20:80 (v/v) Water Acetone Mixtures (20W80A)

Reaction of Tetrabutylammonium Acetate with $(mpa)_2CH^+ BF_4^-$ in 20W80A at 25 °C

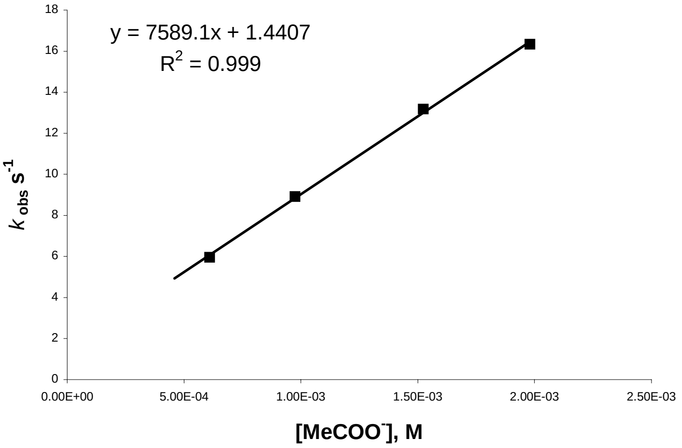
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.00×10^{-5}	6.09×10^{-4}	7.30
2	2.00×10^{-5}	9.75×10^{-4}	10.97
3	2.00×10^{-5}	1.53×10^{-3}	16.06
4	2.00×10^{-5}	1.98×10^{-3}	20.83



$k_{-1} = 9.79 \times 10^3$ M^{-1} s^{-1}

Reaction of Tetrabutylammonium Acetate Anion with $(mor)_2CH^+ BF_4^-$ in 20W80A at 25 °C

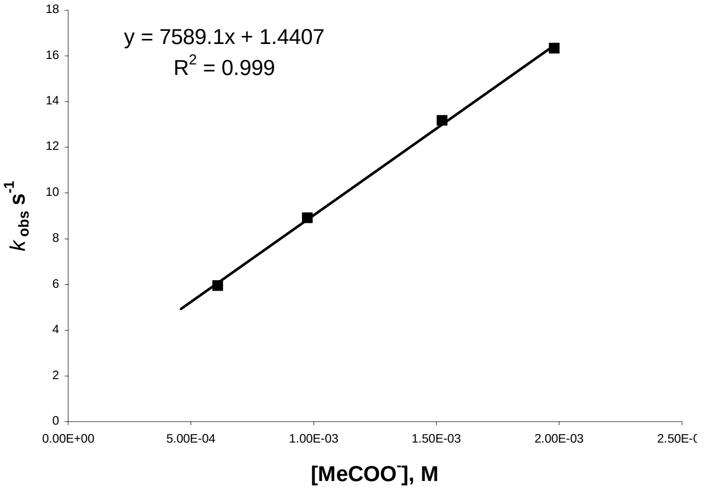
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	1.99×10^{-5}	6.09×10^{-4}	5.96
2	1.99×10^{-5}	9.75×10^{-4}	8.91
3	1.99×10^{-5}	1.53×10^{-3}	13.17
4	1.99×10^{-5}	1.98×10^{-3}	16.33



$k_{-1} = 7.59 \times 10^3$ M^{-1} s^{-1}

Reaction of Tetrabutylammonium Acetate with $(dpa)_2CH^+$ BF_4^- in 20W80A at 25 °C

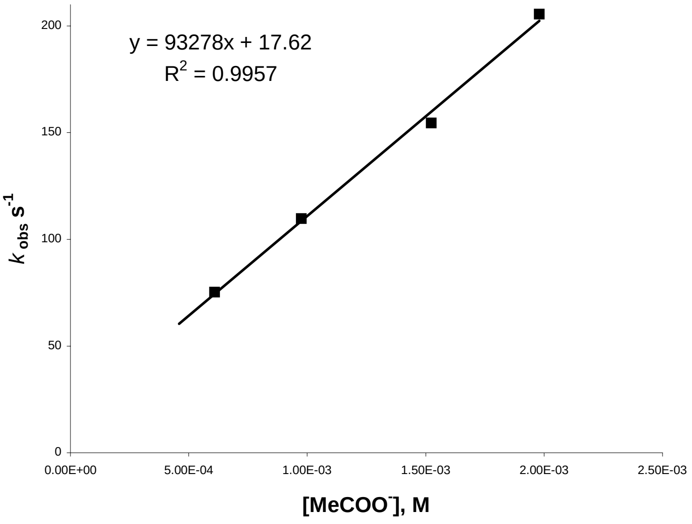
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	2.21×10^{-5}	6.09×10^{-4}	102.67
2	2.21×10^{-5}	9.75×10^{-4}	147.65
3	2.21×10^{-5}	1.53×10^{-3}	203.16
4	2.21×10^{-5}	1.98×10^{-3}	258.01



$\boldsymbol{k_{-1} = 1.12 \times 10^5\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium Acetate with $(mfa)_2CH^+$ BF_4^- in 20W80A at 25 °C

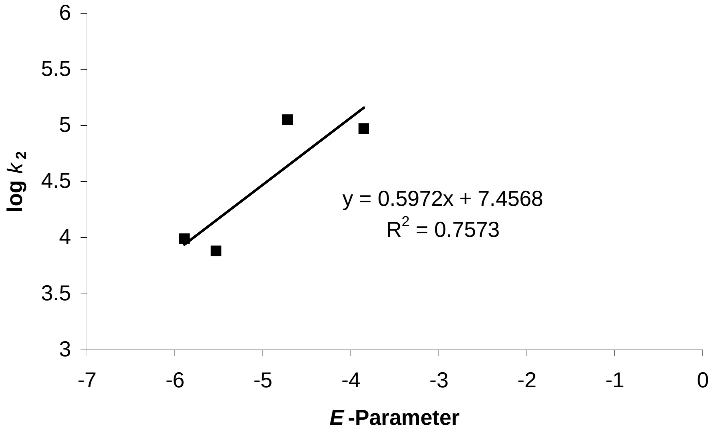
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	1.98×10^{-5}	6.09×10^{-4}	75.33
2	1.98×10^{-5}	9.75×10^{-4}	109.77
3	1.98×10^{-5}	1.53×10^{-3}	154.41
4	1.98×10^{-5}	1.98×10^{-3}	205.52



$\boldsymbol{k_{-1} = 9.33 \times 10^4\ M^{-1}\ s^{-1}}$

Nucleophilicity parameter of the Acetate Anion in 20W80A at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	$\lg k_{-1}$
$(mpa)_2CH^+$	-5.89	9.79×10^3	3.99
$(mor)_2CH^+$	-5.53	7.59×10^3	3.88
$(dpa)_2CH^+$	-4.72	1.12×10^5	5.05
$(mfa)_2CH^+$	-3.85	9.33×10^4	4.97

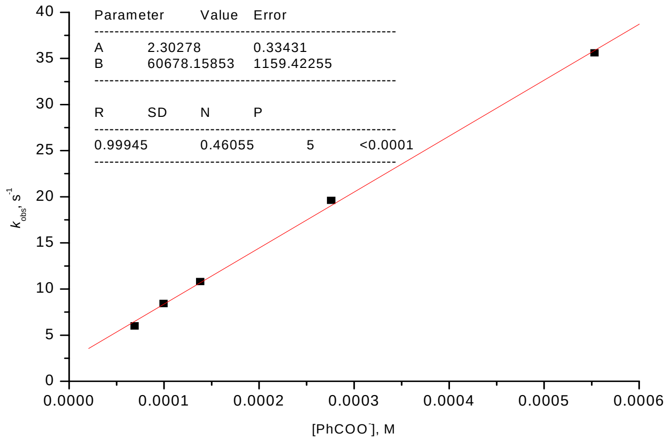


N = 12.49
s = 0.60

3.1 Combination of the Benzoate Anion with Benzhydryl Cations in Acetonitrile

Reaction of Tetrabutylammonium Benzoate with $(lil)_2CH^+$ BF_4^- *in Acetonitrile at 25 °C*

No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	1.02×10^{-5}	6.91×10^{-5}	6.00
2	1.02×10^{-5}	9.95×10^{-5}	8.42
3	1.02×10^{-5}	1.38×10^{-4}	10.8
4	1.02×10^{-5}	2.76×10^{-4}	19.6
5	1.02×10^{-5}	5.53×10^{-4}	35.6

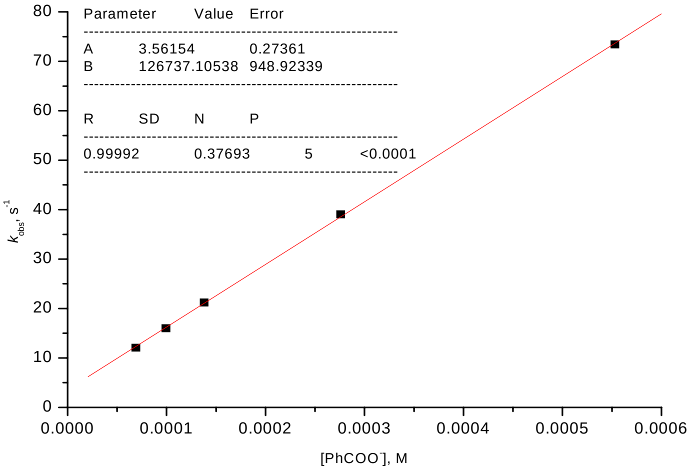


```
Parameter     Value          Error
------------------------------------------------------------
A             2.30278        0.33431
B             60678.15853    1159.42255
------------------------------------------------------------

R             SD             N        P
------------------------------------------------------------
0.99945       0.46055        5        <0.0001
------------------------------------------------------------
```

k_{-1} = 6.07 × 10^4 M^{-1} s^{-1}

Reaction of Tetrabutylammonium Benzoate with $(jul)_2CH^+$ BF_4^- in Acetonitrile at 25 ^{o}C

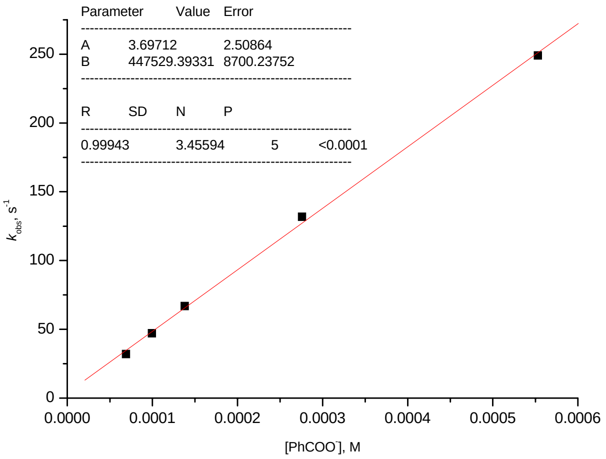
No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s $^{-1}$
1	9.99×10^{-6}	6.91×10^{-5}	12.1
2	9.99×10^{-6}	9.95×10^{-5}	16.0
3	9.99×10^{-6}	1.38×10^{-4}	21.2
4	9.99×10^{-6}	2.76×10^{-4}	39.0
5	9.99×10^{-6}	5.53×10^{-4}	73.4



$k_{-1} = 1.27 \times 10^5$ M^{-1} s^{-1}

Reaction of Tetrabutylammonium Benzoate with $(ind)_2CH^+$ BF_4^- in Acetonitrile at 25 ^{o}C

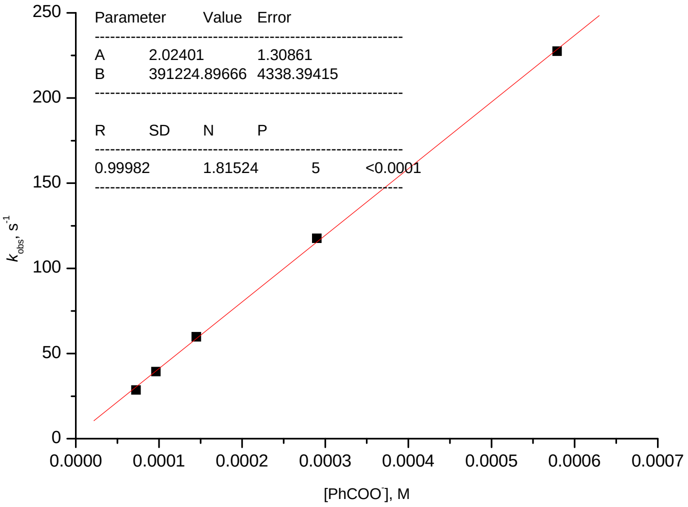
No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s $^{-1}$
1	1.00×10^{-5}	6.91×10^{-5}	31.9
2	1.00×10^{-5}	9.95×10^{-5}	47.1
3	1.00×10^{-5}	1.38×10^{-4}	66.8
4	1.00×10^{-5}	2.76×10^{-4}	131.8
5	1.00×10^{-5}	5.53×10^{-4}	249.1



$k_{-1} = 4.48 \times 10^5$ M $^{-1}$ s $^{-1}$

Reaction of Tetrabutylammonium Benzoate with (ind)$_2$CH$^+$ BF$_4^-$ in Acetonitrile at 20 ^{o}C

No.	[Ar$_2$CH$^+$]$_0$, M	[PhCOO$^-$]$_0$, M	k_{obs}, s^{-1}
1	1.00×10^{-5}	7.24×10^{-5}	28.6
2	1.00×10^{-5}	9.65×10^{-5}	39.4
3	1.00×10^{-5}	1.45×10^{-4}	59.8
4	1.00×10^{-5}	2.90×10^{-4}	117.6
5	1.00×10^{-5}	5.79×10^{-4}	227.5

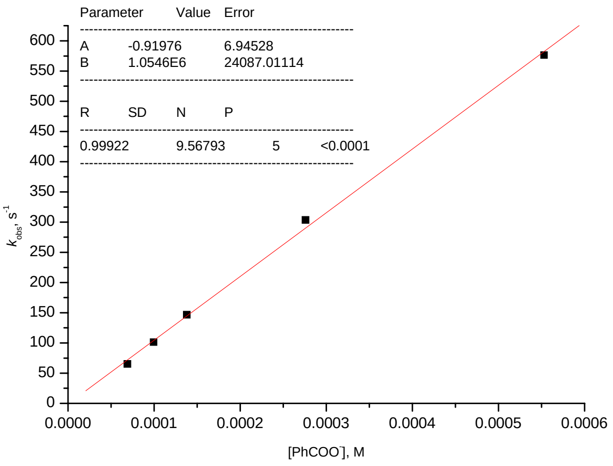


```
Parameter      Value      Error
------------------------------------------------------------
A        2.02401       1.30861
B        391224.89666  4338.39415
------------------------------------------------------------

R        SD        N        P
------------------------------------------------------------
0.99982        1.81524        5        <0.0001
------------------------------------------------------------
```

k_{-1}(20 ^{o}C) = 3.91×10^5 M^{-1} s^{-1}

Reaction of Tetrabutylammonium Benzoate with (thq)$_2$CH$^+$ BF$_4^-$ in Acetonitrile at 25 ^{o}C

No.	[Ar$_2$CH$^+$]$_0$, M	[PhCOO$^-$]$_0$, M	k_{obs}, s^{-1}
1	6.40×10^{-6}	6.91×10^{-5}	65.1
2	6.40×10^{-6}	9.95×10^{-5}	101.2
3	6.40×10^{-6}	1.38×10^{-4}	146.7
4	6.40×10^{-6}	2.76×10^{-4}	303.6
5	6.40×10^{-6}	5.53×10^{-4}	576.4

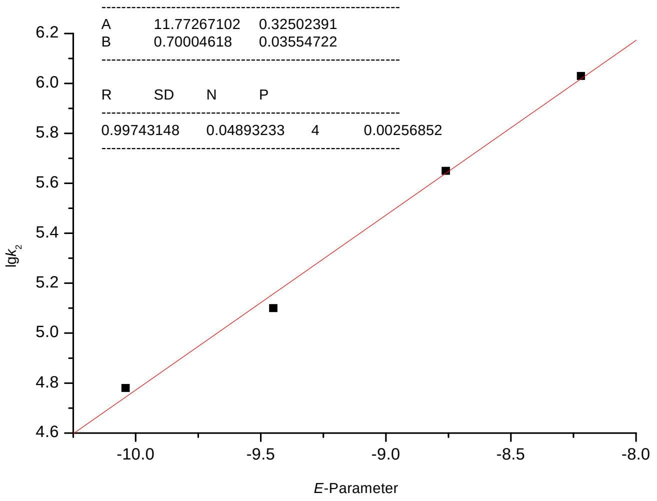


```
Parameter      Value      Error
------------------------------------------------------------
A        -0.91976      6.94528
B        1.0546E6      24087.01114
------------------------------------------------------------

R        SD        N        P
------------------------------------------------------------
0.99922        9.56793        5        <0.0001
------------------------------------------------------------
```

k_{-1} = 1.05×10^6 M^{-1} s^{-1}

Nucleophilicity parameter of the Benzoate Anion in Acetonitrile at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	$\lg k_{-1}$
$(lil)_2CH^+$	-10.04	6.07×10^4	4.78
$(jul)_2CH^+$	-9.45	1.27×10^5	5.10
$(ind)_2CH^+$	-8.76	4.48×10^5	5.65
$(thq)_2CH^+$	-8.22	1.05×10^6	6.03

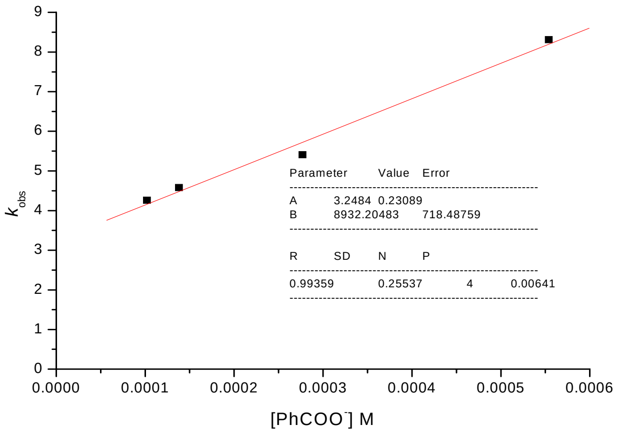


***N* = 16.82**
***s* = 0.70**

3.2 Combination of the Benzoate Anion with Benzhydryl Cations in 10:90 (v/v) Water Acetonitrile Mixtures (10W90AN)

Reaction of Tetrabutylammonium Benzoate with $(mor)_2CH^+$ BF_4^- in 10W90AN at 25 °C

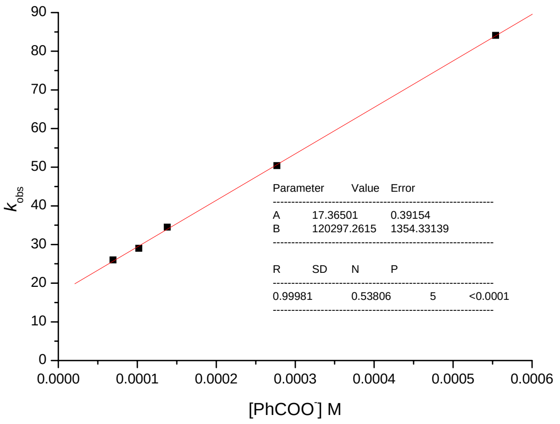
No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	7.65×10^{-6}	1.02×10^{-4}	4.26
2	7.65×10^{-6}	1.38×10^{-4}	4.58
3	7.65×10^{-6}	2.77×10^{-4}	5.41
5	7.65×10^{-6}	5.54×10^{-4}	8.31



k_{-1} = 8.93 × 10^3 $M^{-1}s^{-1}$

Reaction of Tetrabutylammonium Benzoate with $(dpa)_2CH^+$ BF_4^- in 10W90AN at 25 °C

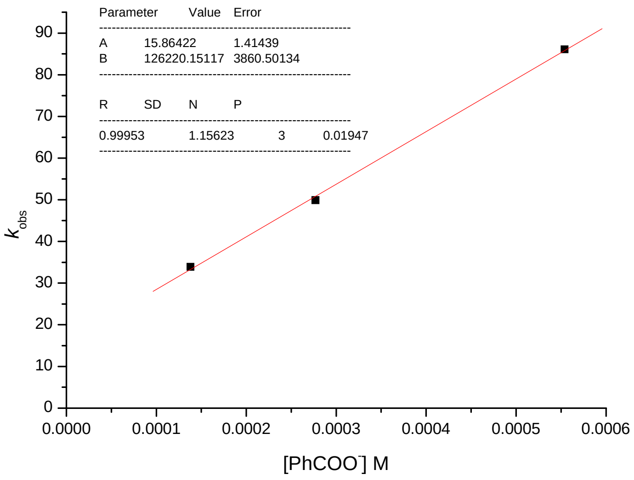
No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	5.90×10^{-6}	6.93×10^{-5}	26.0
2	5.90×10^{-6}	1.02×10^{-4}	29.0
3	5.90×10^{-6}	1.38×10^{-4}	34.5
4	5.90×10^{-6}	2.77×10^{-4}	50.4
5	5.90×10^{-6}	5.54×10^{-4}	84.1



$k_{-1} = 1.20 \times 10^{5}$ M^{-1}s^{-1}

Reaction of Tetrabutylammonium Benzoate with $(mfa)_2CH^+$ BF_4^- in 10W90AN at 25 °C

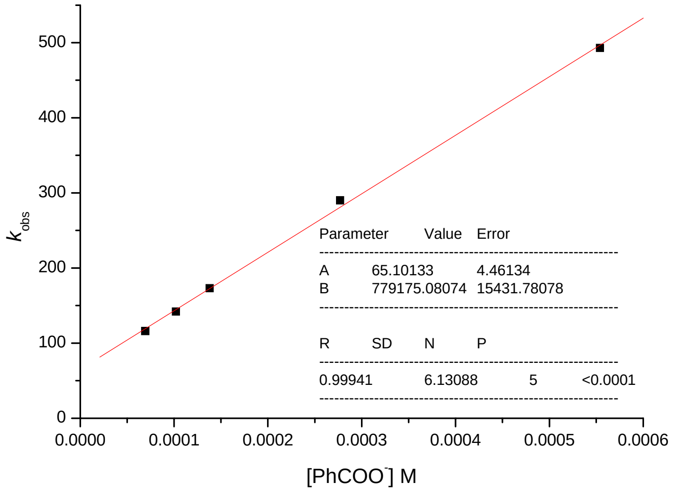
No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	1.16×10^{-5}	1.38×10^{-4}	33.9
2	1.16×10^{-5}	2.77×10^{-4}	49.9
3	1.16×10^{-5}	5.54×10^{-4}	86.1



$k_{-1} = 1.26 \times 10^{5}$ M^{-1}s^{-1}

Reaction of Tetrabutylammonium Benzoate with $(pfa)_2CH^+$ BF_4^- in 10W90AN at 25 °C

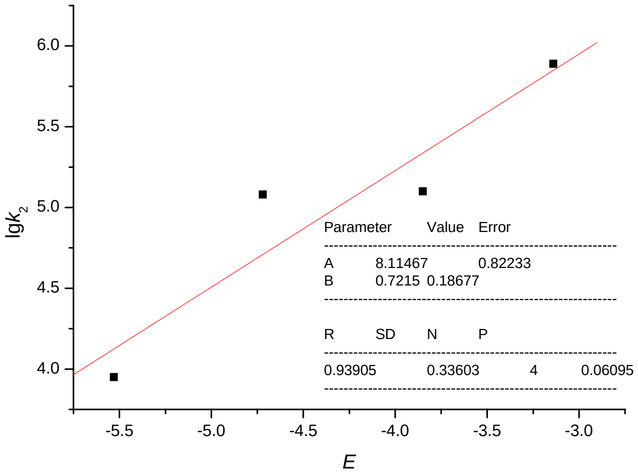
No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	6.73×10^{-6}	6.93×10^{-5}	116
2	6.73×10^{-6}	1.02×10^{-4}	142
3	6.73×10^{-6}	1.38×10^{-4}	173
4	6.73×10^{-6}	2.77×10^{-4}	291
5	6.73×10^{-6}	5.54×10^{-4}	493



$k_{-1} = 7.79 \times 10^5$ $M^{-1}s^{-1}$

Nucleophilicity parameter of the Benzoate Anion in 10W90AN at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	$\lg k_{-1}$
$(mor)_2CH^+$	-5.53	8.93×10^3	3.95
$(dpa)_2CH^+$	-4.72	1.20×10^5	5.08
$(mfa)_2CH^+$	-3.85	1.26×10^5	5.10
$(pfa)_2CH^+$	-3.14	7.79×10^5	5.89

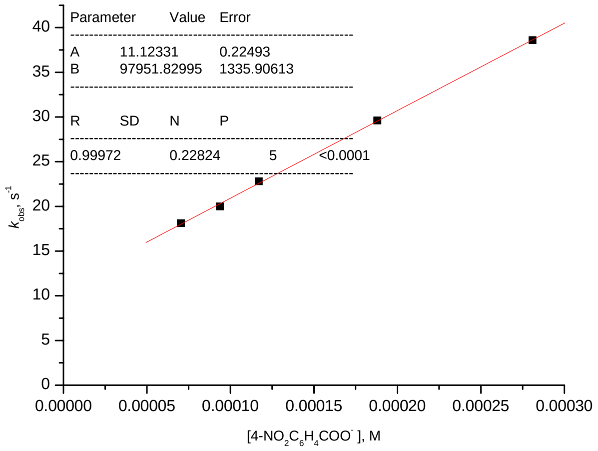


***N* = 11.25**
***s* = 0.72**

4.1 Combination of 4-Nitrobenzoate Anion with Benzhydrylium Cations in Acetonitrile at 25 °C

Reaction of Tetrabutylammonium 4-Nitrobenzoate with $(ind)_2CH^+ BF_4^-$ *in Acetonitrile at 25 °C*

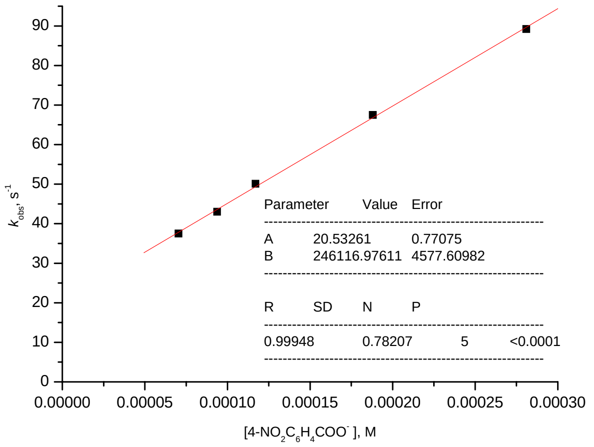
No.	$[Ar_2CH^+]_0$, M	$[4\text{-}NO_2C_6H_4COO^-]_0$, M	k_{obs}, s^{-1}	A_{eq}
1	9.14×10^{-6}	7.04×10^{-5}	18.1	0.75
2	9.14×10^{-6}	9.38×10^{-5}	20.0	0.67
3	9.14×10^{-6}	1.17×10^{-4}	22.8	0.60
4	9.14×10^{-6}	1.88×10^{-4}	29.6	0.46
5	9.14×10^{-6}	2.81×10^{-4}	38.6	0.36



$k_{-1} = 9.80 \times 10^4\ M^{-1}\ s^{-1}$

Reaction of Tetrabutylammonium 4-Nitrobenzoate with $(thq)_2CH^+ BF_4^-$ in Acetonitrile at 25 °C

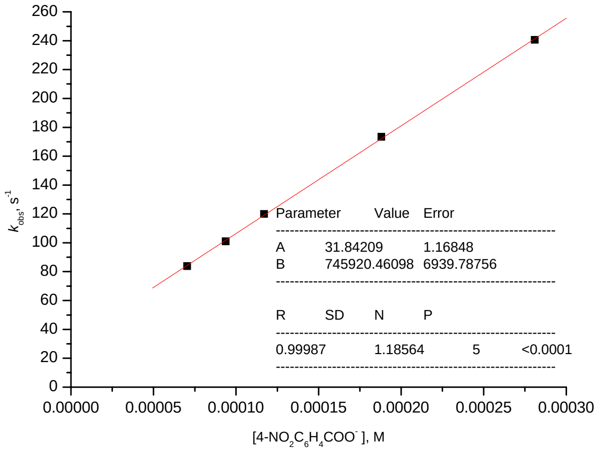
No.	$[Ar_2CH^+]_0$, M	$[4\text{-}NO_2C_6H_4COO^-]_0$, M	k_{obs}, s^{-1}	A_{eq}
1	9.53×10^{-6}	7.04×10^{-5}	37.5	0.51
2	9.53×10^{-6}	9.38×10^{-5}	43.5	0.46
3	9.53×10^{-6}	1.17×10^{-4}	50.1	0.41
4	9.53×10^{-6}	1.88×10^{-4}	67.5	0.31
5	9.53×10^{-6}	2.81×10^{-4}	89.2	0.25



$k_{-1} = 2.46 \times 10^5\ M^{-1}\ s^{-1}$

Reaction of Tetrabutylammonium 4-Nitrobenzoate with (pyr)$_2$CH$^+$ BF$_4^-$ in Acetonitrile at 25 ^{o}C

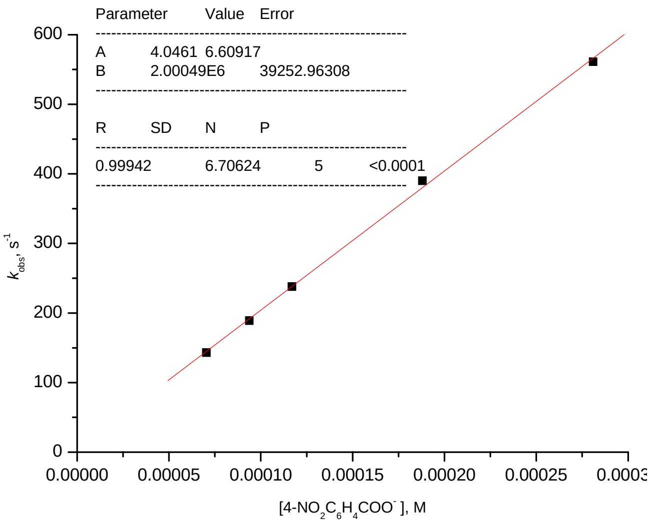
No.	[Ar$_2$CH$^+$]$_0$, M	[4-NO$_2$C$_6$H$_4$COO$^-$]$_0$, M	k_{obs}, s^{-1}	A_{eq}
1	6.81×10^{-6}	7.04×10^{-5}	83.8	0.45
2	6.81×10^{-6}	9.38×10^{-5}	101.0	0.36
3	6.81×10^{-6}	1.17×10^{-4}	120.0	0.31
4	6.81×10^{-6}	1.88×10^{-4}	173.4	0.22
5	6.81×10^{-6}	2.81×10^{-4}	240.6	0.17



$k_{-1} = 7.46 \times 10^5$ M^{-1} s^{-1}

Reaction of Tetrabutylammonium 4-Nitrobenzoate with (dma)$_2$CH$^+$ BF$_4^-$ in Acetonitrile at 25 ^{o}C

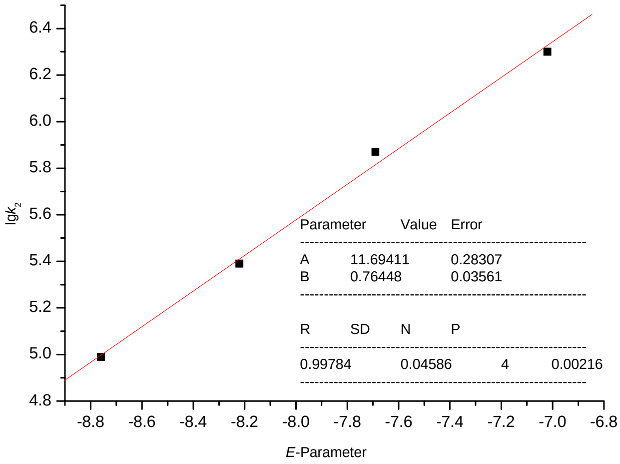
No.	[Ar$_2$CH$^+$]$_0$, M	[4-NO$_2$C$_6$H$_4$COO$^-$]$_0$, M	k_{obs}, s^{-1}
1	9.88×10^{-6}	7.04×10^{-5}	143
2	9.88×10^{-6}	9.38×10^{-5}	189
3	9.88×10^{-6}	1.17×10^{-4}	238
4	9.88×10^{-6}	1.88×10^{-4}	390
5	9.88×10^{-6}	2.81×10^{-4}	561



$k_{-1} = 2.00 \times 10^6$ M^{-1} s^{-1}

Nucleophilicity parameter of the 4-Nitrobenzoate Anion in Acetonitrile at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	$\lg k_{-1}$
$(ind)_2CH^+$	-8.76	9.80×10^4	4.99
$(thq)_2CH^+$	-8.22	2.46×10^5	5.39
$(pyr)_2CH^+$	-7.69	7.46×10^5	5.87
$(dma)_2CH^+$	-7.02	2.00×10^6	6.30

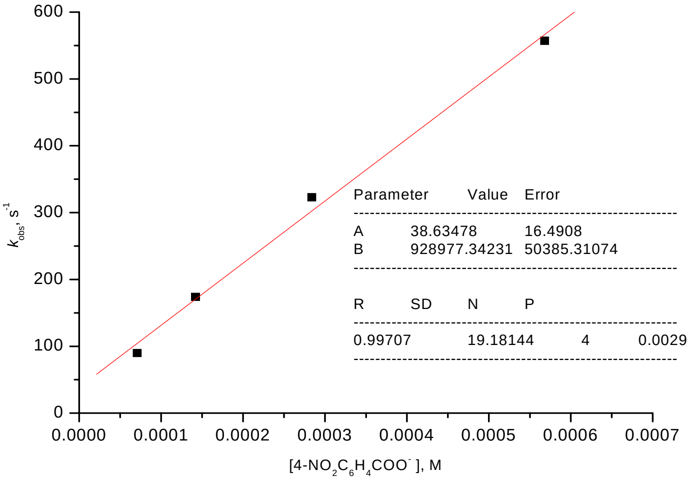


***N* = 15.30**
***s* = 0.76**

4.2 Combination of 4-Nitrobenzoate Anion with Benzhydrylium Cations in Acetone at 25 °C

Reaction of Tetrabutylammonium 4-Nitrobenzoate with $(lil)_2CH^+ BF_4^-$ *in Acetone at 25 °C*

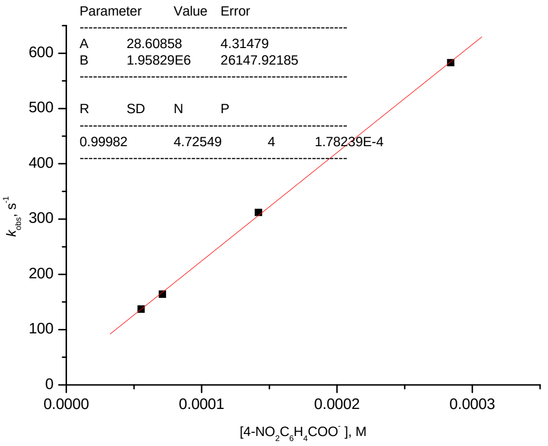
No.	$[Ar_2CH^+]_0$, M	$[4\text{-}NO_2C_6H_4COO^-]_0$, M	k_{obs}, s^{-1}
1	1.05×10^{-5}	7.10×10^{-5}	89.9
2	1.05×10^{-5}	1.42×10^{-4}	174
3	1.05×10^{-5}	2.84×10^{-4}	323
4	1.05×10^{-5}	5.68×10^{-4}	557



$\mathbf{k_{-1} = 9.29 \times 10^5\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium 4-Nitrobenzoate with $(jul)_2CH^+$ BF_4^- *in Acetone at 25* °C

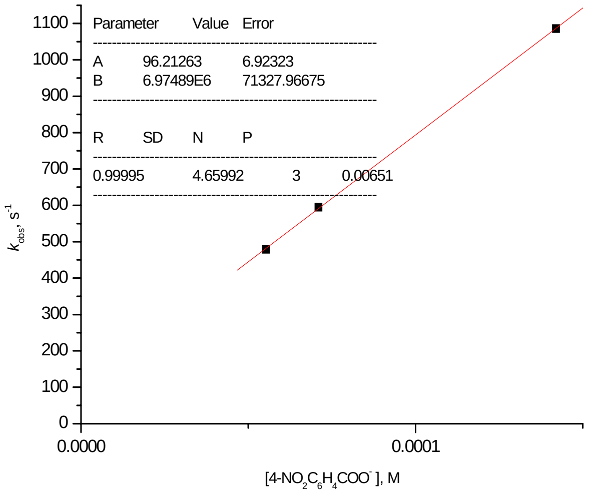
No.	$[Ar_2CH^+]_0$, M	$[4\text{-}NO_2C_6H_4COO^-]_0$, M	k_{obs}, s^{-1}
1	7.02×10^{-6}	5.53×10^{-5}	137
2	7.02×10^{-6}	7.10×10^{-5}	164
3	7.02×10^{-6}	1.42×10^{-4}	312
4	7.02×10^{-6}	2.84×10^{-4}	584



$\boldsymbol{k_{-1} = 1.96 \times 10^6\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium 4-Nitrobenzoate with $(ind)_2CH^+$ BF_4^- *in Acetone at 25* °C

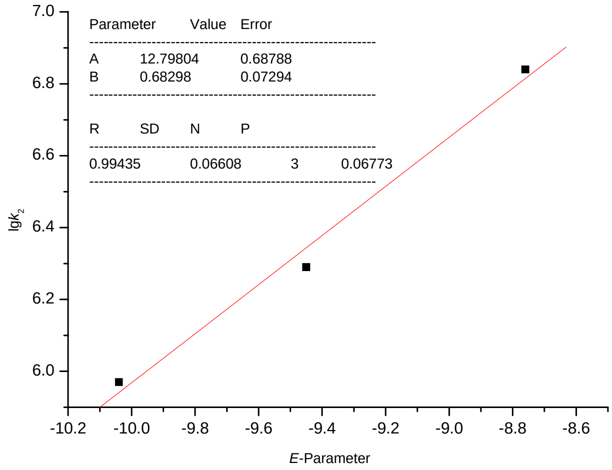
No.	$[Ar_2CH^+]_0$, M	$[4\text{-}NO_2C_6H_4COO^-]_0$, M	k_{obs}, s^{-1}
1	7.45×10^{-6}	5.53×10^{-5}	479
2	7.45×10^{-6}	7.10×10^{-5}	595
3	7.45×10^{-6}	1.42×10^{-4}	1086



$\boldsymbol{k_{-1} = 6.97 \times 10^6\ M^{-1}\ s^{-1}}$

Nucleophilicity parameter of the 4-Nitrobenzoate Anion in Acetone at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	$\lg k_{-1}$
$(lil)_2CH^+$	-10.04	9.29×10^5	5.97
$(jul)_2CH^+$	-9.45	1.96×10^6	6.29
$(ind)_2CH^+$	-8.76	6.97×10^6	6.84

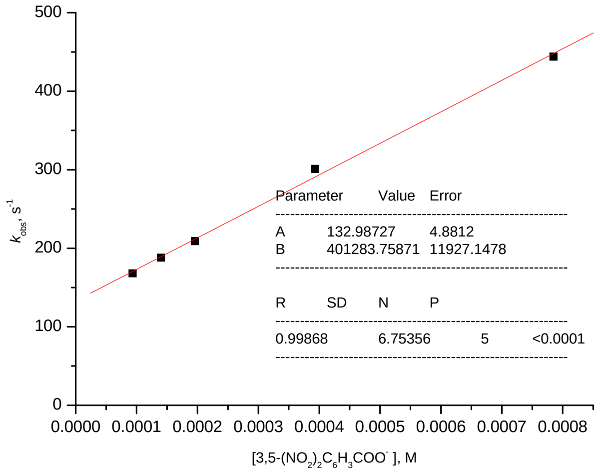


***N* = 18.74**
***s* = 0.68**

5.1 Combination of 3,5-Dinitrobenzoate Anion with Benzhydryl Cations in Acetonitrile at 25 °C

Reaction of Tetrabutylammonium 3,5-Dinitrobenzoate with $(dma)_2CH^+$ BF_4^- in Acetonitrile at 25 °C

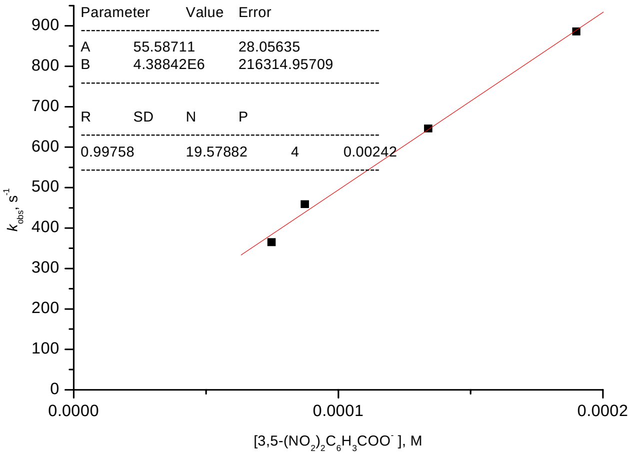
No.	$[Ar_2CH^+]_0$, M	$[3,5\text{-}(NO_2)_2C_6H_3COO^-]_0$, M	k_{obs}, s^{-1}	A_{eq}
1	8.29×10^{-6}	9.35×10^{-5}	168	0.95
2	8.29×10^{-6}	1.40×10^{-4}	188	0.82
3	8.29×10^{-6}	1.96×10^{-4}	209	0.71
4	8.29×10^{-6}	3.93×10^{-4}	301	0.50
5	8.29×10^{-6}	7.85×10^{-4}	444	0.31



$k_{-1} = 4.01 \times 10^5$ M^{-1} s^{-1}

Reaction of Tetrabutylammonium 3,5-Dinitrobenzoate with (mpa)$_2$CH$^+$ BF$_4^-$ in Acetonitrile at 25 ^{o}C

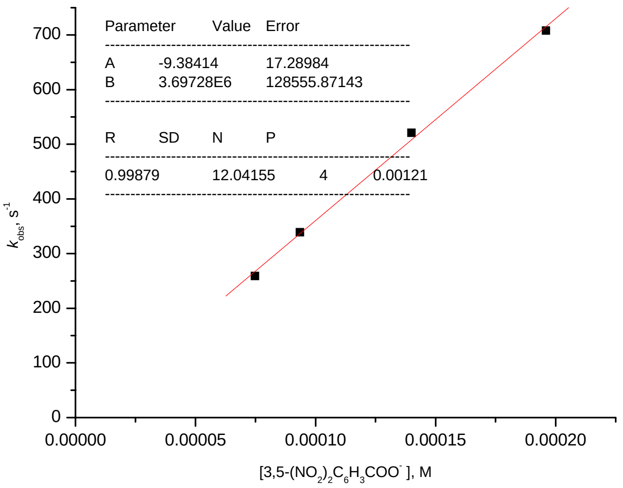
No.	[Ar$_2$CH$^+$]$_0$, M	[3,5-(NO$_2$)$_2$C$_6$H$_3$COO$^-$]$_0$, M	k_{obs}, s^{-1}
1	1.23×10^{-5}	7.48×10^{-5}	365
2	1.23×10^{-5}	8.74×10^{-5}	459
3	1.23×10^{-5}	1.34×10^{-4}	646
4	1.23×10^{-5}	1.90×10^{-4}	886



k_{-1} = 4.39 × 10^6 M^{-1} s^{-1}

Reaction of Tetrabutylammonium 3,5-Dinitrobenzoate with (mor)$_2$CH$^+$ BF$_4^-$ in Acetonitrile at 25 ^{o}C

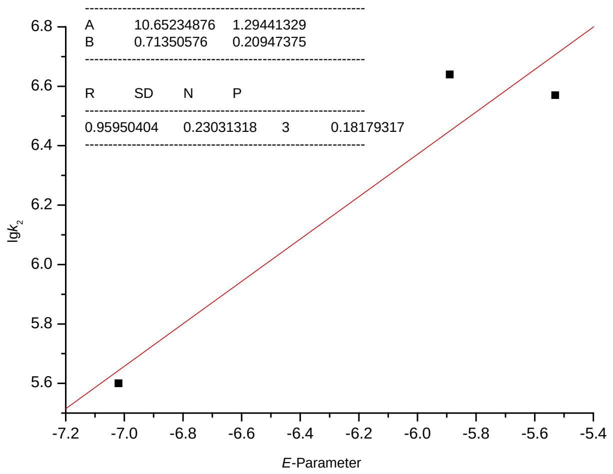
No.	[Ar$_2$CH$^+$]$_0$, M	[3,5-(NO$_2$)$_2$C$_6$H$_3$COO$^-$]$_0$, M	k_{obs}, s^{-1}
1	1.08×10^{-5}	7.48×10^{-5}	259
2	1.08×10^{-5}	9.35×10^{-5}	339
3	1.08×10^{-5}	1.40×10^{-4}	521
4	1.08×10^{-5}	1.96×10^{-4}	708



k_{-1} = 3.70 × 10^6 M^{-1} s^{-1}

Nucleophilicity parameter of the 3,5-Dinitrobenzoate Anion in Acetonitrile at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	lgk_{-1}
$(dma)_2CH^+$	-7.02	4.01×10^5	5.60
$(mpa)_2CH^+$	-5.89	4.39×10^6	6.64
$(mor)_2CH^+$	-5.53	3.70×10^6	6.57

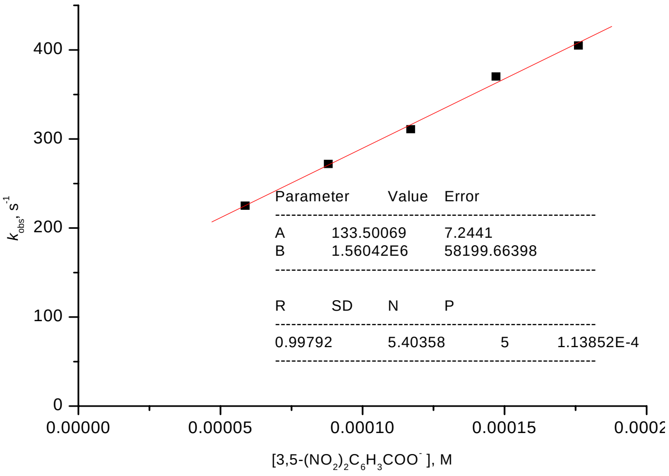


N = 14.93
s = 0.71

5.2 Combination of the 3,5-Dinitrobenzoate Anion with Benzhydrylium Cations in Acetone at 25 °C

Reaction of Tetrabutylammonium 3,5-Dinitrobenzoate with $(ind)_2CH^+$ BF_4^- in Acetone at 25 °C

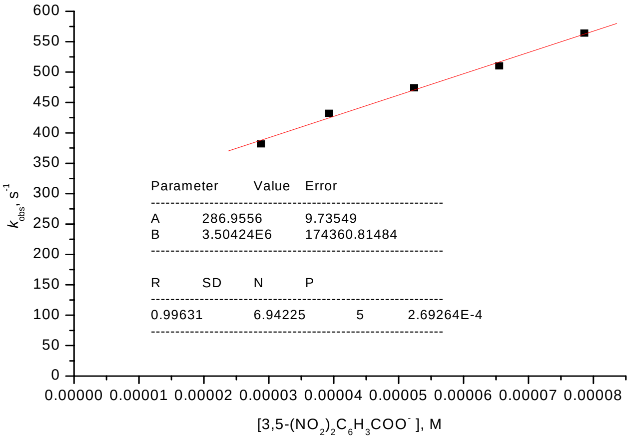
No.	$[Ar_2CH^+]_0$, M	$[3,5\text{-}(NO_2)_2C_6H_3COO^-]_0$, M	k_{obs}, s^{-1}	A_{eq}
1	7.45×10^{-6}	5.87×10^{-5}	225	0.56
2	7.45×10^{-6}	8.80×10^{-5}	271	0.50
3	7.45×10^{-6}	1.17×10^{-4}	312	0.43
4	7.45×10^{-6}	1.47×10^{-4}	371	0.38
5	7.45×10^{-6}	1.76×10^{-4}	405	0.33



$k_{-1} = 1.56 \times 10^6\ M^{-1}\ s^{-1}$

Reaction of Tetrabutylammonium 3,5-Dinitrobenzoate with $(thq)_2CH^+\ BF_4^-$ *in Acetone at 25 °C*

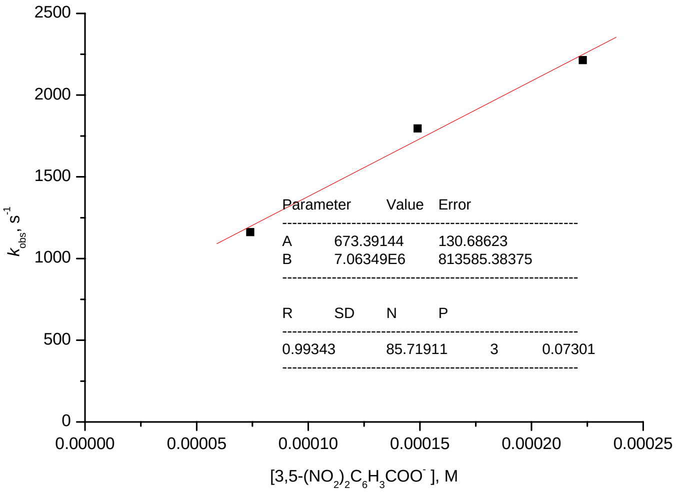
No.	$[Ar_2CH^+]_0$, M	$[3,5\text{-}(NO_2)_2C_6H_3COO^-]_0$, M	k_{obs}, s^{-1}	A_{eq}
1	4.04×10^{-6}	2.88×10^{-5}	382	0.27
2	4.04×10^{-6}	3.93×10^{-5}	432	0.24
3	4.04×10^{-6}	5.24×10^{-5}	475	0.21
4	4.04×10^{-6}	6.55×10^{-5}	510	0.20
5	4.04×10^{-6}	7.86×10^{-5}	564	0.18



$k_{-1} = 3.50 \times 10^6$ M^{-1} s^{-1}

Reaction of Tetrabutylammonium 3,5-Dinitrobenzoate with $(pyr)_2CH^+\ BF_4^-$ *in Acetone at 25 °C*

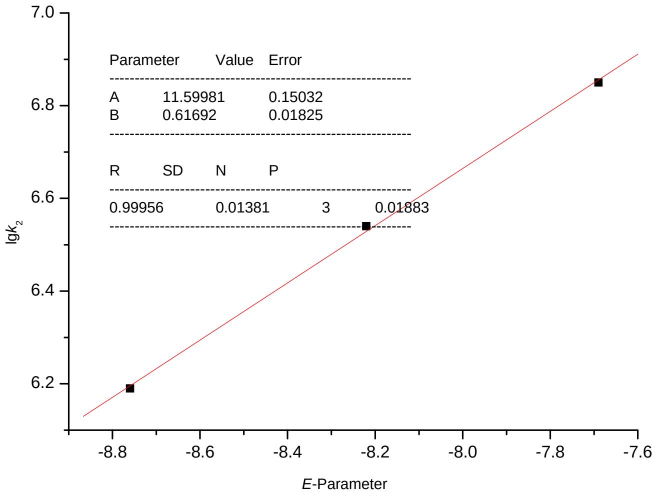
No.	$[Ar_2CH^+]_0$, M	$[3,5\text{-}(NO_2)_2C_6H_3COO^-]_0$, M	k_{obs}, s^{-1}	A_{eq}
1	1.49×10^{-5}	7.40×10^{-5}	1161	0.17
2	1.49×10^{-5}	1.49×10^{-4}	1796	0.10
3	1.49×10^{-5}	2.23×10^{-4}	2213	0.07



$k_{-1} = 7.06 \times 10^6$ M^{-1} s^{-1}

Nucleophilicity parameter of the 3,5-Dinitrobenzoate Anion in Acetone at 25 °C

Ar_2CH^+	E	k_{-1}, $M^{-1}s^{-1}$	$\lg k_{-1}$
$(ind)_2CH^+$	-8.76	1.56×10^6	6.19
$(thq)_2CH^+$	-8.22	3.50×10^6	6.54
$(pyr)_2CH^+$	-7.69	7.06×10^6	6.85



N = 18.80
s = 0.62

6. Determination of Ionization Rates. Because benzhydrylium carboxylates, which are derived from highly stabilized benzhydrylium cations, cannot be isolated, the double mixing technique was employed. In the first mixer, a solution of $Ar_2CH^+BF_4^-$ 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-$Bu_4N^+RCO_2^-$ 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 $Ar_2CH–O_2CR$. The ionizations are followed photometrically at the absorption maxima of Ar_2CH^+. The concentrations of the generated benzhydrylium carboxylates are between 2.5×10^{-6} mol/L and 1.0×10^{-5} mol/L, the excess of carboxylate ions varied between 7.5 and 110 equivalents of the benzhydryl carboxylate. Each measurement was repeated at least five times with variable excess of the carboxylate ions. The observed rate constants, with one solvent/nucleofuge-system as exception, did not change with the amount of added carboxylate and so k_1 represents the average of all accomplished measurements.

Ionization rate constants k_1 for 10W90A with acetate as leaving group were obtained as intercepts of the plots of k_{obs} versus the concentration of n-$Bu_4N^+AcO^-$, whereas k_{-1} for the combination reaction was obtained from the slope.

6.1 Ionization of Benzhydryl Acetates in 20:80 (v/v) Water Acetonitrile Mixtures (20W80AN)

Ionization of (lil)$_2$CH–OAc in 20W80AN at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	1.00×10^{-5}	4.02×10^{-5}	3.58
2	1.00×10^{-5}	5.93×10^{-5}	3.61
3	1.00×10^{-5}	1.30×10^{-4}	3.64
4	1.00×10^{-5}	2.69×10^{-4}	3.64
5	1.00×10^{-5}	4.74×10^{-4}	3.70

$k_1 = (3.63 \pm 0.04)$ s^{-1}

Ionization of (jul)$_2$CH–OAc in 20W80AN at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	5.04×10^{-6}	3.47×10^{-6}	19.4
2	2.52×10^{-6}	5.99×10^{-6}	19.7
3	5.04×10^{-6}	2.90×10^{-5}	19.4
4	5.04×10^{-6}	4.60×10^{-5}	19.3
5	5.04×10^{-6}	6.30×10^{-5}	19.2
6	5.04×10^{-6}	1.31×10^{-4}	21.4
7	5.04×10^{-6}	2.47×10^{-4}	19.7

$k_1 = (19.73 \pm 0.70)$ s^{-1}

Ionization of (ind)$_2$CH–OAc in 20W80AN at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	5.07×10^{-6}	2.14×10^{-6}	2.05
2	5.07×10^{-6}	4.85×10^{-6}	2.24
3	5.07×10^{-6}	9.36×10^{-6}	2.14
4	5.07×10^{-6}	2.38×10^{-5}	2.28
5	5.07×10^{-6}	5.27×10^{-5}	2.31
6	5.07×10^{-6}	1.36×10^{-4}	2.27
7	5.07×10^{-6}	2.65×10^{-4}	2.29

$k_1 = (2.23 \pm 0.09)$ s^{-1}

Ionization of (thq)$_2$CH–OAc in 20W80AN at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	5.03×10^{-6}	2.18×10^{-6}	6.10
2	5.03×10^{-6}	2.39×10^{-5}	6.22
3	5.03×10^{-6}	5.27×10^{-5}	5.99
4	5.03×10^{-6}	1.36×10^{-4}	5.88
5	5.03×10^{-6}	2.66×10^{-4}	5.84
6	2.52×10^{-6}	2.68×10^{-4}	5.18

$k_1 = (5.87 \pm 0.33)$ s^{-1}

Ionization of $(pyr)_2CH–OAc$ *in 20W80AN at 25* ^oC

No.	Before ionization		k_{obs}, s^{-1}
	[Ar_2CHOAc], M	[$MeCOO^-$], M	
1	5.48×10^{-6}	2.55×10^{-5}	8.31
2	5.48×10^{-6}	3.32×10^{-5}	8.62
3	5.48×10^{-6}	7.18×10^{-5}	8.61
4	5.48×10^{-6}	9.99×10^{-5}	8.72

$k_1 = (8.57 \pm 0.15)$ s^{-1}

Ionization of $(dma)_2CH–OAc$ *in 20W80AN at 25* ^oC

No.	Before ionization		k_{obs}, s^{-1}
	[Ar_2CHOAc], M	[$MeCOO^-$], M	
1	5.73×10^{-6}	4.87×10^{-6}	1.77
2	5.73×10^{-6}	3.65×10^{-5}	1.80
3	5.73×10^{-6}	7.86×10^{-5}	1.79
4	5.73×10^{-6}	1.63×10^{-4}	1.77
5	5.73×10^{-6}	3.11×10^{-4}	1.74

$k_1 = (1.77 \pm 0.02)$ s^{-1}

6.2 Ionization of Benzhydryl Acetates in 40:60 (v/v) Water Acetonitrile Mixtures (40W60AN)

Ionization of $(lil)_2CH–OAc$ in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	[Ar_2CHOAc], M	[$MeCOO^-$], M	
1	9.95×10^{-6}	4.23×10^{-6}	6.89
2	9.95×10^{-6}	3.87×10^{-5}	6.88
3	9.95×10^{-6}	5.90×10^{-5}	6.89
4	9.95×10^{-6}	1.28×10^{-4}	6.89
5	9.95×10^{-6}	2.66×10^{-4}	6.94
6	9.95×10^{-6}	5.41×10^{-4}	6.93

$k_1 = (6.90 \pm 0.02)$ s^{-1}

Ionization of $(jul)_2CH–OAc$ in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	[Ar_2CHOAc], M	[$MeCOO^-$], M	
1	9.93×10^{-6}	4.26×10^{-6}	39.8
2	9.93×10^{-6}	3.87×10^{-5}	39.7
3	9.93×10^{-6}	5.90×10^{-5}	39.9
4	9.93×10^{-6}	1.28×10^{-4}	39.7
5	9.93×10^{-6}	2.66×10^{-4}	39.9
6	9.93×10^{-6}	5.41×10^{-4}	40.3

$k_1 = (39.9 \pm 0.20)$ s^{-1}

Ionization of $(ind)_2CH–OAc$ in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	[Ar_2CHOAc], M	[$MeCOO^-$], M	
1	9.98×10^{-6}	4.01×10^{-5}	4.55
2	9.98×10^{-6}	1.40×10^{-4}	4.51
3	9.98×10^{-6}	3.91×10^{-4}	4.51

$k_1 = (4.52 \pm 0.02)$ s^{-1}

Ionization of $(thq)_2CH–OAc$ in 40W60AN at 25 °C

No.	Before ionization $[Ar_2CHOAc]$, M	 $[MeCOO^-]$, M	k_{obs}, s^{-1}
1	9.96×10^{-6}	4.01×10^{-5}	13.5
2	9.96×10^{-6}	1.40×10^{-4}	13.4
3	9.96×10^{-6}	3.91×10^{-4}	13.4

$k_1 = (13.4 \pm 0.05)\ s^{-1}$

Ionization of $(pyr)_2CH–OAc$ in 40W60AN at 25 °C

No.	Before ionization $[Ar_2CHOAc]$, M	 $[MeCOO^-]$, M	k_{obs}, s^{-1}
1	9.06×10^{-6}	3.58×10^{-5}	22.0
2	9.06×10^{-6}	1.71×10^{-4}	22.2
3	9.06×10^{-6}	3.50×10^{-4}	21.9

$k_1 = (22.0 \pm 0.12)\ s^{-1}$

Ionization of $(dma)_2CH–OAc$ in 40W60AN at 25 °C

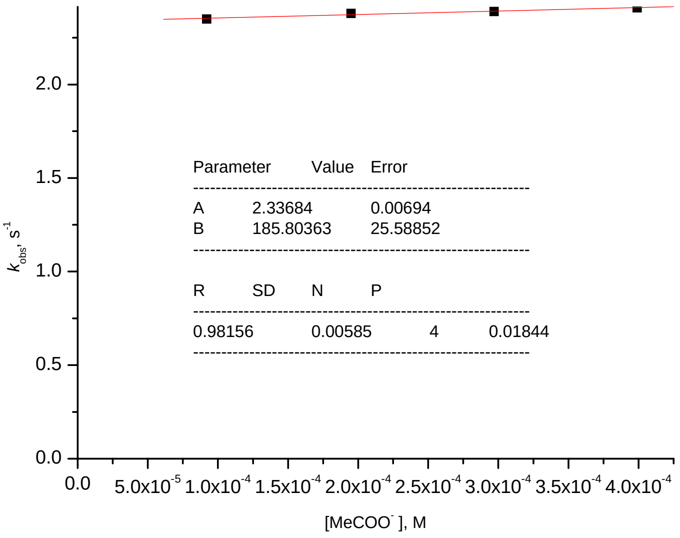
No.	Before ionization $[Ar_2CHOAc]$, M	 $[MeCOO^-]$, M	k_{obs}, s^{-1}
1	8.70×10^{-6}	3.62×10^{-5}	4.52
2	8.70×10^{-6}	1.71×10^{-4}	4.58
3	8.70×10^{-6}	3.51×10^{-4}	4.53

$k_1 = (4.54 \pm 0.03)\ s^{-1}$

6.3 Ionization of Benzhydryl Acetates in 10:90 (v/v) Water Acetone Mixtures (10W90A)

Ionization of $(jul)_2CH–OAc$ in 10W90A at 25 °C

No.	Before ionization $[Ar_2CHOAc]$, M	 $[MeCOO^-]$, M	k_{obs}, s^{-1}
1	9.92×10^{-6}	9.20×10^{-5}	2.35
2	9.92×10^{-6}	1.95×10^{-4}	2.38
3	9.92×10^{-6}	2.97×10^{-4}	2.39
4	9.92×10^{-6}	3.99×10^{-4}	2.41

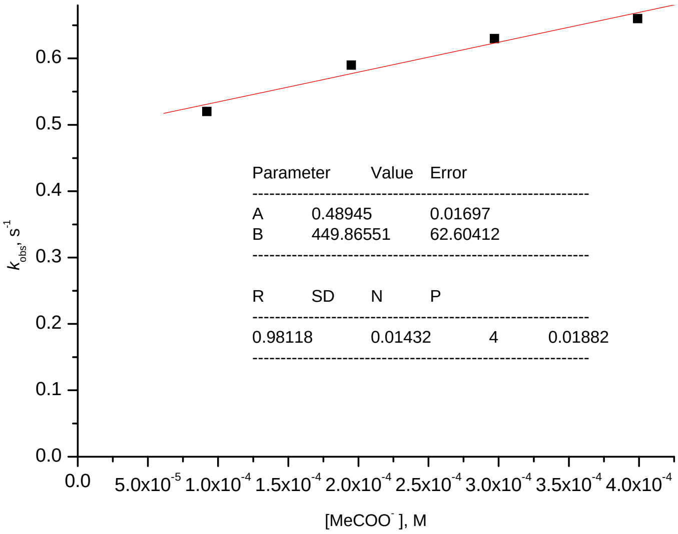


```
Parameter        Value    Error
------------------------------------------------------------
A        2.33684        0.00694
B        185.80363      25.58852
------------------------------------------------------------

R        SD        N        P
------------------------------------------------------------
0.98156        0.00585        4        0.01844
------------------------------------------------------------
```

$k_1 = 2.34\ s^{-1}$
$k_{-1} = 1.85 \times 10^2\ M^{-1}\ s^{-1}$

Ionization of $(ind)_2CH–OAc$ in 10W90A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CHOAc]$, M	$[MeCOO^{-}]$, M	
1	1.00×10^{-5}	9.20×10^{-5}	0.52
2	1.00×10^{-5}	1.95×10^{-4}	0.59
3	1.00×10^{-5}	2.97×10^{-4}	0.63
4	1.00×10^{-5}	3.99×10^{-4}	0.66



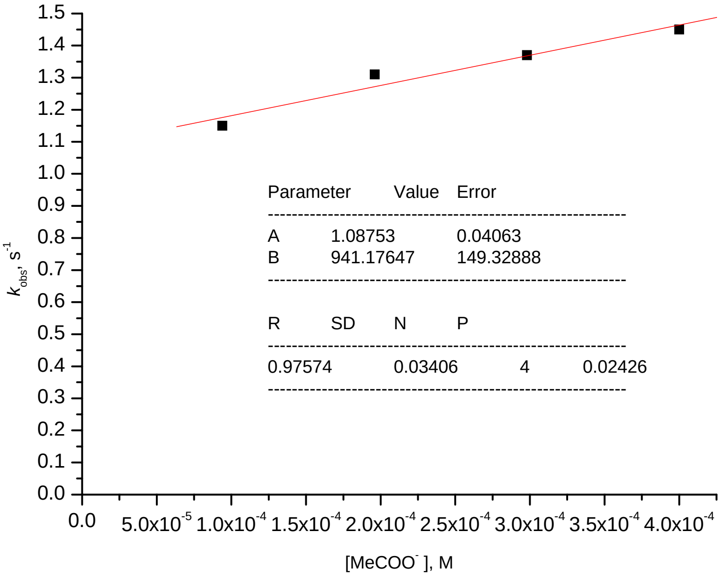
```
Parameter        Value      Error
-----------------------------------------------------------
A        0.48945        0.01697
B        449.86551      62.60412
-----------------------------------------------------------

R        SD        N        P
-----------------------------------------------------------
0.98118        0.01432        4        0.01882
-----------------------------------------------------------
```

$k_1 = 0.49\ s^{-1}$

$k_{-1} = 4.50 \times 10^2\ M^{-1}\ s^{-1}$

Ionization of $(thq)_2CH–OAc$ in 10W90A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CHOAc]$, M	$[MeCOO^{-}]$, M	
1	8.70×10^{-6}	9.40×10^{-5}	1.15
2	8.70×10^{-6}	1.96×10^{-4}	1.31
3	8.70×10^{-6}	2.98×10^{-4}	1.37
4	8.70×10^{-6}	4.00×10^{-4}	1.45



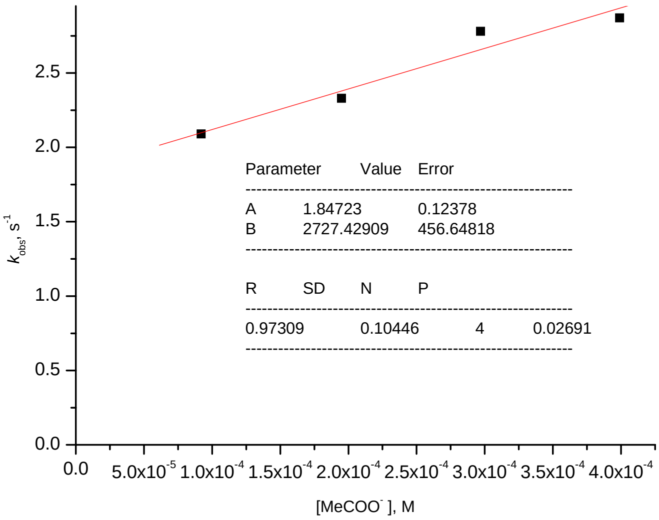
```
Parameter        Value      Error
-----------------------------------------------------------
A        1.08753        0.04063
B        941.17647      149.32888
-----------------------------------------------------------

R        SD        N        P
-----------------------------------------------------------
0.97574        0.03406        4        0.02426
-----------------------------------------------------------
```

$k_1 = 1.09\ s^{-1}$

$k_{-1} = 9.41 \times 10^2\ M^{-1}\ s^{-1}$

Ionization of $(pyr)_2CH–OAc$ in 10W90A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CHOAc]$, M	$[MeCOO^-]$, M	
1	1.00×10^{-5}	9.20×10^{-5}	2.09
2	1.00×10^{-5}	1.95×10^{-4}	2.33
3	1.00×10^{-5}	2.97×10^{-4}	2.87
4	1.00×10^{-5}	3.99×10^{-4}	2.78



$\boldsymbol{k_1 = 1.85\ s^{-1}}$

$\boldsymbol{k_{-1} = 2.73 \times 10^3\ M^{-1}\ s^{-1}}$

Ionization of $(dma)_2CH–OAc$ in 10W90A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CHOAc]$, M	$[MeCOO^-]$, M	
1	9.88×10^{-6}	9.20×10^{-5}	0.85
2	9.88×10^{-6}	1.95×10^{-4}	1.15
3	9.88×10^{-6}	2.97×10^{-4}	1.19
4	9.88×10^{-6}	3.99×10^{-4}	1.15

$k_1 = (1.08 \pm 0.14)\ s^{-1}$

6.4 Ionization of Benzhydryl Acetates in 20:80 (v/v) Water Acetone Mixtures (20W80A)

Ionization of $(lil)_2CH–OAc$ in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CHOAc]$, M	$[MeCOO^-]$, M	
1	9.98×10^{-6}	8.95×10^{-5}	2.24
2	9.98×10^{-6}	1.89×10^{-4}	2.24
3	9.98×10^{-6}	3.88×10^{-4}	2.24

$k_1 = (2.24 \pm 0.00)\ s^{-1}$

Ionization of $(jul)_2CH–OAc$ in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CHOAc]$, M	$[MeCOO^-]$, M	
1	9.95×10^{-6}	8.94×10^{-5}	8.33
2	9.95×10^{-6}	1.89×10^{-4}	8.40
3	9.95×10^{-6}	3.88×10^{-4}	8.39

$k_1 = (8.37 \pm 0.03)\ s^{-1}$

Ionization of $(\mathrm{ind})_2\mathrm{CH–OAc}$ in 20W80A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	$[\mathrm{Ar_2CHOAc}]$, M	$[\mathrm{MeCOO^-}]$, M	
1	9.91×10^{-6}	8.95×10^{-5}	1.40
2	9.91×10^{-6}	1.89×10^{-4}	1.41
3	9.91×10^{-6}	3.88×10^{-4}	1.43

$k_1 = (1.40 \pm 0.01)$ s^{-1}

Ionization of $(\mathrm{thq})_2\mathrm{CH–OAc}$ in 20W80A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	$[\mathrm{Ar_2CHOAc}]$, M	$[\mathrm{MeCOO^-}]$, M	
1	9.93×10^{-6}	8.94×10^{-5}	3.30
2	9.93×10^{-6}	1.89×10^{-4}	3.36
3	9.93×10^{-6}	3.88×10^{-4}	3.42

$k_1 = (3.36 \pm 0.05)$ s^{-1}

Ionization of $(\mathrm{pyr})_2\mathrm{CH–OAc}$ in 20W80A at 25 $^{\circ}$C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	$[\mathrm{Ar_2CHOAc}]$, M	$[\mathrm{MeCOO^-}]$, M	
1	6.20×10^{-6}	6.77×10^{-5}	4.87
2	6.20×10^{-6}	1.42×10^{-4}	4.95
3	6.20×10^{-6}	2.89×10^{-4}	5.04

$k_1 = (4.95 \pm 0.07)$ s^{-1}

Ionization of $(\mathrm{dma})_2\mathrm{CH–OAc}$ in 20W80A at 25 $^{\circ}$C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	$[\mathrm{Ar_2CHOAc}]$, M	$[\mathrm{MeCOO^-}]$, M	
1	6.14×10^{-6}	6.78×10^{-5}	2.10
2	6.14×10^{-6}	1.42×10^{-4}	2.21
3	6.14×10^{-6}	2.89×10^{-4}	2.36

$k_1 = (2.22 \pm 0.11)$ s^{-1}

6.5 Ionization of Benzhydryl Acetates in 40:60 (v/v) Water Acetone Mixtures (40W60A)

Ionization of $(\mathrm{lil})_2\mathrm{CH–OAc}$ in 40W60A at 25 $^{\circ}$C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	$[\mathrm{Ar_2CHOAc}]$, M	$[\mathrm{MeCOO^-}]$, M	
1	9.86×10^{-6}	8.95×10^{-5}	13.5
2	9.86×10^{-6}	1.89×10^{-4}	13.5
3	9.86×10^{-6}	3.88×10^{-4}	13.7

$k_1 = (13.6 \pm 0.09)$ s^{-1}

Ionization of $(\mathrm{jul})_2\mathrm{CH–OAc}$ in 40W60A at 25 $^{\circ}$C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	$[\mathrm{Ar_2CHOAc}]$, M	$[\mathrm{MeCOO^-}]$, M	
1	9.95×10^{-6}	8.94×10^{-5}	61.0
2	9.95×10^{-6}	1.89×10^{-4}	61.2
3	9.95×10^{-6}	3.88×10^{-4}	62.4

$k_1 = (61.5 \pm 0.62)$ s^{-1}

Ionization of (ind)$_2$CH–OAc in 40W60A at 25 °C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	9.91×10^{-6}	8.95×10^{-5}	9.35
2	9.91×10^{-6}	1.89×10^{-4}	9.37
3	9.91×10^{-6}	3.88×10^{-4}	9.52

$k_1 = (9.41 \pm 0.08)$ s^{-1}

Ionization of (thq)$_2$CH–OAc in 40W60A at 25 °C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	9.93×10^{-6}	8.94×10^{-5}	24.4
2	9.93×10^{-6}	1.89×10^{-4}	25.0
3	9.93×10^{-6}	3.88×10^{-4}	25.4

$k_1 = (24.9 \pm 0.41)$ s^{-1}

Ionization of (pyr)$_2$CH–OAc in 40W60A at 25 °C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	6.20×10^{-6}	6.77×10^{-5}	35.5
2	6.20×10^{-6}	1.42×10^{-4}	36.0
3	6.20×10^{-6}	2.89×10^{-4}	36.3

$k_1 = (35.9 \pm 0.33)$ s^{-1}

Ionization of (dma)$_2$CH–OAc in 40W60A at 25 °C

No.	Before ionization		$k_{1\psi}$, s^{-1}
	[Ar$_2$CHOAc], M	[MeCOO$^-$], M	
1	6.14×10^{-6}	6.78×10^{-5}	9.25
2	6.14×10^{-6}	1.42×10^{-4}	9.32
3	6.14×10^{-6}	2.89×10^{-4}	9.32

$k_1 = (9.30 \pm 0.03)$ s^{-1}

7.1 Ionization of Benzhydryl Benzoates in 20:80 (v/v) Water Acetonitrile Mixtures (20W80AN)

Ionization of (lil)$_2$CH-OBz in 20W80AN at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	1.02×10^{-5}	8.93×10^{-5}	9.61
2	1.02×10^{-5}	1.89×10^{-4}	9.58
3	1.02×10^{-5}	3.88×10^{-4}	9.54

$k_1 = (9.58 \pm 0.03)$ s^{-1}

Ionization of (jul)$_2$CH-OBz in 20W80AN at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	9.99×10^{-6}	8.94×10^{-5}	44.9
2	9.99×10^{-6}	1.89×10^{-4}	44.8
3	9.99×10^{-6}	3.88×10^{-4}	45.0

$k_1 = (44.9 \pm 0.08)$ s^{-1}

Ionization of (ind)$_2$CH-OBz in 20W80AN at 25 °C

No.	Before ionization [Ar$_2$CH-OBz], M	 [BzO$^-$], M	k_{obs}, s^{-1}
1	1.00×10^{-5}	8.94×10^{-5}	5.16
2	1.00×10^{-5}	1.89×10^{-4}	5.18
3	1.00×10^{-5}	3.88×10^{-4}	5.13

$k_1 = (5.16 \pm 0.02)$ s^{-1}

Ionization of (thq)$_2$CH-OBz in 20W80AN at 25 °C

No.	Before ionization [Ar$_2$CH-OBz], M	 [BzO$^-$], M	k_{obs}, s^{-1}
1	6.40×10^{-6}	9.30×10^{-5}	14.8
2	6.40×10^{-6}	1.83×10^{-4}	14.7
3	6.40×10^{-6}	3.92×10^{-4}	14.7

$k_1 = (14.7 \pm 0.05)$ s^{-1}

Ionization of (pyr)$_2$CH-OBz in 20W80AN at 25 °C

No.	Before ionization [Ar$_2$CH-OBz], M	 [BzO$^-$], M	k_{obs}, s^{-1}
1	8.78×10^{-6}	6.36×10^{-5}	21.1
2	8.78×10^{-6}	9.17×10^{-5}	21.0
3	8.78×10^{-6}	1.36×10^{-4}	21.2
4	8.78×10^{-6}	2.81×10^{-4}	21.2
5	8.78×10^{-6}	5.70×10^{-4}	21.1

$k_1 = (21.1 \pm 0.07)$ s^{-1}

Ionization of (dma)$_2$CH-OBz in 20W80AN at 25 °C

No.	Before ionization [Ar$_2$CH-OBz], M	 [BzO$^-$], M	k_{obs}, s^{-1}
1	1.00×10^{-5}	6.24×10^{-5}	4.29
2	1.00×10^{-5}	9.05×10^{-5}	4.22
3	1.00×10^{-5}	1.35×10^{-4}	4.26
4	1.00×10^{-5}	2.80×10^{-4}	4.26
5	1.00×10^{-5}	5.69×10^{-4}	4.36

$k_1 = (4.28 \pm 0.05)$ s^{-1}

7.2 Ionization of Benzhydryl Benzoates in 40:60 (v/v) Water Acetonitrile Mixtures (40W60AN)

Ionization of (lil)$_2$CH-OBz in 40W60AN at 25 °C

No.	Before ionization [Ar$_2$CH-OBz], M	 [BzO$^-$], M	k_{obs}, s^{-1}
1	1.02×10^{-5}	8.93×10^{-5}	12.0
2	1.02×10^{-5}	1.89×10^{-4}	11.9
3	1.02×10^{-5}	3.88×10^{-4}	11.8

$k_1 = (11.9 \pm 0.08)$ s^{-1}

Ionization of $(jul)_2$CH-OBz in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	9.99×10^{-6}	8.94×10^{-5}	68.6
2	9.99×10^{-6}	1.89×10^{-4}	67.3
3	9.99×10^{-6}	3.88×10^{-4}	67.8

$k_1 = (67.9 \pm 0.53)\ s^{-1}$

Ionization of $(ind)_2$CH-OBz in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	1.00×10^{-5}	8.94×10^{-5}	5.16
2	1.00×10^{-5}	1.89×10^{-4}	5.18
3	1.00×10^{-5}	3.88×10^{-4}	5.13

$k_1 = (5.16 \pm 0.02)\ s^{-1}$

Ionization of $(thq)_2$CH-OBz in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	6.40×10^{-6}	9.30×10^{-5}	24.6
2	6.40×10^{-6}	1.83×10^{-4}	24.6
3	6.40×10^{-6}	3.92×10^{-4}	24.3

$k_1 = (24.5 \pm 0.14)\ s^{-1}$

Ionization of $(pyr)_2$CH-OBz in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	8.78×10^{-6}	6.36×10^{-5}	36.2
2	8.78×10^{-6}	9.17×10^{-5}	36.0
3	8.78×10^{-6}	1.36×10^{-4}	36.3
4	8.78×10^{-6}	2.81×10^{-4}	35.6
5	8.78×10^{-6}	5.70×10^{-4}	35.9

$k_1 = (36.0 \pm 0.25)\ s^{-1}$

Ionization of $(dma)_2$CH-OBz in 40W60AN at 25 ^oC

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	1.00×10^{-5}	6.24×10^{-5}	7.67
2	1.00×10^{-5}	9.05×10^{-5}	7.57
3	1.00×10^{-5}	1.35×10^{-4}	7.53
4	1.00×10^{-5}	2.80×10^{-4}	7.63
5	1.00×10^{-5}	5.69×10^{-4}	7.69

$k_1 = (7.62 \pm 0.06)\ s^{-1}$

7.3 Ionization of Benzhydryl Benzoates in 20:80 (v/v) Water Acetone Mixtures (20W80A)

Ionization of $(lil)_2CH$-OBz in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	9.86×10^{-6}	8.99×10^{-5}	4.92
2	9.86×10^{-6}	1.90×10^{-4}	4.95
3	9.86×10^{-6}	3.89×10^{-4}	5.00
4	9.86×10^{-6}	4.10×10^{-4}	5.01

$k_1 = (4.97 \pm 0.04)\ s^{-1}$

Ionization of $(jul)_2CH$-OBz in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	9.95×10^{-6}	8.99×10^{-5}	19.4
2	9.95×10^{-6}	1.90×10^{-4}	19.8
3	9.95×10^{-6}	3.89×10^{-4}	19.8
	9.95×10^{-6}	4.10×10^{-4}	19.8

$k_1 = (19.7 \pm 0.17)\ s^{-1}$

Ionization of $(ind)_2CH$-OBz in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	9.91×10^{-6}	8.99×10^{-5}	2.87
2	9.91×10^{-6}	1.90×10^{-4}	2.87
3	9.91×10^{-6}	3.89×10^{-4}	2.91
4	9.91×10^{-6}	4.10×10^{-4}	2.91

$k_1 = (2.89 \pm 0.02)\ s^{-1}$

Ionization of $(thq)_2CH$-OBz in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	9.93×10^{-6}	8.99×10^{-5}	7.01
2	9.93×10^{-6}	1.90×10^{-4}	7.07
3	9.93×10^{-6}	3.89×10^{-4}	7.28
4	9.93×10^{-6}	4.10×10^{-4}	7.19

$k_1 = (7.14 \pm 0.10)\ s^{-1}$

Ionization of $(pyr)_2CH$-OBz in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	6.20×10^{-6}	6.77×10^{-5}	9.48
2	6.20×10^{-6}	1.41×10^{-4}	9.90
3	6.20×10^{-6}	2.33×10^{-5}	10.1

$k_1 = (9.83 \pm 0.26)\ s^{-1}$

Ionization of $(dma)_2CH$-OBz in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}OBz]$, M	$[BzO^-]$, M	
1	1.00×10^{-5}	6.77×10^{-5}	3.34
2	1.00×10^{-5}	1.42×10^{-4}	3.50
3	1.00×10^{-5}	1.95×10^{-5}	3.62

$k_1 = (3.49 \pm 0.12)\ s^{-1}$

7.4 Ionization of Benzhydryl Benzoates in 40:60 (v/v) Water Acetone Mixtures (40W60A)

Ionization of (lil)$_2$CH-OBz in 40W60A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	9.86×10^{-6}	8.99×10^{-5}	18.8
2	9.86×10^{-6}	1.90×10^{-4}	19.4
3	9.86×10^{-6}	3.89×10^{-4}	19.5
	9.86×10^{-6}	4.10×10^{-4}	19.6

$k_1 = (19.3 \pm 0.31)$ s^{-1}

Ionization of (jul)$_2$CH-OBz in 40W60A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	9.95×10^{-6}	8.99×10^{-5}	94.3
2	9.95×10^{-6}	1.90×10^{-4}	95.0
3	9.95×10^{-6}	3.89×10^{-4}	94.7
4	9.95×10^{-6}	4.10×10^{-4}	96.0

$k_1 = (95.0 \pm 0.63)$ s^{1}

Ionization of (ind)$_2$CH-OBz in 40W60A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	9.91×10^{-6}	8.99×10^{-5}	13.6
2	9.91×10^{-6}	1.90×10^{-4}	13.7
3	9.91×10^{-6}	3.89×10^{-4}	13.8
4	9.91×10^{-6}	4.10×10^{-4}	13.9

$k_1 = (13.8 \pm 0.03)$ s^{-1}

Ionization of (thq)$_2$CH-OBz in 40W60A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	9.93×10^{-6}	8.99×10^{-5}	36.2
2	9.93×10^{-6}	1.90×10^{-4}	35.9
3	9.93×10^{-6}	3.89×10^{-4}	36.5
	9.93×10^{-6}	4.10×10^{-4}	36.7

$k_1 = (36.3 \pm 0.30)$ s^{-1}

Ionization of (pyr)$_2$CH-OBz in 40W60A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	6.20×10^{-6}	6.77×10^{-5}	50.1
2	6.20×10^{-6}	1.41×10^{-4}	49.4
3	6.20×10^{-6}	2.89×10^{-4}	52.1

$k_1 = (50.5 \pm 1.14)$ s^{-1}

Ionization of (dma)$_2$CH-OBz in 40W60A at 25 $^{\circ}$C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-OBz], M	[BzO$^-$], M	
1	6.14×10^{-6}	6.77×10^{-5}	12.5
2	6.14×10^{-6}	1.42×10^{-4}	12.9
3	6.14×10^{-6}	2.89×10^{-4}	12.8

$k_1 = (12.7 \pm 0.17)$ s^{-1}

8.1 Ionization of Benzhydryl 4–Nitrobenzoates in 10:90 (v/v) Water Acetone Mixtures (10W90A)

Ionization of (lil)$_2$CH-PNB in 10W90A at 25 °C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	9.43×10^{-6}	6.33×10^{-5}	53.3
2	9.43×10^{-6}	1.36×10^{-4}	51.5
3	9.43×10^{-6}	2.82×10^{-4}	51.8

k_1 = (52.2±0.79) s^{-1}

Ionization of (jul)$_2$CH-PNB in 10W90A at 25 °C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	8.73×10^{-6}	6.40×10^{-5}	165
2	8.73×10^{-6}	1.37×10^{-4}	163
3	8.73×10^{-6}	2.82×10^{-4}	160

k_1 = (163±2.05) s^{-1}

Ionization of (ind)$_2$CH-PNB in 10W90A at 25 °C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	7.30×10^{-6}	6.54×10^{-5}	25.9
2	7.30×10^{-6}	1.38×10^{-4}	25.8
3	7.30×10^{-6}	2.84×10^{-4}	26.1

k_1 = (25.9±0.12) s^{-1}

Ionization of (thq)$_2$CH-PNB in 10W90A at 25 °C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	6.31×10^{-6}	6.64×10^{-5}	55.6
2	6.31×10^{-6}	1.39×10^{-4}	56.0
3	6.31×10^{-6}	2.90×10^{-4}	56.1

k_1 = (55.9±0.21) s^{-1}

Ionization of (pyr)$_2$CH-PNB in 10W90A at 25 °C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	5.69×10^{-6}	6.70×10^{-5}	66.2
2	5.69×10^{-6}	1.40×10^{-4}	66.2
3	5.69×10^{-6}	2.85×10^{-4}	65.4

k_1 = (65.9±0.37) s^{-1}

Ionization of (dma)$_2$CH-PNB in 10W90A at 25 °C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	7.41×10^{-6}	6.53×10^{-5}	19.9
2	7.41×10^{-6}	1.38×10^{-4}	20.2
3	7.41×10^{-6}	2.84×10^{-4}	21.6

k_1 = (20.6±0.74) s^{-1}

8.2 Ionization of Benzhydryl 4–Nitrobenzoates in 20:80 (v/v) Water Acetone Mixtures (20W80A)

Ionization of (lil)$_2$CH-PNB in 20W80A at 25 ^{o}C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	9.43×10^{-6}	6.33×10^{-5}	105
2	9.43×10^{-6}	1.36×10^{-4}	101
3	9.43×10^{-6}	2.82×10^{-4}	103

k_1 = (103±1.63) s^{-1}

Ionization of (jul)$_2$CH-PNB in 20W80A at 25 ^{o}C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	8.73×10^{-6}	6.40×10^{-5}	355
2	8.73×10^{-6}	1.37×10^{-4}	353
3	8.73×10^{-6}	2.82×10^{-4}	350

k_1 = (353±2.05) s^{-1}

Ionization of (ind)$_2$CH-PNB in 20W80A at 25 ^{o}C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	7.30×10^{-6}	6.54×10^{-5}	56.2
2	7.30×10^{-6}	1.38×10^{-4}	55.6
3	7.30×10^{-6}	2.84×10^{-4}	55.7

k_1 = (55.8±0.26) s^{-1}

Ionization of (pyr)$_2$CH-PNB in 20W80A at 25 ^{o}C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	6.34×10^{-6}	7.03×10^{-5}	155
2	6.34×10^{-6}	1.47×10^{-4}	157
3	6.34×10^{-6}	3.01×10^{-4}	157

k_1 = (156±0.94) s^{-1}

Ionization of (dma)$_2$CH-PNB in 20W80A at 25 ^{o}C

No.	Before ionization [Ar$_2$CH-PNB], M	 [PNB$^-$]$_0$, M	k_{obs}, s^{-1}
1	7.45×10^{-6}	6.92×10^{-5}	37.9
2	7.45×10^{-6}	1.46×10^{-4}	38.1
3	7.45×10^{-6}	2.99×10^{-4}	38.5

k_1 = (38.2±0.25) s^{-1}

8.3 Ionization of Benzhydryl 4–Nitrobenzoates in 40:60 (v/v) Water Acetone Mixtures (40W60A)

Ionization of $(pyr)_2CH$-PNB in 40W60A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}PNB]$, M	$[PNB^-]_0$, M	
1	6.34×10^{-6}	7.03×10^{-5}	696
2	6.34×10^{-6}	1.47×10^{-4}	689
3	6.34×10^{-6}	3.01×10^{-4}	719

$k_1 = (702 \pm 12.82)\ s^{-1}$

Ionization of $(dma)_2CH$-PNB in 40W60A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}PNB]$, M	$[PNB^-]_0$, M	
1	7.45×10^{-6}	6.92×10^{-5}	177
2	7.45×10^{-6}	1.46×10^{-4}	176
3	7.45×10^{-6}	2.99×10^{-4}	176

$k_1 = (176 \pm 0.47)\ s^{-1}$

9.1 Ionization of Benzhydryl 3,5–Dinitrobenzoates in 10:90 (v/v) Water Acetone Mixtures (10W90A)

Ionization of $(pyr)_2CH$-DNB in 10W90A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}DNB]$, M	$[DNB^-]_0$, M	
1	4.58×10^{-6}	9.80×10^{-5}	1044
2	4.58×10^{-6}	1.42×10^{-4}	1067

$k_1 = (1055 \pm 11.50)\ s^{-1}$

Ionization of $(dma)_2CH$-DNB in 10W90A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	$[Ar_2CH\text{-}DNB]$, M	$[DNB^-]_0$, M	
1	7.16×10^{-6}	6.61×10^{-5}	252
2	7.16×10^{-6}	9.56×10^{-5}	253
3	7.16×10^{-6}	1.39×10^{-4}	254

$k_1 = (253 \pm 0.82)\ s^{-1}$

9.2 Ionization of Benzhydryl 3,5–Dinitrobenzoates in 20:80 (v/v) Water Acetone Mixtures (20W80A)

Ionization of (dma)$_2$CH-DNB in 20W80A at 25 °C

No.	Before ionization		k_{obs}, s^{-1}
	[Ar$_2$CH-DNB], M	[DNB$^-$]$_0$, M	
1	7.16×10^{-6}	6.61×10^{-5}	483
2	7.16×10^{-6}	9.56×10^{-5}	480
3	7.16×10^{-6}	1.39×10^{-4}	478

$k_1 = (480 \pm 2.05)$ s^{-1}

10. Salt Effects of Ionization of Benzhydryl Acetates in 20:80 (v/v) Water Acetone and Acetonitrile Mixtures (20W80A & 20W80AN).

As all ionization experiments of this investigation had to be performed in the presence of variable concentrations of the carboxylate ions ([n-Bu$_4$N$^+$RCO$_2^-$] < 2×10^{-6} M^{-1}), the effect of the ion strength on the ionization rates was studied systematically. The first seven entries of Table S2.1 show that variation of the acetate concentration neither affected the final absorbance nor had an influence on the ionization rate constants. A marginal rate acceleration (about 20%) was observed when the reaction was carried out in the presence of a high concentration of an inert salt (0.25 M NaClO$_4$, entries 8-11 of Table S2.1).

Table S2.1. First-Order Rate Constants for the Ionization of (ind)$_2$CH-OAc in 20W80AN at 25 °C in the Presence of Variable Concentrations of Tetrabutylammonium Acetate and Sodium Perchlorate.

Entry	[(ind)$_2$CH-OAc]$_0$, M	[AcO$^-$], M	[NaClO$_4$], M	A_{end}^{a}	k_{obs}, s^{-1}
1	5.07×10^{-6}	2.14×10^{-6}	0	0.56	2.05
2	5.07×10^{-6}	4.85×10^{-6}	0	0.55	2.24
3	5.07×10^{-6}	9.36×10^{-6}	0	0.56	2.14
4	5.07×10^{-6}	2.38×10^{-5}	0	0.57	2.28
5	5.07×10^{-6}	5.27×10^{-5}	0	0.55	2.31
6	5.07×10^{-6}	1.36×10^{-4}	0	0.56	2.27
7	5.07×10^{-6}	2.65×10^{-4}	0	0.57	2.29
8	9.87×10^{-6}	9.10×10^{-5}	0.25	1.18	2.57
9	9.87×10^{-6}	1.91×10^{-4}	0.25	1.17	2.63
10	9.87×10^{-6}	2.92×10^{-4}	0.25	1.17	2.68
11	9.87×10^{-6}	3.25×10^{-4}	0.25	1.17	2.67

^{a} Absorbance after ionization.

A similar behavior was found in 80% aqueous acetone (Table S2.2). While the final absorbances were hardly affected by the presence of small concentrations of acetate ions and by variable concentrations of NaClO4 and LiClO4, in the presence of 0.24 M NaClO4 a 20% increase of the ionization rate constant was observed (entries 4-7). Lithium ions had a stronger effect (entries 8-11), as shown by the almost doubling of the ionization rate in the presence of 0.25 M LiClO4.

Table S2.2. First Order Rate Constants for the Ionization of $(ind)_2CH$-OAc in 20W80A at 25 °C in the Presence of Variable Concentrations of Tetrabutylammonium Acetate, Sodium Perchlorate and Lithium Perchlorate.

Entry	$[(ind)_2CH\text{-OAc}]_0$, M	$[AcO^-]$, M	$[M^+ClO_4^-]$, M	A_{end}[a]	k_{obs}, s^{-1}
1	9.91×10^{-6}	8.95×10^{-5}	0	1.15	1.40
2	9.91×10^{-6}	1.89×10^{-4}	0	1.16	1.41
3	9.91×10^{-6}	3.88×10^{-4}	0	1.15	1.43
4	9.78×10^{-6}	3.60×10^{-5}	0.10 (Na^+)	1.07	1.42
5	9.78×10^{-6}	3.60×10^{-5}	0.14 (Na^+)	1.08	1.42
6	9.78×10^{-6}	3.60×10^{-5}	0.19 (Na^+)	1.07	1.57
7	9.78×10^{-6}	3.60×10^{-5}	0.24 (Na^+)	1.05	1.74
8	9.39×10^{-6}	3.30×10^{-5}	0.05 (Li^+)	0.96	1.47
9	9.39×10^{-6}	3.30×10^{-5}	0.15 (Li^+)	0.94	1.82
10	9.39×10^{-6}	3.30×10^{-5}	0.20 (Li^+)	0.94	2.37
11	9.39×10^{-6}	3.30×10^{-5}	0.25 (Li^+)	0.95	2.54

[a] Absorbance after ionization.

The small effects on ionization rates show that variation of ion strength due to variable concentrations of Bu4N+ AcO– (2×10^{-6} – 6×10^{-4} M) can be neglected. This finding is in line with earlier studies of salt effects. Winstein reported that added non-common-ion salts cause linear salt effects on the ionization rates (eq S2.1).

$$k_{salt} = k_0 (1 + b[\text{salt}]) \qquad \text{(S2.1)}$$

In eq S1 k_{salt} and k_0 are first order rate constants with and without added salt and b depends on solvent, added salt, temperature and substrate.

From the solvolysis rates of (ind)$_2$CHOAc in 20W80A (Table 2.5, chapter 2) one calculates b = 5.6 for $LiClO_4$ and b = 3.2 for $NaClO_4$ in agreement with b values reported earlier for the effect of $LiClO_4$ on the solvolysis of benzhydryl chloride (b = 4.6) and *p*-chlorobenzhydryl chloride (b = 4.7) in 20W80A.[S2]

b describes the magnitude of solvolysis rate enhancement by non-common ion salts, which becomes quite large in solvents of low ionizing power like diethyl ether or neat acetone. Thus, a value of b = 47[S3] has been reported for the heterolysis of *p*-methoxyneophyl tosylates in pure acetone (ε = 20.70 at 25 °C)[S4] and of b = 14.5 for *p*-nitrobenzoates[S5] in ether (ε = 4.2 at 25 °C), respectively. Small values of b as in this work were generally found in ethanol or aqueous acetone. Thus, Dvorko[S6] reported b = 2.2 for benzhydryl bromide in acetonitrile and Shaji[S7] reports b = 3.7 at 20 °C for solvolysis of *m*-nitrophenyldiphenylmethyl benzoate in ethanol for the addition of $LiClO_4$. Olson found an increase of rate from 58% for the solvolysis of *t*-butyl chloride in 10W90A by adding 0.1 M $LiClO_4$ (equals b = 5.8).[S8] For the same system Manege found b values of 2.3 and 3.7 for addition of 1 M $LiClO_4$ and 2 M $LiClO_4$, respectively.[S9] Isobornyl chloride solvolysis at 0 °C in 30% aqeous methanol in presence of $NaClO_4$ gives b ~1.7 and the heterolysis in 45W55A with $LiClO_4$ b ~2.[S10]

References

(S1) a) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Heck, R.; Robinson, G. C. *J. Am. Chem. Soc.* 1956, *78*, 328-335. b) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* 1956, *78*, 2780-2784. c) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* 1956, *78*, 2763-2767.

(S2) Diaz, A. F.; Assamunt, N. *Tetrahedron* 1974, *30*, 797-800.

(S3) Perrin, C. L.; Pressing, J. *J. Am. Chem. Soc.* 1971, *93*, 5705-5710.

(S4) Coetzee, J. F.; Chang, T. H. *Pure Appl. Chem.* 1986, *58*, 1535-1540.

(S5) Winstein, S.; Friedrich, E. C.; Smith, S. *J. Am. Chem. Soc.* 1964, *86*, 305-307.

(S6) Dvorko, G. F.; Ponomareva, E. A.; Ponomarev, N. E. *Russ. J. Gen. Chem.* 2006, *76*, 1368-1385.

(S7) Nair, M. R.; Shaji, V. R. *Indian J. Chem.* 1988, *27A*, 242-243.

(S8) Spieth, F.; Olson, A. R. *J. Am. Chem. Soc.* 1955, *77*, 1412-1417.

(S9) Manege, L. C.; Ueda, T.; Hojo, M.; Fujio, M. *J. Chem. Soc. Perkin 2.* 1998, 1961-1966.

(S10) Bunton, C. A.; Del Pesco, T. W.; Dunlop, A. M.; Yang, K.-U. *J. Org. Chem.* 1971, *36*, 887-897.

–Appendix–

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

Problems with the Determination of Some Ion Combination Rate Constants k_{-1}

As mentioned in chapter 2, some plots of the pseudo first-order rate constants for the reactions of benzhydrylium ions with carboxylate ions against the carboxylate concentrations show a considerable positive intercept as illustrated by Figure A.1. 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 do not proceed quantitatively. As expressed by eq. A.1, the observed rate constants for reversible reactions equal the sum of forward and backward reactions.[A1]

$$k_{obs} = k_1 + k_{-1}[\mathrm{RCO_2}^-] \qquad \text{(A.1)}$$

As pointed out in chapter 2, the intercept taken from Figure A.1 ($k_1 = 11.1$ s^{-1}) closely resembles the ionization constant $k_1 = 9.07$ s^{-1} which is calculated as 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}.[A2] If the intercept is small compared with k_{obs}, the agreement between the ionization constants derived in these two different ways is less satisfactory.

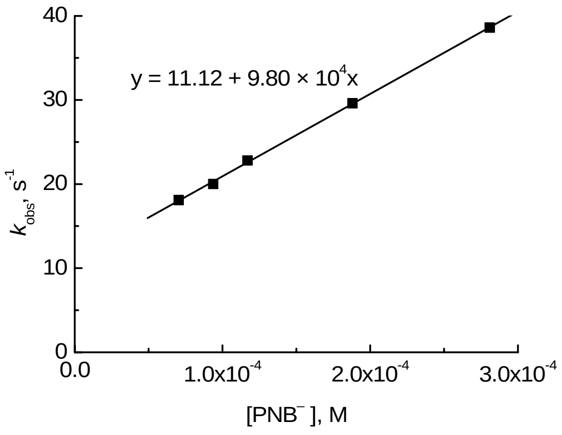


Figure A.1. Linear correlation of the first-order rate constants k_{obs} for the reaction of $(\mathrm{ind})_2\mathrm{CH}^+$ with PNB^- in acetonitrile versus the concentration of n-$\mathrm{Bu}_4\mathrm{N}^+\mathrm{PNB}^-$.

The kinetics of the reactions of benzhydrylium ions with carboxylate ions in aqueous solvents 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. In addition, they showed a large intercept; attempts to differentiate the parallel processes were unsuccesful.

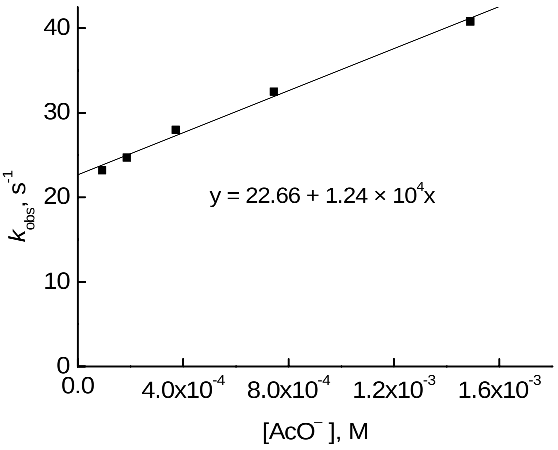


Figure A.2. Linear correlation of the first-order rate constants for the reaction of $(\mathrm{mfa})_2\mathrm{CH}^+$ with AcO^- in 20W80AN versus the concentration of n-$\mathrm{Bu}_4\mathrm{N}^+\mathrm{AcO}^-$.

Figure A.2 shows an example for a linear correlation with a large positive intercept on the ordinate (22.66 s^{-1}), which can neither be explained by the rate constant k_1 of the solvolysis of the corresponding benzhydryl carboxylate, $(mfa)_2CH–OAc$ ($k_1 = 2.60 \times 10^{-2}$ s^{-1}) nor by the rate constant k_{Solv} of the benzhydrylium ion reacting with the aqueous solvent ($N_{20W80AN} = 5.02$;[A3] $s_{20W80AN} = 0.89$;[A3] $E(mfa)_2CH^+ = –3.85$[A4] => $k_{Solv} = 11.5$ s^{-1}). For that reason, Table A.1 gives a few carbocation carboxylate combination rate constants in aqueous solvents, which show significant intercepts and have therefore been omitted from the originally published data.[A2]

Table A.1. Second-Order Rate Constants for Reactions of Benzhydryl Cations with Carboxylate at 25 °C.

Nucleophile	Solvent	Cation	k_{-1}, $M^{-1}s^{-1}$
AcO^-	10W90AN	$(mpa)_2CH^+$	1.02×10^4
		$(mor)_2CH^+$	1.17×10^4
	20W80AN	$(mpa)_2CH^+$	1.85×10^3
		$(mor)_2CH^+$	1.02×10^3
		$(dpa)_2CH^+$	1.10×10^4
		$(mfa)_2CH^+$	1.24×10^4
BzO^-	20W80AN	$(mor)_2CH^+$	4.32×10^3
		$(dpa)_2CH^+$	1.37×10^4
		$(mfa)_2CH^+$	2.43×10^4
		$(pfa)_2CH^+$	1.49×10^5

The resulting nucleophilicity parameters for the AcO^- and BzO^- anion of the combination reactions listed in Table A.1 are listed in Table A.2.

Table A.2. Nucleophilicity Parameters (25 °C) of Carboxylate Ions in Different Solvents.

$R–CO_2^−$	Solvent	N_{25} [a]	s_{25} [a]
$AcO^−$	10W90AN	12.03	0.64
	20W80AN	10.80	0.63
$BzO^−$	20W80AN	11.58	0.60

[a] Due the compatibility with the heterolysis rate constants determined in this work all of these rate constants 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* parameter in Table A.2.

Comparison of Nucleophilicities

In a recent publication we have reported nucleophilicity parameters *N* for chloride and bromide ions in various solvents.[A5] While the chloride ion is slightly more nucleophilic (N = 17.2) than acetate (N = 16.90) and benzoate (N = 16.82) in pure acetonitrile, the addition of water to acetonitrile diminishes the nucleophilicities of acetate and benzoate to a larger extent than the nucleophilicity of chloride, with the result that in aqueous acetonitrile, chloride is considerably more nucleophilic than these carboxylates (Figure A.3). Richard and Pearson reported the same order of nucleophilicities of chloride and acetate toward tritylium ions[A6] and methyl halides[A7]. The reason why esters of carboxylic acids can be synthesized by reaction of alkyl chlorides with carboxylate anions thus is not due to the relative nucleophilicities of the two ions. It can be explained by the considerably higher nucleofugality of the chloride ion compared to carboxylate anions. Please note that *N* provides only a rough guide to the relative nucleophilic reactivities of the carboxylate ions. The small differences in *s* lead to the relative nucleophilic reactivities that are slightly dependent on the nature of the electrophilic reaction partner.

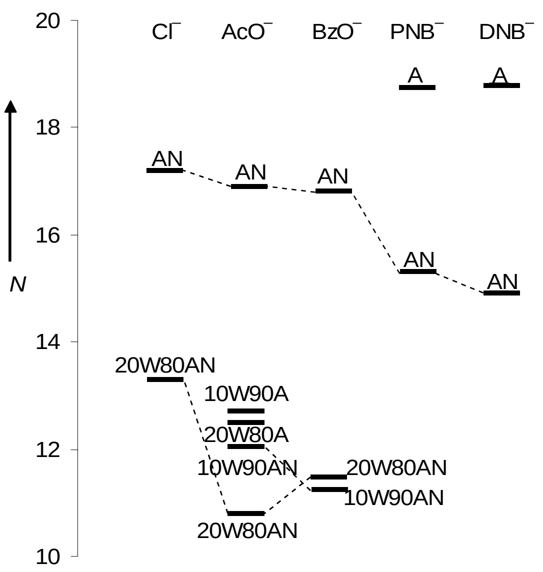


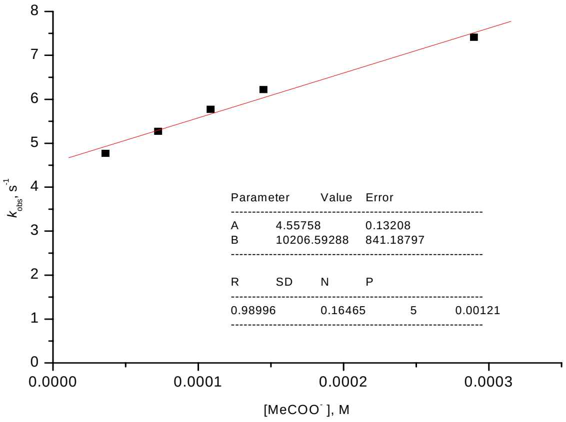
Figure A.3. Comparison of the reactivities of carboxylate anions (N_{25} values) with the chloride ion (N values) in different solvents.

Appendix – Experimental Section

1.1 Combination of the Acetate Anion with Benzhydryl Cations in 20:80 (v/v) Water Acetonitrile Mixtures (10W90AN)

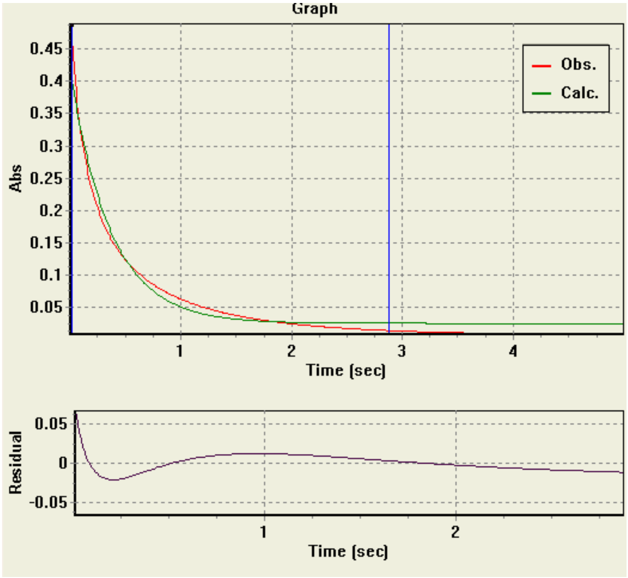
Reaction of Tetrabutylammonium Acetate with $(mpa)_2CH^+$ BF_4^- in 10W90AN at 25 ^{o}C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	5.57×10^{-6}	3.62×10^{-5}	2.92
2	5.57×10^{-6}	7.24×10^{-5}	4.77
3	5.57×10^{-6}	1.09×10^{-4}	5.27
4	5.57×10^{-6}	1.45×10^{-4}	5.77
5	5.57×10^{-6}	2.90×10^{-4}	7.40



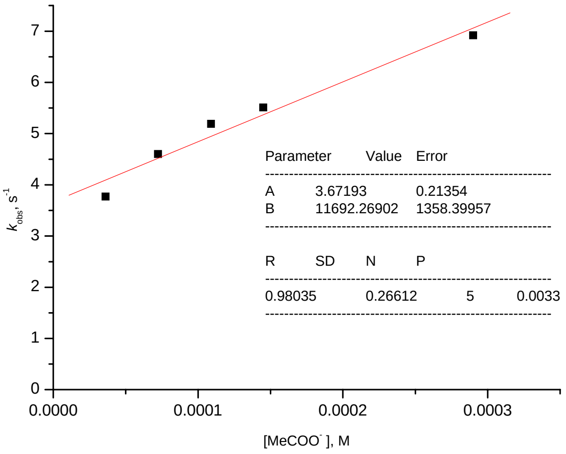
```
Parameter       Value       Error
------------------------------------------------------------
A           4.55758         0.13208
B           10206.59288     841.18797
------------------------------------------------------------

R           SD          N           P
------------------------------------------------------------
0.98996         0.16465         5           0.00121
------------------------------------------------------------
```

k_{-1} = 1.02 × 10^4 M^{-1} s^{-1}



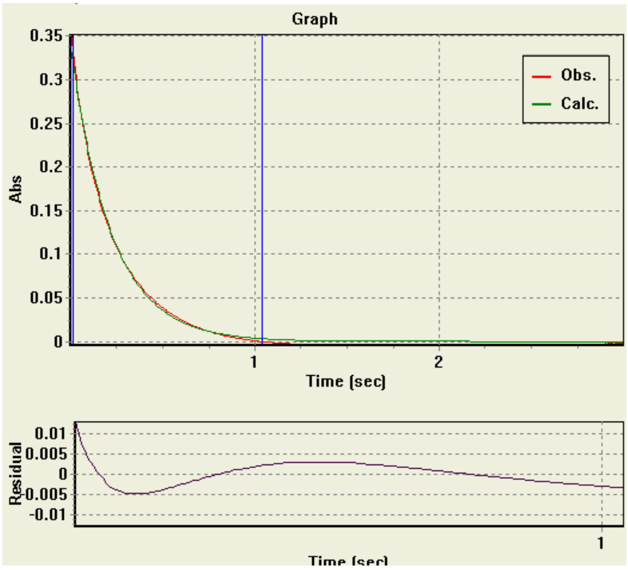
Reaction of Tetrabutylammonium Acetate with $(mor)_2CH^+$ BF_4^- in 10W90AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	3.72 × 10^{-6}	3.62 × 10^{-5}	3.77
2	3.72 × 10^{-6}	7.24 × 10^{-5}	4.60
3	3.72 × 10^{-6}	1.09 × 10^{-4}	5.19
4	3.72 × 10^{-6}	1.45 × 10^{-4}	5.51
5	3.72 × 10^{-6}	2.90 × 10^{-4}	6.92
6	3.72 × 10^{-6}	5.43 × 10^{-4}	9.13



```
Parameter       Value       Error
------------------------------------------------------------
A           3.67193         0.21354
B           11692.26902     1358.39957
------------------------------------------------------------

R           SD          N           P
------------------------------------------------------------
0.98035         0.26612         5           0.0033
------------------------------------------------------------
```

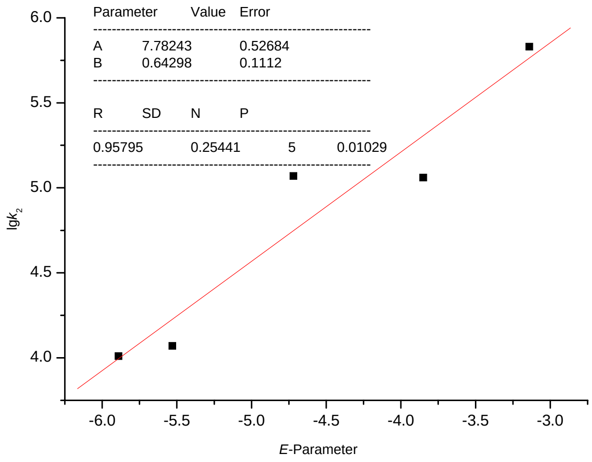
k_{-1} = 1.17 × 10^4 M^{-1} s^{-1}



Nucleophilicity parameter of the Acetate Anion in 10W90AN at 25 °C

Ar_2CH^+	*E*	k_{-1}, $M^{-1}s^{-1}$	lgk_{-1}
$(mpa)_2CH^+$	-5.89	1.02×10^4	4.01
$(mor)_2CH^+$	-5.53	1.17×10^4	4.07
$(dpa)_2CH^{+a}$	-4.72	1.17×10^5	5.07
$(mfa)_2CH^{+a}$	-3.85	1.15×10^5	5.06
$(pfa)_2CH^{+a}$	-3.14	6.87×10^5	5.83

[a] from ref. [2]

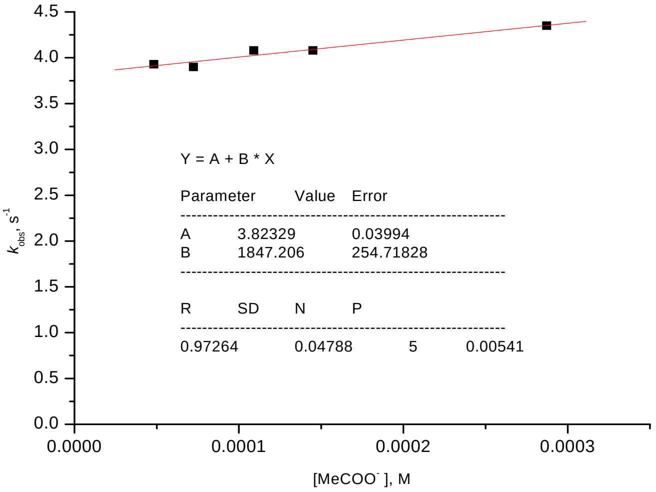


***N* = 12.03**
***s* = 0.64**

1.2 Combination of the Acetate Anion with Benzhydryl Cations in 20:80 (v/v) Water Acetonitrile Mixtures (20W80AN)

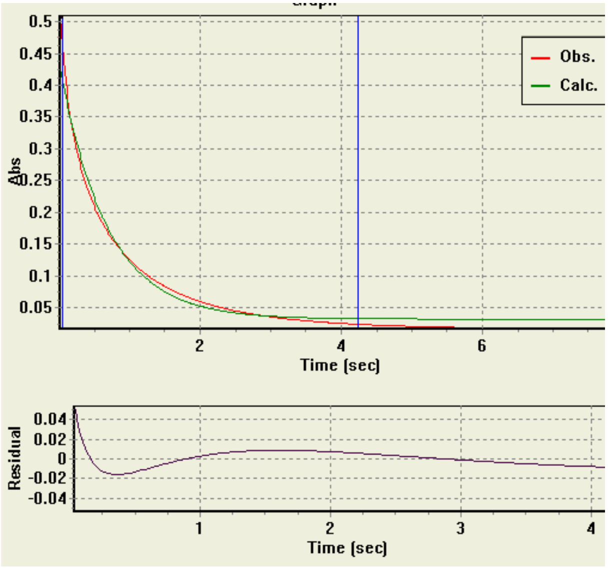
Reaction of Tetrabutylammonium Acetate with $(mpa)_2CH^+$ BF_4^- in 20W80AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	5.69×10^{-6}	4.83×10^{-5}	3.93
2	5.69×10^{-6}	7.24×10^{-5}	3.90
3	5.69×10^{-6}	1.09×10^{-4}	4.08
4	5.69×10^{-6}	1.45×10^{-4}	4.08
5	5.69×10^{-6}	2.90×10^{-4}	4.35



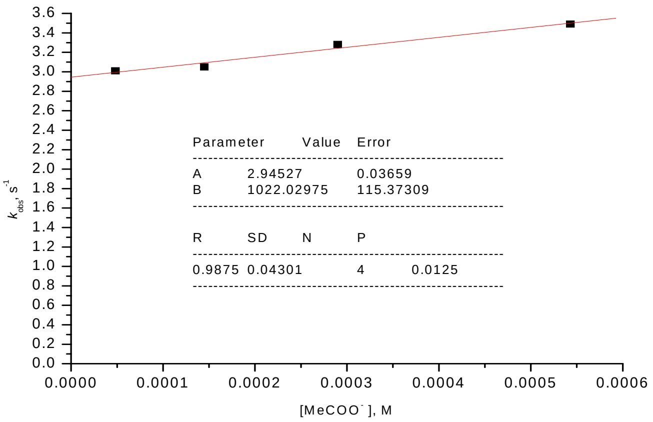
```
Y = A + B * X

Parameter     Value      Error
------------------------------------------------
A          3.82329     0.03994
B          1847.206    254.71828
------------------------------------------------

R          SD        N        P
------------------------------------------------
0.97264    0.04788      5     0.00541
```

k_{-1} = 1.85 × 10^3 M^{-1} s^{-1}



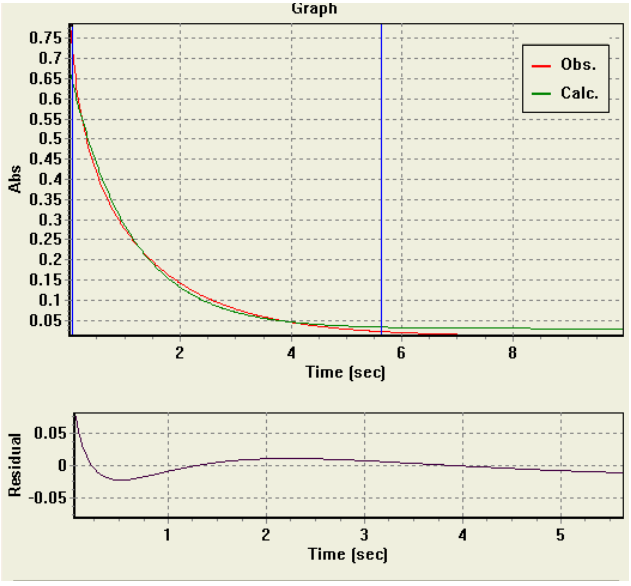
Reaction of Tetrabutylammonium Acetate with $(mor)_2CH^+$ BF_4^- in 20W80AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	7.90×10^{-6}	4.83×10^{-5}	3.02
2	7.90×10^{-6}	1.45×10^{-4}	3.05
5	7.90×10^{-6}	2.90×10^{-4}	3.28
4	7.90×10^{-6}	5.43×10^{-4}	3.49



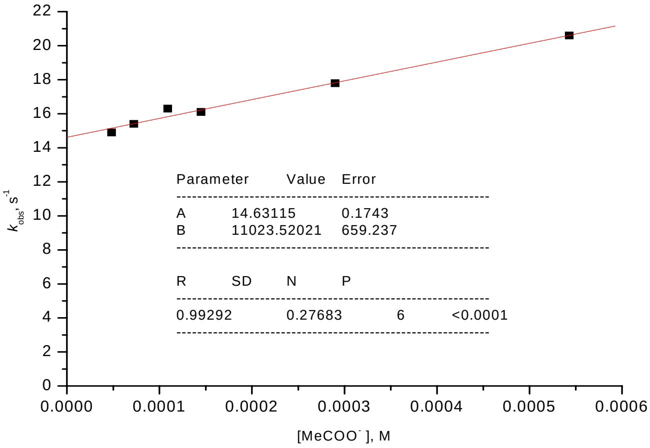
```
Parameter     Value        Error
------------------------------------------------
A          2.94527       0.03659
B          1022.02975    115.37309
------------------------------------------------

R          SD        N        P
------------------------------------------------
0.9875  0.04301      4        0.0125
------------------------------------------------
```

k_{-1} = 1.02 × 10^3 M^{-1} s^{-1}



Reaction of Tetrabutylammonium Acetate with (dpa)$_2$CH$^+$ BF$_4^-$ in 20W80AN at 25 ^{o}C

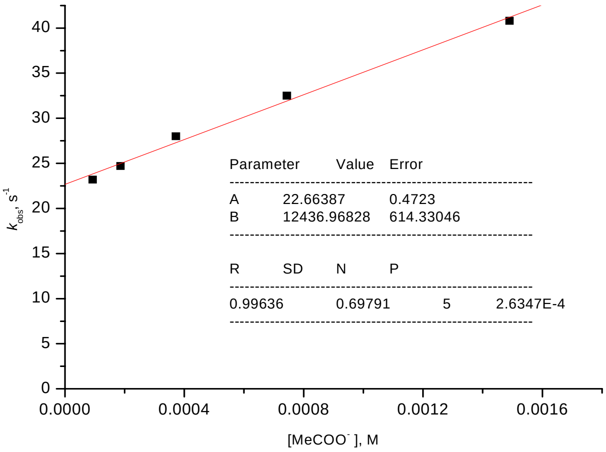
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	5.75×10^{-6}	4.83×10^{-5}	14.9
2	5.75×10^{-6}	7.24×10^{-5}	15.4
3	5.75×10^{-6}	1.09×10^{-4}	16.3
4	5.75×10^{-6}	1.45×10^{-4}	16.1
5	5.75×10^{-6}	2.90×10^{-4}	17.8
6	5.75×10^{-6}	5.43×10^{-4}	20.6



$\mathbf{k_{-1} = 1.10 \times 10^4\ M^{-1}\ s^{-1}}$

Reaction of Tetrabutylammonium Acetate with (mfa)$_2$CH$^+$ BF$_4^-$ in 20W80AN at 25 ^{o}C

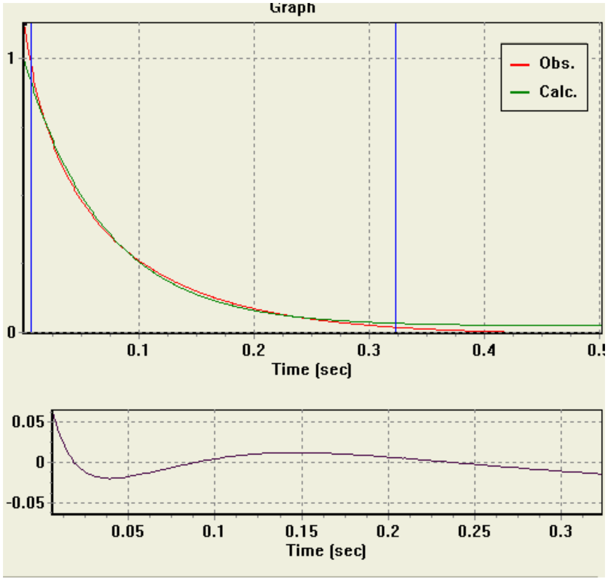
No.	$[Ar_2CH^+]_0$, M	$[MeCOO^-]_0$, M	k_{obs}, s^{-1}
1	8.04×10^{-6}	9.30×10^{-5}	23.2
2	8.04×10^{-6}	1.86×10^{-4}	24.7
3	8.04×10^{-6}	3.72×10^{-4}	28.0
4	8.04×10^{-6}	7.44×10^{-4}	32.5
5	8.04×10^{-6}	1.49×10^{-4}	40.8



Parameter	Value	Error
A	22.66387	0.4723
B	12436.96828	614.33046

R	SD	N	P
0.99636	0.69791	5	2.6347E-4

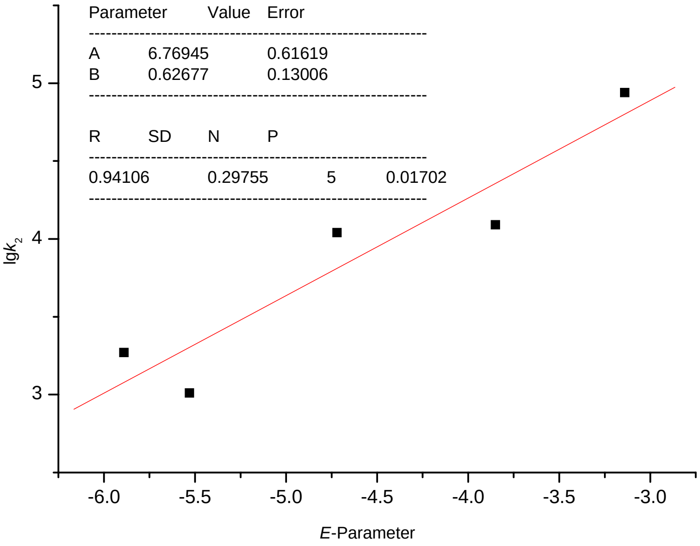
k_{-1} = 1.24 × 10^4 M^{-1} s^{-1}



Nucleophilicity parameter of the Acetate Anion in 20W80AN at 25 °C

Ar$_2$CH$^+$	E	k_{-1}, M^{-1} s^{-1}	lgk_{-1}
(mpa)$_2$CH$^+$	-5.89	1.85 × 10^3	3.27
(mor)$_2$CH$^+$	-5.53	1.02 × 10^3	3.01
(dpa)$_2$CH$^+$	-4.72	1.10 × 10^4	4.04
(mfa)$_2$CH$^+$	-3.85	1.24 × 10^4	4.09
(pfa)$_2$CH^{+a}	-3.14	8.67 × 10^4	4.94

[a] from ref. [2]



Parameter	Value	Error
A	6.76945	0.61619
B	0.62677	0.13006

R	SD	N	P
0.94106	0.29755	5	0.01702

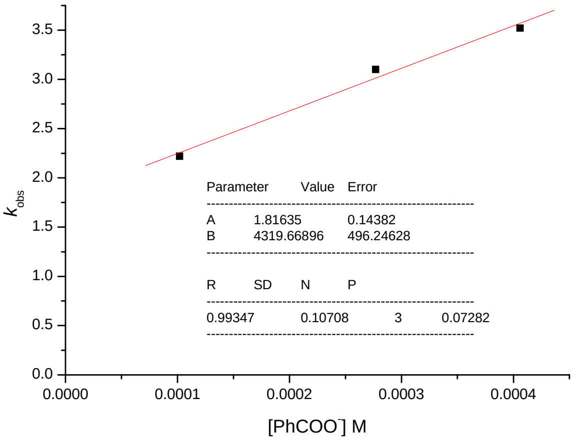
***N* = 10.80**
***s* = 0.63**

2. Combination of the Benzoate Anion with Benzhydryl Cations in 20:80 (v/v) Water Acetonitrile Mixtures (20W80AN)

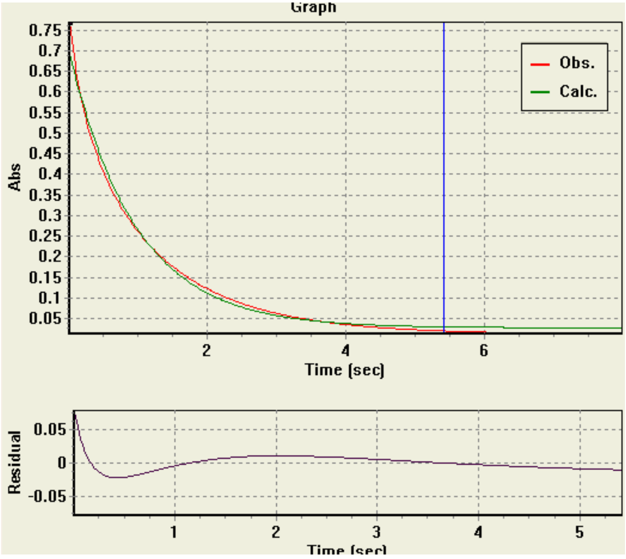
Reaction of Tetrabutylammonium Benzoate with $(mor)_2CH^+ BF_4^-$ in 20W80AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	7.65×10^{-6}	1.02×10^{-4}	2.22
2	7.65×10^{-6}	2.77×10^{-4}	3.10
3	7.65×10^{-6}	4.06×10^{-4}	3.52

$k_{-1} = 4.32 \times 10^3$ M^{-1} s^{-1}



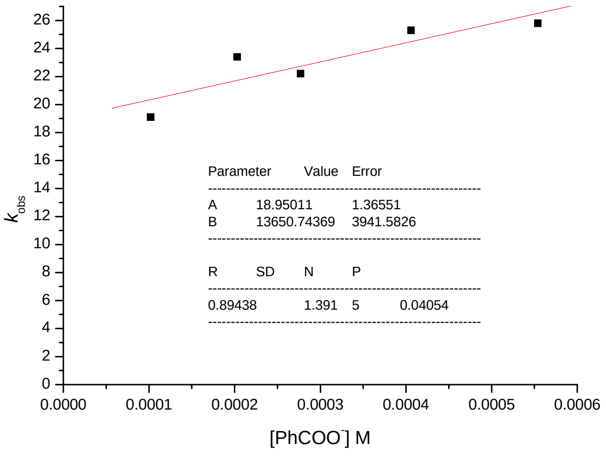
```
Parameter      Value      Error
------------------------------------------------
A         1.81635         0.14382
B         4319.66896      496.24628
------------------------------------------------
R         SD        N        P
------------------------------------------------
0.99347   0.10708   3        0.07282
------------------------------------------------
```



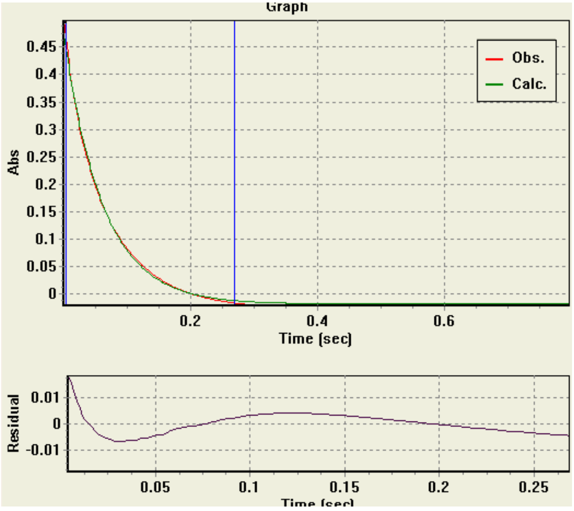
Reaction of Tetrabutylammonium Benzoate with $(dpa)_2CH^+ BF_4^-$ in 20W80AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	5.90×10^{-6}	1.02×10^{-4}	19.1
2	5.90×10^{-6}	2.03×10^{-4}	23.4
3	5.90×10^{-6}	2.77×10^{-4}	22.2
4	5.90×10^{-6}	4.06×10^{-4}	25.3
5	5.90×10^{-6}	5.54×10^{-4}	25.8

$k_{-1} = 1.37 \times 10^4$ $M^{-1}s^{-1}$

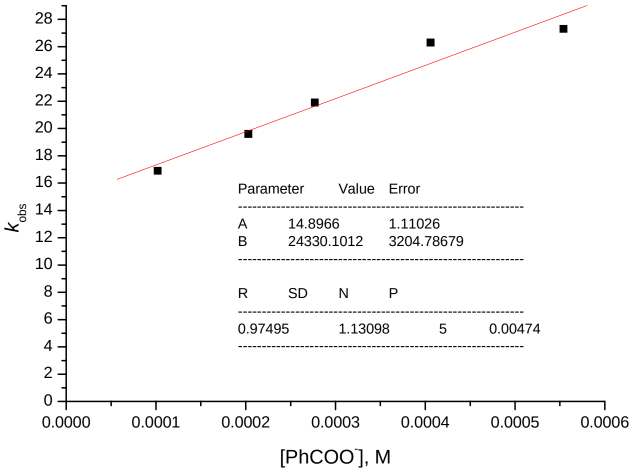


```
Parameter      Value      Error
------------------------------------------------
A         18.95011        1.36551
B         13650.74369     3941.5826
------------------------------------------------
R         SD        N        P
------------------------------------------------
0.89438   1.391     5        0.04054
------------------------------------------------
```

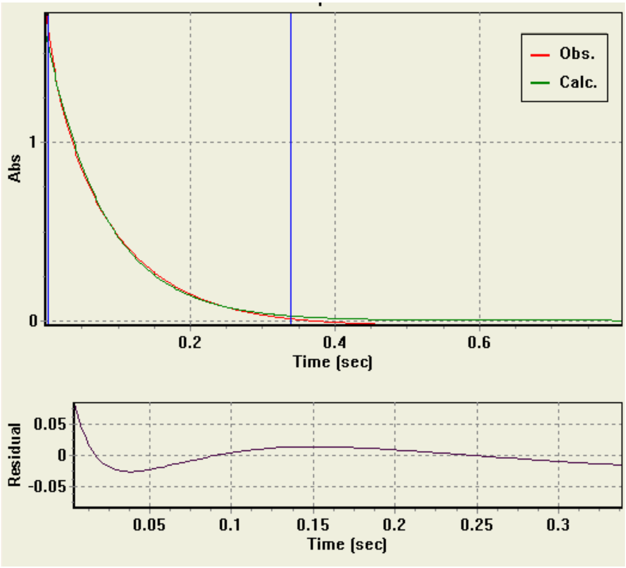


Reaction of Tetrabutylammonium Benzoate with $(mfa)_2CH^+$ BF_4^- in 20W80AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	1.16×10^{-5}	1.02×10^{-4}	16.9
2	1.16×10^{-5}	2.03×10^{-4}	19.6
3	1.16×10^{-5}	2.77×10^{-4}	21.9
4	1.16×10^{-5}	4.06×10^{-4}	26.3
5	1.16×10^{-5}	5.54×10^{-4}	27.3

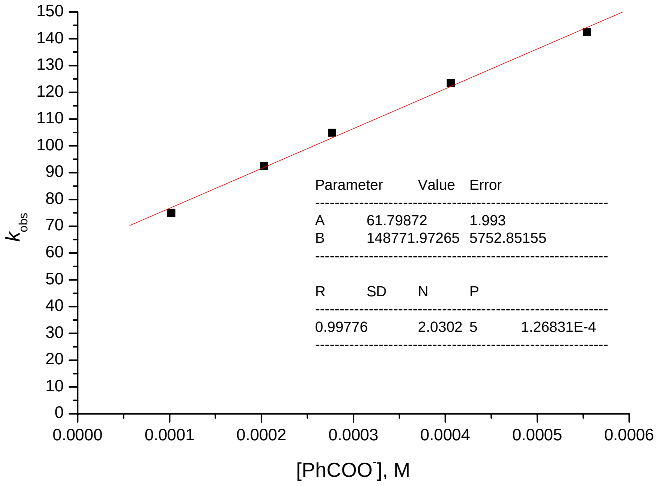


$k_{-1} = 2.43 \times 10^4$ $M^{-1}s^{-1}$

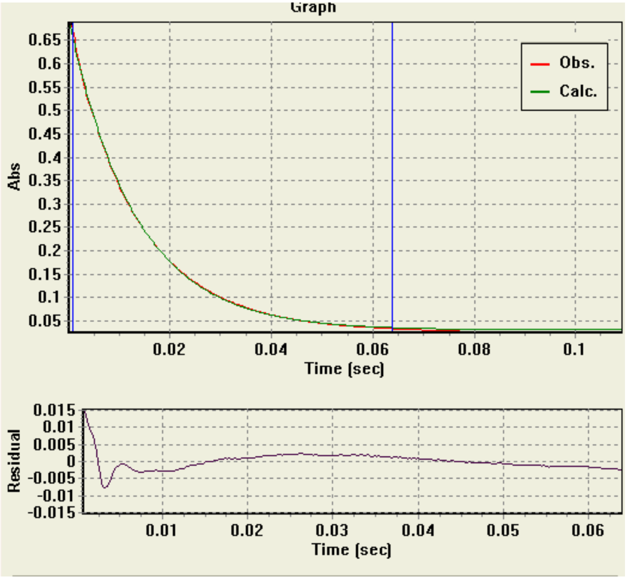


Reaction of Tetrabutylammonium Benzoate with $(pfa)_2CH^+$ BF_4^- in 20W80AN at 25 °C

No.	$[Ar_2CH^+]_0$, M	$[PhCOO^-]_0$, M	k_{obs}, s^{-1}
1	6.73×10^{-6}	1.02×10^{-4}	75.0
2	6.73×10^{-6}	2.03×10^{-4}	92.5
3	6.73×10^{-6}	2.77×10^{-4}	104.9
4	6.73×10^{-6}	4.06×10^{-4}	123.5
5	6.73×10^{-6}	5.54×10^{-4}	142.3

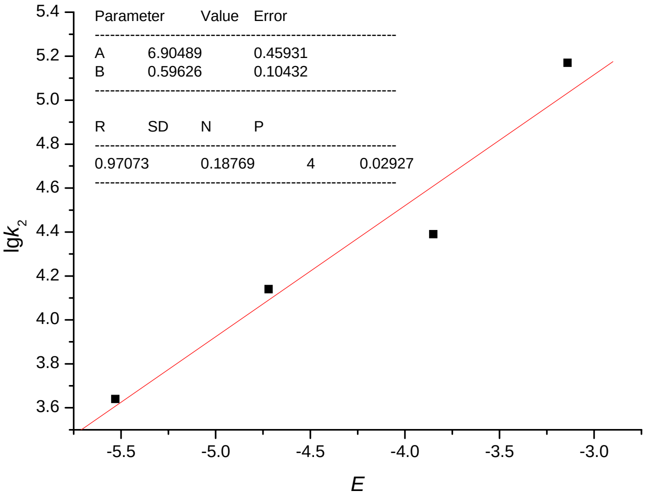


$k_{-1} = 1.49 \times 10^5$ M^{-1}s^{-1}



Nucleophilicity parameter of the Benzoate Anion in 20W80AN at 25 °C

Ar_2CH^+	*E*	k_{-1}, M^{-1}s^{-1}	$\lg k_{-1}$
$(mor)_2CH^+$	-5.53	4.32×10^3	3.64
$(dpa)_2CH^+$	-4.72	1.37×10^4	4.14
$(mfa)_2CH^+$	-3.85	2.43×10^4	4.39
$(pfa)_2CH^+$	-3.14	1.49×10^5	5.17



***N* = 11.58**

***s* = 0.60**

References

(A1) 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.

(A2) Schaller, H. F.; Tishkov, A. A.; Feng, X.; Mayr, H. *J. Am. Chem. Soc.* **2008**, *130*, 3012-3022.

(A3) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174-5181.

(A4) 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.

(A5) Minegishi, S.; Loos, R.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2005**, *127*, 2641-2649.

(A6) Richard, J. P.; Toteva, M. M.; Crugeiras, J. *J. Am. Chem. Soc.* **2000**, *122*, 1664-1674.

(A7) Pearson, R. G.; Sobel, H. R.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319-26.

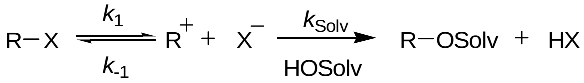
“Carbocation Watching” in Solvolysis Reactions

Schaller, H. F.; Mayr, H. *Angew. Chem.* **2008**, *120*, 4022-4025; *Angew. Chem. Int. Ed.* **2008**, *47*, 3958-3961.

Introduction

Mechanisms of S_N1 reactions have been one of the most intensively studied topics in Organic Chemistry during the middle of the 20th century.[1]

Scheme 3.1. Typical Solvolysis Reaction.



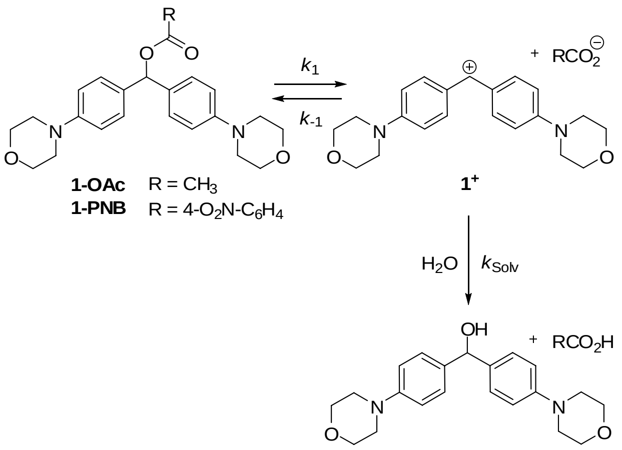
These reactions typically proceed with slow formation of the carbocations, followed by fast subsequent reactions with the solvent (Scheme 3.1). Detailed mechanistic studies by Winstein[2] have shown that intermediate carbocations can recombine with the leaving group at the ion-pair or free-ion stage before being trapped by the solvent. Since fast kinetic methods were not available at that time, most information on the relative rates of ionization, ion recombination, and reaction of the intermediate carbocation with the solvent has been derived indirectly from measurement of gross solvolysis rates.

Recently we have shown that the ionization rates of covalent benzhydryl esters can be observed photometrically if the resulting carbocations are highly stabilized and do not undergo subsequent reactions with the solvent.[3] On the other hand, we have also reported that the trifluoroethanolysis of chloro-bis-(*p*-methoxyphenyl)methane proceeds with instantaneous formation of the carbocation, the combination of which with trifluoroethanol could be followed photometrically with a stopped-flow instrument.[4] Based on these results it was predicted that it should be possible to design systems where both, ionization and follow-up reaction, can be measured. We have now realized such systems and report on the first solvolysis reactions where the formation of carbocations and their subsequent disappearance in aqueous acetone and acetonitrile can be measured directly and fitted by the kinetic model depicted in Scheme 3.2.

Results and Discussion

When water was added to the colorless solution of 4,4'-bis(morpholino)benzhydryl acetate **1-OAc** in acetonitrile, the solution rapidly turned blue, then faded again within a couple of minutes. A video demonstrating such “carbocation watching” is provided at http://www.wiley-vch.de/contents/jc_2002/2008/z800354_s.html (see also Demonstration Experiment).

Scheme 3.2. Solvolysis Reaction of 4,4'-Bis(morpholino)benzhydryl Carboxylates in Aqueous Acetone or Acetonitrile.



Photometric monitoring of this process showed that the maximum of the carbocation concentration was reached after 7 s in 80 % aqueous acetonitrile. From the absorbance one could derive that at this point, the concentration of the carbocation corresponded to approximately 3 % of the initial substrate concentration. The fact that the blue color appears much faster than it disappears indicates that the small maximum concentration of the carbocation must be due to fast recombination of the carbocations with the acetate anions. Due to the involvement of several rate and equilibrium constants (partial dissociation of acetic acid) we were not able to find a kinetic model which fits the resulting plot of the carbocation concentration vs. time (Figure S3.6, Experimental Section). However, the corresponding reaction in the presence of di*iso*propyl-methylamine (($(i\text{Pr})_2\text{NMe}$), which shows a similar absorbance-time correlation (Figure 3.1), could be fitted to the kinetic model shown in Scheme 3.1. The resulting rate constants and the GEPASI[5] fit of the carbocation concentration are shown in Figure 3.1.

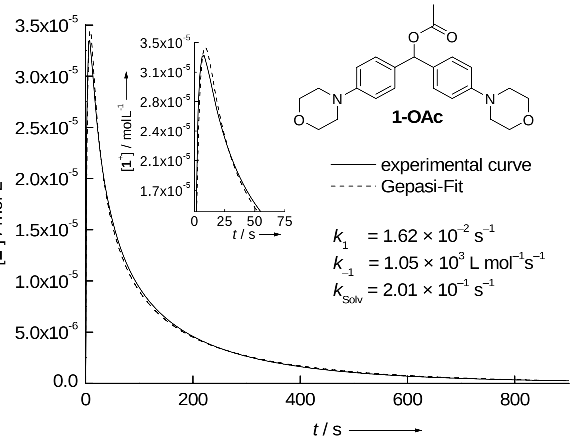
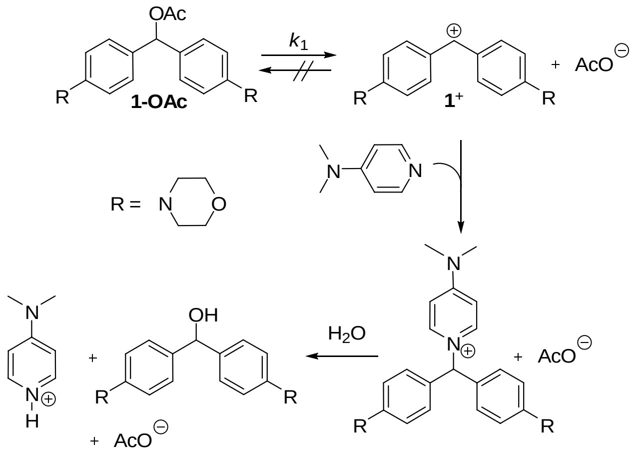


Figure 3.1. Formation and consumption of the blue 4,4'-bis(morpholino)benzhydrylium ion $\mathbf{1}^+$ (monitored photometrically at 612 nm) during the solvolysis of 4,4'-bis(morpholino)benzhydryl acetate **1-OAc** (1.09 mmol L^{-1}) in 80 % aqueous acetonitrile in the presence of $(i\text{Pr})_2\text{NMe}$ (5.24 mmol L^{-1}) at 25 °C.

When the solvolysis reaction of **1-OAc** was followed conductimetrically under the same conditions, a continuous increase of the ion-concentration (see Experimental Section, Figure S3.4) was observed. Assuming a direct proportionality between conductivity and the concentration of $[(i\text{Pr})_2\text{NHMe}]^+\text{OAc}^-$, this curve was fitted by GEPASI to give values for $k_{-1} = 1.09 \times 10^3$ L mol^{-1} s^{-1} and $k_{\text{Solv}} = 2.01 \times 10^{-1}$ s^{-1} (see Figure S3.4, Experimental Section) which are almost identical to those derived photometrically, while the value for the ionization constant $k_1 = 2.13 \times 10^{-2}$ s^{-1} was 25 % larger than that derived from the absorbance of the intermediate carbocation (compare Figure 3.1).[6] The value of k_{Solv} derived from Figures 3.1 and the conductimetrical curve is similar to that previously reported for the hydrolysis of $\mathbf{1}^+\text{BF}_4^-$ in 80 % aqueous acetonitrile (0.251 s^{-1} at 20 °C).[7]

The high degree of reversibility of the ionization step (mass law effect, common ion rate depression) implies that the increase of conductivity does not follow an exponential function (Figure S3.3). However, when the solvolysis of 4,4'-bis(morpholino)benzhydryl acetate **1-OAc** (0.62 mmol L^{-1}) was performed in the presence of 4-(dimethylamino)pyridine (DMAP, 5.02 mmol L^{-1}) or quinuclidine (5.24 mmol L^{-1}) the solution did not turn blue, and a mono-exponential increase of conductivity was observed (Figures S3.1 and S3.2) due to quantitative trapping of the intermediate carbocations by these amines (Scheme 3.3).[8]

Scheme 3.3. Trapping of the intermediate benzhydrylium ions by DMAP.



The resulting first-order rate constants, $k_1 = 2.04 \times 10^{-2}\ s^{-1}$ (in the presence of DMAP) and $2.01 \times 10^{-2}\ s^{-1}$ (in the presence of quinuclidine) were the same (within the experimental error) as those derived from Figures 3.1 and S3.4, where the intermediate carbocations were visible.

In the presence of extra tetrabutylammonium acetate, the ionization equilibrium lies far on the side of the covalent benzhydryl acetates; therefore, we were not able to study the solvolysis of 4,4'-bis(morpholino)benzhydryl acetate **1-OAc** photometrically at constant acetate anion concentrations.

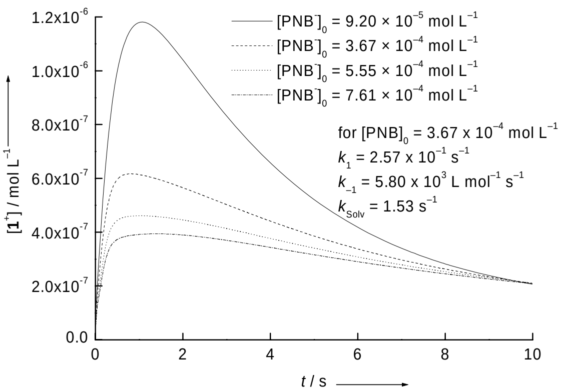


Figure 3.2. Formation and consumption of the blue 4,4'-bis(morpholino)benzhydrylium ion $\mathbf{1}^+$ (monitored photometrically at 612 nm) during the heterolysis of 4,4'-bis(morpholino)benzhydryl *p*-nitrobenzoate **1-PNB** (1.04×10^{-5} mol L^{-1}) in 80 % aqueous acetone in the presence of different amounts of *n*-$Bu_4N^+PNB^-$ at 25 °C.

However, the ionization equilibria of the corresponding *p*-nitrobenzoates lie more on the side of the ions, and it was possible to study their solvolyses at almost constant concentrations of *p*-nitrobenzoate anions (PNB^-). Figure 3.2 shows that the maximum concentration of the intermediate carbocation, which is reached after 0.7 to 1.0 s, decreases with increasing concentrations of *n*-$Bu_4N^+PNB^-$. The maxima of the curves correspond to stationary points, where

$$\frac{d[\mathbf{1}^+]}{dt} = k_1[\mathbf{1\text{-}PNB}] - k_{-1}[\mathbf{1}^+][\mathbf{PNB}^-] - k_{\mathrm{Solv}}[\mathbf{1}^+] = 0 \qquad (3.1)$$

or

$$\frac{[\mathbf{1}^+]}{[\mathbf{1\text{-}PNB}]} = \frac{k_1}{k_{-1}[\mathbf{PNB}^-] + k_{\mathrm{Solv}}} \qquad (3.2)$$

In accordance with eq 3.2, the maxima of the concentrations of the carbocations decrease as the concentrations of the carboxylate anions grow. At a concentration of 9.20×10^{-5} mol L^{-1} of *n*-$Bu_4N^+PNB^-$, the observed carbocation absorbance corresponds to a concentration of $\mathbf{1}^+$ which is approximately 12 % of the initial concentration of **1-PNB**. Figure 3.2 shows that the curves corresponding to higher carbocation concentrations decline faster, resulting in a crossing of the graphs at 10 s. This observation reflects the common-ion effect: At high carboxylate anion concentrations, the gross hydrolysis reactions proceed more slowly, and small equilibrium concentrations of carbocations are preserved for an extended period of time.

The individual curves of Figure 3.2, except the one with the lowest concentration of n-$Bu_4N^+PNB^-$, can satisfactorily be fitted by the kinetic model of Scheme 3.1. From all curves of Figure 3.2 GEPASI derives the same value of $k_{Solv} = (1.49 \pm 0.4)$ s^{-1}, which is 1.5 times larger than that reported for the hydrolysis of 4,4'-bis(morpholino)benzhydrylium tetrafluoroborate in the same solvent at 20 °C.[7] The other rate constants depend slightly on the ionic strengths of the solutions (Experimental Section). Thus the ion-combination constant k_{-1} decreases from (5800 ± 50) M^{-1} s^{-1} at $[PNB^-]_0$ = 0.37 mmol L^{-1} to (2980 ± 50) M^{-1} s^{-1} at $[PNB^-]_0$ = 0.76 mmol L^{-1}. The unexpected finding that the ionization rate constant k_1 is also calculated to decrease from 0.257 s^{-1} (for $[PNB^-]_0$ = 0.37 mmol L^{-1}) to 0.161 s^{-1} (for $[PNB^-]_0$ = 0.76 mmol L^{-1}) may be explained by the fact that ion-pairing, which is more important in the more concentrated salt solutions, is not considered in our kinetic model, which generally assumes $[PNB^-]_0 = [n\text{-}Bu_4N^+PNB^-]_0$.

When the solvolyses of 4,4'-bis(morpholino)benzhydryl p-nitrobenzoate **1-PNB** were studied in 60 % aqueous acetone at variable p-nitrobenzoate anion concentrations, similar absorbance/time correlations were observed, but the concentration maxima of the intermediate carbocations were higher (corresponding to 27–32 % ionization) and less affected by the carboxylate anion concentration (Figure 3.3). As expected, the ionization equilibria lie more on the side of the ions in the more polar solvent.

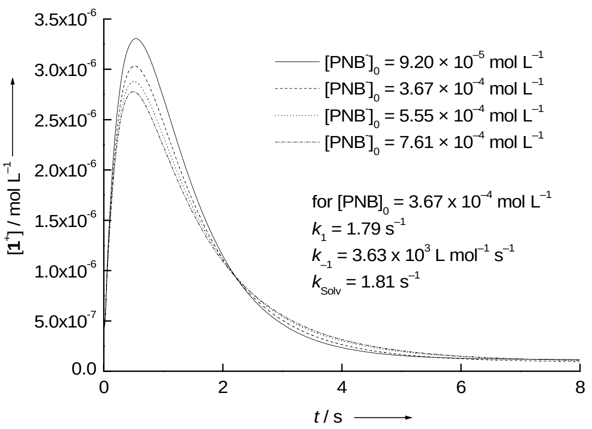
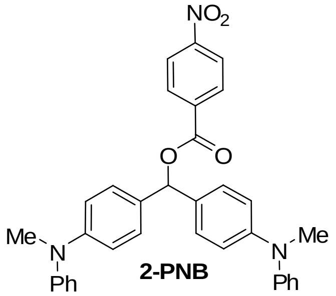


Figure 3.3. Formation and consumption of the blue 4,4'-bis(morpholino)benzhydrylium ion $\mathbf{1}^+$ (monitored photometrically at 612 nm) during the heterolysis of **1-PNB** (1.04×10^{-5} mol L^{-1}) in 60 % aqueous acetone in the presence of different amounts of n-$Bu_4N^+PNB^-$ at 25 °C.

The same values for k_1 and k_{Solv} are derived from the different curves and k_{-1} is calculated to decrease by 27 % when [PNB^-] increases from 0.37 mmol L^{-1} to 0.76 mmol L^{-1} (Experimental Section). In line with expectation, the variation of ion strength is less important in the more polar solvent.

Comparison of the rate constants in 80 % aqueous acetone (Figure 3.2) and 60 % aqueous acetone (Figure 3.3) shows that the doubling of the water concentration increases the ionization constant k_1 by a factor of 7 while k_{-1} and k_{Solv} remain almost constant. In accordance with this finding we had previously reported that the nucleophilicities of 80 % and 90 % aqueous acetone (k_{Solv}) are almost identical.[9]

“Carbocation watching” was also possible during the solvolysis of the benzhydrylium *p*-nitrobenzoate **2-PNB** in 80 % and 60 % aqueous acetone. Due to the fact that replacement of the morpholino groups by the *N*-methylanilino groups accelerates ionization (k_1) more than it affects ion recombination (k_{-1}) (cf. Figures 3.2–3.4), larger equilibrium concentrations of benzhydrylium ions are produced when **2-PNB** is solvolyzed under the same conditions as **1-PNB**. As a consequence of the higher concentration of the intermediate carbocations, the agreement of the individual rate constants k_1, k_{-1} and k_{Solv} obtained at different carboxylate anion concentrations is much better than in the case of **1** (Experimental Section).



2-PNB

20W80A
$k_1 = 1.00\ \mathrm{s}^{-1}$
$k_{-1} = 1.30 \times 10^4\ \mathrm{M}^{-1}\mathrm{s}^{-1}$
$k_{\mathrm{Solv}} = 1.51\ \mathrm{s}^{-1}$

40W60A
$k_1 = 6.36\ \mathrm{s}^{-1}$
$k_{-1} = 3.96 \times 10^3\ \mathrm{M}^{-1}\mathrm{s}^{-1}$
$k_{\mathrm{Solv}} = 1.59\ \mathrm{s}^{-1}$

Figure 3.4. Rate constants for the solvolysis of the 4,4'-bis(methylphenylamino)benzhydryl *p*-nitrobenzoate **2-PNB** (9.48×10^{-4} mol L^{-1}) in 80 % and 60 % aqueous acetone in the presence of 3.67×10^{-4} mol L^{-1} *n*-$Bu_4N^+PNB^-$.

Conclusion

S_N2C^+ reactions, postulated more than 50 years ago by Ingold,[10] have thus been established as the missing link between conventional S_N1 reactions, where carbocations appear as short-lived intermediates, and the domain of stable carbocations where subsequent reactions of carbocations do not occur.[3, 11] Our philicity[12] and fugality[13] scales can be employed to identify the range where the change of mechanism occurs.

Demonstration Experiment

A colorless solution is obtained by dissolving 4,4'-bis(morpholino)benzhydryl acetate **1-OAc** (≈ 10 mg) in acetone (8 mL) at room temperature. When 8 mL of water are added, the solution turns blue (4,4'-bis(morpholino)benzhydrylium ion $\mathbf{1}^+$) and subsequently fades within about 80 s (formation of the colorless benzhydrol). A video of this experiment is provided at http://www.wiley-vch.de/contents/jc_2002/2008/z800354_s.html.

References

(1) a) Streitwieser, Jr. A. in *Solvolytic Displacement Reactions*, McGraw-Hill, New York, **1962**; b) *Carbonium Ions,* Vol. 1–5 (Eds.: Olah, G. A.; Schleyer, P. v. R.), Wiley-Interscience, New York, **1968-1976**; c) Ingold, C. K. *Structure and Mechanism in Organic Chemistry, 2nd ed*, Cornell Univ. Press, Ithaca, NY, **1969**; d) Vogel, P. *Carbocation Chemistry*, Elsevier, Amsterdam, **1985**. e) *Advances in Carbocation Chemistry,* Vol. 1 (Ed.: Creary, X.), JAI, Greenwich, **1989**. f) *Advances in Carbocation Chemistry,* Vol. 2 (Ed.: Coxon, J.), JAI, Greenwich, **1995**.

(2) a) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Heck, R.; Robinson, G. C. *J. Am. Chem. Soc.* **1956**, *78*, 328–335. b) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89–173. c) Raber, D. J.; Harris, J. M.; Schleyer P. v. R.; in *Ions and Ion Pairs in Organic Reactions,* Vol. 2, (Ed.: Szwarc, M.), Wiley, New York, **1974**.

(3) Schaller, H. F.; Tishkov, A. A.; Feng, X.; Mayr, H. *J. Am. Chem. Soc.* **2008**, *130*, 3012-3022.

(4) Mayr, H.; Minegishi, S. *Angew. Chem.* **2002**, *114*, 4674–4676; *Angew. Chem. Int. Ed.* **2002**, *41*, 4493-4495.

(5) a) Mendes, P. *Comput. Appl. Biosci.* **1993**, *9*, 563–571. b) Mendes, P. *Trends Biochem. Sci.* **1997**, *22*, 361–363. c) Mendes, P.; Kell, D. *Bioinformatics* **1998**, *14*, 869–883.

(6) In the initial phase of the reaction, the conductivity is partially due to the presence of the benzhydrylium ions. Since the maximum of the benzhydryliums ions is only 3 % of the initial concentration of benzhydryl acetate, we have neglected the fact that the specific conductivity of benzhydrylium ions differs from that of trialkyl-ammonium ions.

(7) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174-5181.

(8) The occurrence of S_N2 reactions under these conditions can be excluded: Streidl, N.; Antipova, A.; Mayr, H. unpublished results.

(9) Denegri, B.; Minegishi, S.; Kronja, O.; Mayr, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 2302-2305.

(10) Gelles, E.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1954**, 2918-2929.

(11) *Stable Carbocation Chemistry,* (Eds.: Prakash, G. K. S.; Schleyer, P. v. R.), Wiley-Interscience, New York, **1997**.

(12) a) 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. b) Lucius, R.; Loos, R.; Mayr, H. *Angew. Chem.* **2002**, *114*, 97-102; *Angew. Chem. Int. Ed.* **2002**, *41*, 91-95. c) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66-77.

(13) a) 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. b) Denegri, B.; Ofial, A. R.; Juric, S.; Streiter, A.; Kronja, O.; Mayr, H. *Chem. Eur. J.* **2006**, *12*, 1657-1666. c) Denegri, B.; Kronja, O. *J. Org. Chem.* **2007**, *72*, 8427-8433.

–Experimental Section–

“Carbocation Watching” in Solvolysis Reactions

Schaller, H. F.; Mayr, H. *Angew. Chem.* **2008**, *120*, 4022-4025; *Angew. Chem. Int. Ed.* **2008**, *47*, 3958-3961.

General

Materials. Commercially available acetonitrile, water (HPLC-gradient grade, VWR), and acetone (extra dry, Acros) were used without further purification for all experiments.

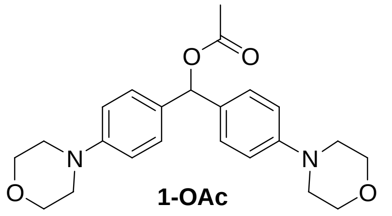
Mixtures of solvents are given as (v/v) and the solvents are abbreviated: A = acetone, AN = acetonitrile, W = water. For example the solvent mixture 20W80AN refers to a mixture of water and acetonitrile in a ratio of 20/80 (v/v).

N,*N*-Diisopropylmethylamine ((iPr)$_2$NMe, ≥ 98 %, Fluka) was distilled, quinuclidine (≥ 97 %, Fluka) and 4-(dimethylamino)pyridine (DMAP, > 99 %, Aldrich) were used without further purification.

The benzhydrylium tetrafluoroborates Ar_2CH^+ BF_4^- were prepared as described before.[S1]

The covalent benzhydryl carboxylates **1-PNB** and **2-PNB** which are derived from highly stabilized benzhydrylium ions (**1**$^+$ and **2**$^+$) and good nucleofuges (PNB$^-$) cannot be isolated.

4,4'-Bis(morpholino)benzhydryl acetate (**1-OAc**). A mixture of 4,4'-bis(morpholino)benzhydrol (354 mg, 1.0 mmol), DMAP (0.1 equiv, 12 mg, 0.10 mmol), and freshly distilled triethylamine (1.2 equiv, 101 mg, 1.00 mmol) in dry benzene (5 mL) was stirred for 5 min under nitrogen atmosphere before acetic anhydride (1 equiv) was added. Stirring was continued for 5 h at room temperature. Then pentane (5 mL) was added, and the reaction mixture was washed quickly with 0.2 M hydrochloric acid (10 mL), saturated aq. $NaHCO_3$ (10 mL), and water. The organic phase was dried ($MgSO_4$) and filtered. Then the solvent was evaporated in vacuo (T < 30°C). The residue was crystallized from diethyl ether/pentane to give **1-OAc** (258 mg, 65 %) as a colorless powder.



1-OAc

^{1}H NMR (200 MHz, C_6D_6): δ = 1.73 (s, 3 H, CH_3), 2.65 (t, 8 H, J = 3.5 Hz, NCH_2), 3.46 (t, 8 H, J = 3.5 Hz, OCH_2), 6.63 (d, 4H, J = 8.7 Hz, ArH), 7.21 (s, 1 H, Ar_2CH), 7.38 ppm (d, 4 H, J = 8.7 Hz, ArH); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 21.3 (q, CH_3), 49.6 (t, NCH_2), 67.2 (t, OCH_2), 77.2 (d, Ar_2CH), 116.1 (d, Ar), 129.1 (d, Ar), 132.9 (s, Ar), 151.7 (s, Ar), 169.9 ppm (s, CO_2).

Kinetics

Solvolysis Reactions by Conductometry. For the conductometric monitoring of the solvolysis reactions of **1-OAc** in 20W80AN a WTW LTA 1/NS Pt electrode connected to a Tacussel CD 810 conductometer was used.[S2] To freshly prepared aqueous solvent mixtures (20W80AN, 25 mL) amine was added and the mixtures were thermostated (25.0 ± 0.1 °C) prior to the injection of a small volume (75–150 µL) of a 0.2 M stock solution of **1-OAc** in CH_2Cl_2. The increase of the conductance (G) was then recorded.

Solvolysis Reactions by Conventional UV-Vis-Photometry. For the UV-Vis-photometric investigation of the solvolysis reactions of **1-OAc** in 20W80AN a conventional UV-Vis-photometry setup was used (J&M TIDAS diode array spectrophotometer connected through fiber optic cables with standard SMA connectors to a Hellma 661.060-UV quartz Suprasil immersion probe with 5 mm light path). To freshly prepared aqueous solvent mixtures (20W80AN, 25 mL) a specific amount of amine was added and the mixtures were thermostated (25.0 ± 0.1 °C) prior to the injection of a small volume (75–150 µL) of a stock solution of **1-OAc** in CH_2Cl_2.

Solvolysis Reactions by Stopped-Flow UV-Vis-Photometry. The covalent benzhydryl carboxylates **1-PNB** and **2-PNB**, which are derived from highly stabilized benzhydrylium ions (**1**$^+$ and **2**$^+$) and good nucleofuges (PNB^-), cannot be isolated. Therefore the double mixing mode of a stopped-flow instrument (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software) was employed to generate the covalent benzhydryl esters by first mixing a solution of $Ar_2CH^+BF_4^-$ in acetone with a solution of 10 to 80 equiv. of n-$Bu_4N^+PNB^-$ in the same solvent. After a delay time of 1 s, the colorless solution of the resulting covalent Ar_2CH-PNB was combined in a second mixing step with an equal volume of *aqueous* acetone, which provoked the ionization of Ar_2CH–PNB. The ionizations were followed photometrically at the absorption maxima of Ar_2CH^+. The concentrations of the generated benzhydrylium carboxylates were between (2.5–10) × 10^{-6} mol L^{-1}. The excess of carboxylate ions varied between 10 and 80 equiv. of the Ar_2CH-PNB.

Evaluation of Kinetic Measurement by GEPASI software. Whenever we were not able to analyze the kinetic traces by a fit to a single-exponential function, we used the "evolutionary programming" optimization method implemented in the GEPASI software (version 3.30)[S3] to calculate the rate constants k_1, k_{-1}, and k_{Solv}.

For this procedure the experimentally measured time-dependent conductance or absorption curves must be converted to concentration vs. time curves. In case of the conductometric measurements, a calibration curve for n-$Bu_4N^+AcO^-$ in 20W80AN was used for this conversion. Differences of the specific conductivities of Ar_2CH^+, R_3NH^+, and R_4N^+ have been neglected. Absorptions were converted to the corresponding concentrations of Ar_2CH^+ by using the absorption coefficients.[S4]

Besides the experimentally obtained kinetic curves (conc vs. time), a set of equations (see below) that describes a simple S_N1 solvolysis reaction (Scheme 3.1, chapter 3) was used as input for the GEPASI software. Then, the "evolutionary programming" method of GEPASI searches for a global minimum of the sum of squares of residuals *ssq* (eq (S3.1)) of the adjustable variables (= rate constants k_1, k_{-1}, and k_{Solv}), the experimental kinetic curves, and the initial concentrations of the involved species.

$$ssq = \sum_i \left(\frac{y_i - y_i^*}{w_i} \right)^2 \qquad \text{eq (S3.1)}$$

In Equation (S3.1), y_i are the measured values of the variables, y^*_i are the simulated values of the variables and w_i are weighting constants. The weighting constants are used to scale all variables to similar values so that they have equal weight on the fit. The smaller *ssq*, the better the fit.

Conductimetric Investigation of the Solvolysis Reactions of 1-OAc in 20W80AN in Presence of Different Amines

The solvolysis reactions of **1-OAc** in 20W80AN (at 25 °C) were monitored by following the increase of the conductivity of the reaction mixtures.

In the presence of added DMAP or quinuclidine (Scheme 3.3), the first-order rate constants k_1 (s^{-1}) for the solvolysis reactions of **1-OAc** were obtained by least-squares fitting of the single exponential equation $y = A_1\exp(-x/t_1) + y_0$ (with $1/t_1 = k_1$) to the conductance data (Figures S3.1 and S3.2).

In presence of diisopropyl-methylamine ($(i\mathrm{Pr})_2\mathrm{NMe}$), however, the increase of conductivity during the solvolysis reaction of **1-OAc** in 20W80AN cannot be described by a single exponential function (Figure S3.3) and a fit calculated by GEPASI according to Scheme 3.1 was applied to analyze the kinetics (Figure S3.4).

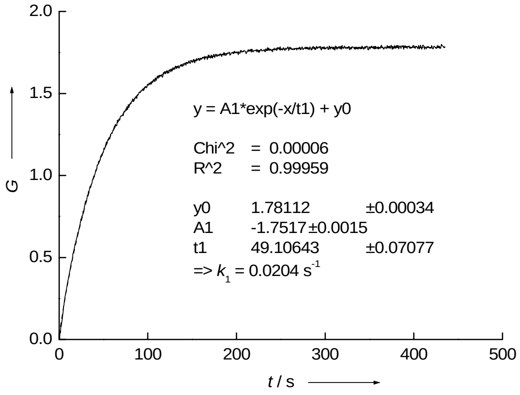


Figure S3.1. Increase of conductivity during the solvolysis of **1-OAc** (0.622 mM) in 20W80AN at 25 °C in the presence of DMAP (5.02 mM). Superposition of experimental curve (black) and exponential fit (dashed).

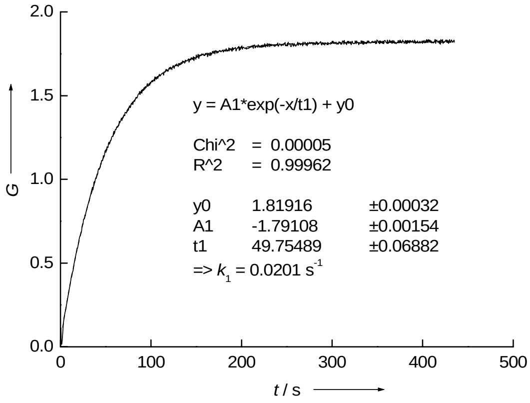


Figure S3.2. Increase of conductivity during the solvolysis of **1-OAc** (0.622 mM) in 20W80AN at 25 °C in the presence of quinuclidine (5.24 mM). Superposition of experimental curve (black) and exponential fit (dashed).

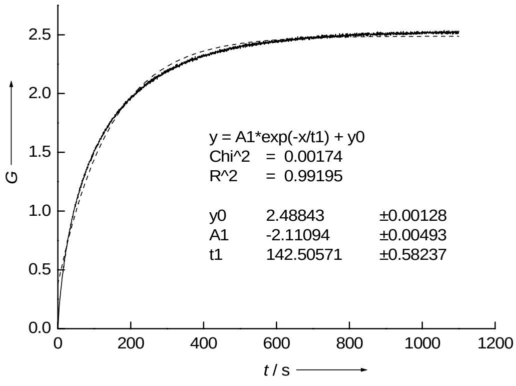


Figure S3.3. Increase of conductivity during the solvolysis of **1-OAc** (0681 mM) in 20W80AN at 25 °C in the presence of $(i\text{Pr})_2$NMe (5.24 mM). The superposition of experimental curve (black) and exponential fit (dashed) shows systematic deviations.

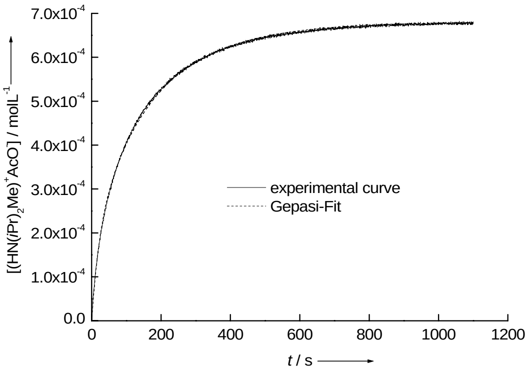


Figure S3.4. Increase of conductivity during the solvolysis of **1-OAc** (0.681 mM) in 20W80AN at 25 °C in the presence of $(i\text{Pr})_2$NMe (0.524 mM). The superposition of experimental curve (black) and a fit calculated by GEPASI (dashed, *ssq* = 1.04 × 10^{-8}) according to Scheme 3.1 delivers the rate constants:

$k_1 = (2.13 \pm 0.00) \times 10^{-2}\ \text{s}^{-1}$;

$k_{-1} = (1.09 \pm 0.04) \times 10^{3}\ \text{M}^{-1}\ \text{s}^{-1}$;

$k_{\text{Solv}} = (2.01 \pm 0.07) \times 10^{-1}\ \text{s}^{-1}$.

Photometric Investigation of the Solvolysis Reaction of 1-OAc in 20W80AN

The solvolysis reactions of **1-OAc** in 20W80AN (at 25 °C) were monitored by conventional UV-Vis-photometry. The increase and subsequent decay of the absorbance at 612 nm (Figure S3.5) was used for the GEPASI analysis of the kinetics of the solvolysis reaction according to Scheme 3.1.

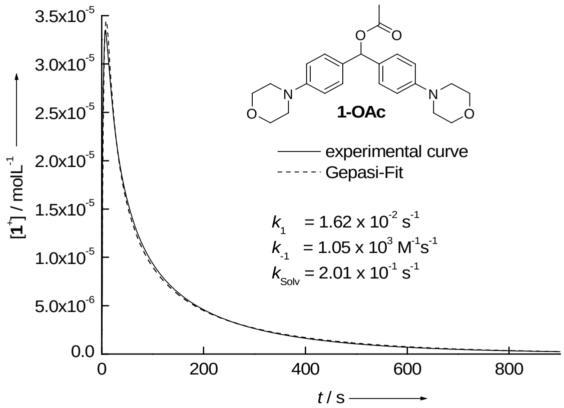


Figure S3.5. Formation and consumption of the blue carbocation **1**$^+$ (monitored at 612 nm, conventional UV-Vis-photometry, absorptions are converted to concentrations of **1**$^+$) during the heterolysis of **1-OAc** (1.09 mM) in 20W80AN at 25 °C in the presence of (iPr)2NMe (5.24 mM). The superposition of experimental curve (black) and a fit calculated by GEPASI (red, ssq = 1.33 × 10-10) according to Scheme 3.1 delivers the rate constants: $k_1 = (1.62 \pm 0.00) \times 10^{-2}$ s^{-1}; k_{-1} = $(1.05 \pm 0.04) \times 10^3$ M^{-1} s^{-1}; $k_{\text{Solv}} = (2.01 \pm 0.07) \times 10^{-1}$ s^{-1} (Figure 3.1, chapter 3).

Without added (iPr)$_2$NMe, the solvolysis reaction **1-OAc** in 20W80AN (Figure S3.6) could not be analyzed by GEPASI within the framework of Scheme 3.1 (chapter 3), probably because of the involvement of several rate and equilibrium constants (partial dissociation of acetic acid).

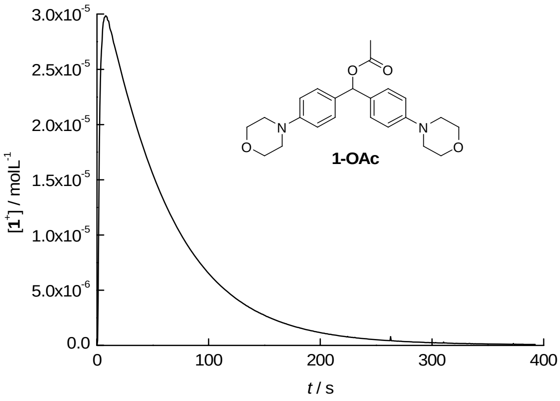
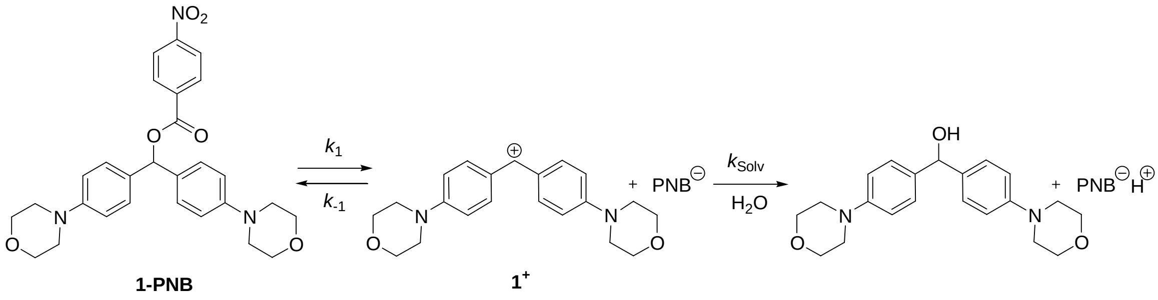


Figure S3.6. Formation and consumption of the blue carbocation $\mathbf{1}^+$ (monitored at 612 nm, conventional UV-Vis-photometry, absorptions are converted to concentrations of $\mathbf{1}^+$) during the heterolysis of **1-OAc** (0.908 mM) in 20W80AN at 25 °C.

Photometric Investigation of the Solvolysis Reactions of 1-PNB in 20W80A

The solvolysis reactions of **1-PNB** in 20W80A (at 25 °C) were monitored by stopped-flow UV-Vis-photometry. The increase and subsequent decay of the absorbance at 612 nm (Figure S3.7) was used for the GEPASI analysis of the kinetics of the solvolysis reaction according to Scheme 3.1 (Table S3.1).



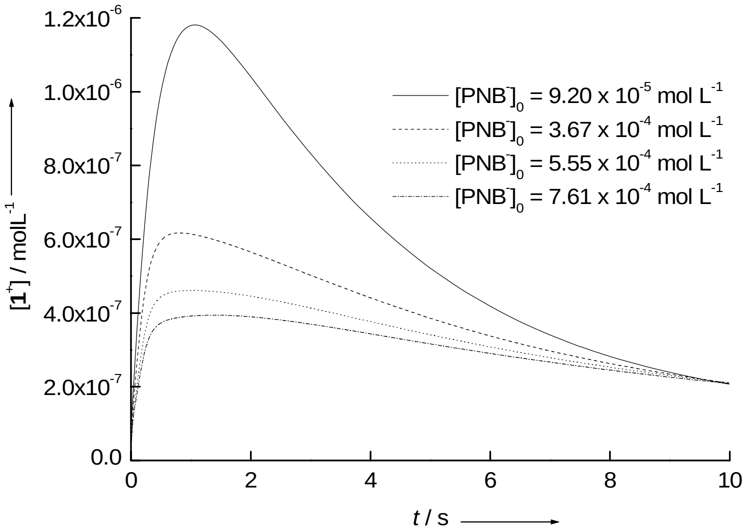


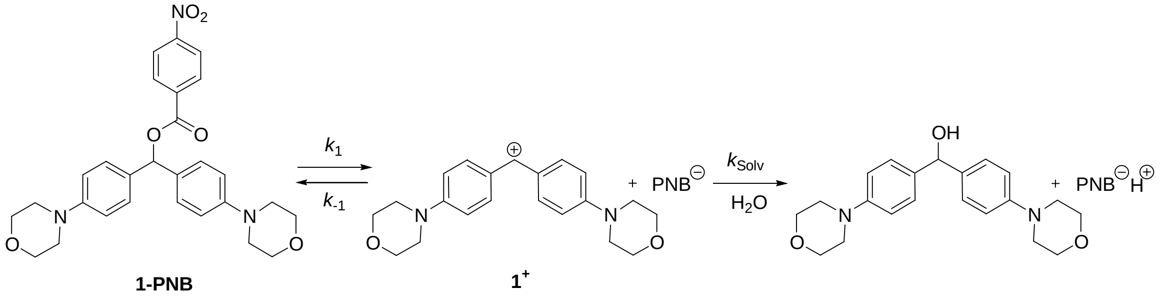
Figure S3.7. Formation and consumption of the blue carbocation $\mathbf{1}^+$ (monitored at 612 nm, stopped-flow technique, absorptions are converted to concentrations of $\mathbf{1}^+$) during the heterolysis of **1-PNB** (1.04×10^{-5} M) in 20W80A at 25 °C in the presence of different amounts of $nBu_4N^+PNB^-$ (Figure 3.3, chapter 3).

Table S3.1. Variation of the *p*-nitrobenzoate concentration and effect on the rate constants k_1, k_{-1}, and k_{Solv} (obtained from an analysis of the kinetic curves shown in Figure S3.7 by GEPASI) of the solvolysis reactions of **1-PNB** in 20W80A at 25 °C.

[**1-PNB**]$_0$ [M]	[PNB$^-$]$_0$ [M]	k_1 [s^{-1}]	k_{-1} [M^{-1} s^{-1}]	k_{Solv} [s^{-1}]	*ssq*
1.04×10^{-5}	9.20×10^{-5}	-	-	-	-
1.04×10^{-5}	3.67×10^{-4}	$(2.57 \pm 0.00) \times 10^{-1}$	$(5.80 \pm 0.05) \times 10^{3}$	1.53 ± 0.00	2.07×10^{-14}
1.04×10^{-5}	5.55×10^{-4}	$(1.92 \pm 0.00) \times 10^{-1}$	$(4.00 \pm 0.05) \times 10^{3}$	1.50 ± 0.00	3.14×10^{-14}
1.04×10^{-5}	7.61×10^{-4}	$(1.61 \pm 0.00) \times 10^{-1}$	$(2.98 \pm 0.05) \times 10^{3}$	1.43 ± 0.00	4.22×10^{-14}

Photometric Investigation of the Solvolysis Reactions of 1-PNB in 40W60A

The solvolysis reactions of **1-PNB** in 40W60A (at 25 °C) were monitored by stopped-flow UV-Vis-photometry. The increase and subsequent decay of the absorbance at 612 nm (Figure S3.8) was used for the GEPASI analysis of the kinetics of the solvolysis reaction according to Scheme 13. (Table S3.2).



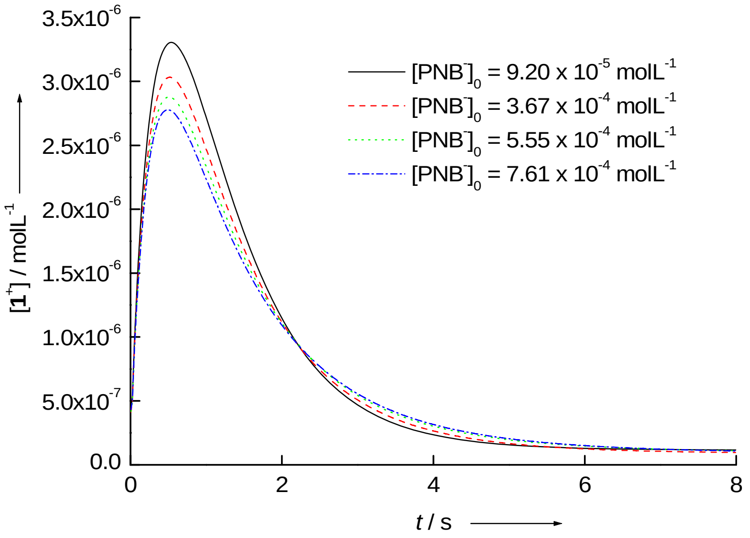


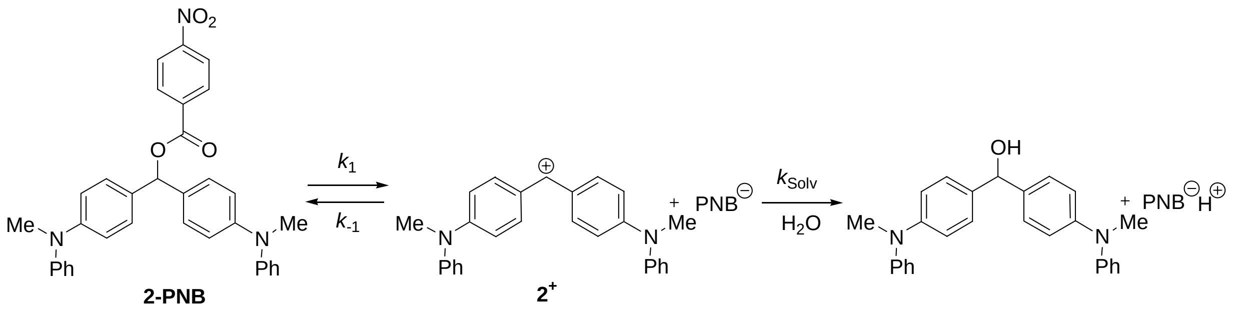
Figure S3.8. Formation and consumption of the blue carbocation 1^+ (monitored at 612 nm, stopped-flow technique, absorptions are converted to concentrations of 1^+) during the heterolysis of **1-PNB** (1.04×10^{-5} M) in 40W60A at 25 °C in the presence of different amounts of $n\text{Bu}_4\text{N}^+\text{PNB}^-$ (Figure 3.4, chapter 3).

Table S3.2. Variation of the *p*-nitrobenzoate concentration and effect on the rate constants k_1, k_{-1}, and k_{Solv} (obtained from an analysis of the kinetic curves shown in Figure S3.8 by Gepasi) of the solvolysis reactions of **1-PNB** in 40W60A at 25 °C.

[**1-PNB**]$_0$ [M]	[PNB$^-$]$_0$ [M]	k_1 [s^{-1}]	k_{-1} [M^{-1} s^{-1}]	k_{Solv} [s^{-1}]	*ssq*
1.04×10^{-5}	9.20×10^{-5}	-	-	-	-
1.04×10^{-5}	3.67×10^{-4}	1.79 ± 0.01	$(3.63 \pm 0.06) \times 10^3$	1.81 ± 0.00	1.49×10^{-12}
1.04×10^{-5}	5.55×10^{-4}	1.79 ± 0.00	$(3.10 \pm 0.05) \times 10^3$	1.81 ± 0.00	1.74×10^{-12}
1.04×10^{-5}	7.61×10^{-4}	1.81 ± 0.01	$(2.62 \pm 0.04) \times 10^3$	1.84 ± 0.00	1.58×10^{-12}

Photometric Investigation of the Solvolysis Reactions of 2-PNB in 20W80A

The solvolysis reactions of **2-PNB** in 20W80A (at 25 °C) were monitored by stopped-flow UV-Vis-photometry. The increase and subsequent decay of the absorbance at 613 nm (Figure S3.9) was used for the GEPASI analysis of the kinetics of the solvolysis reaction according to Scheme 3.1 (Table S3.3).



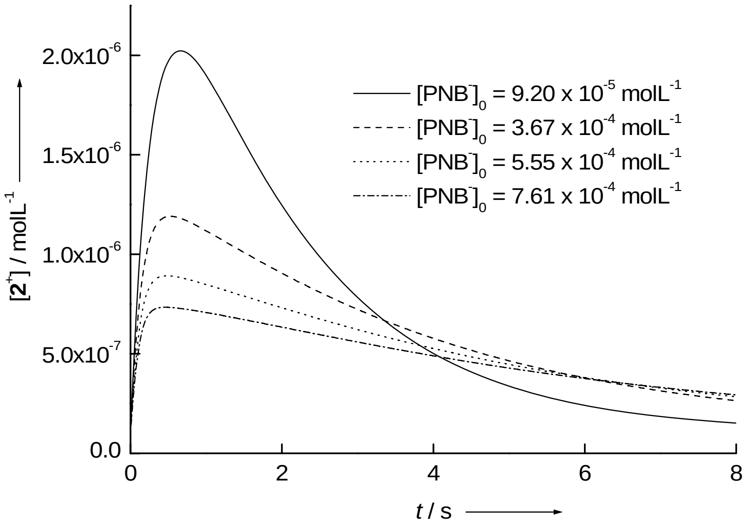


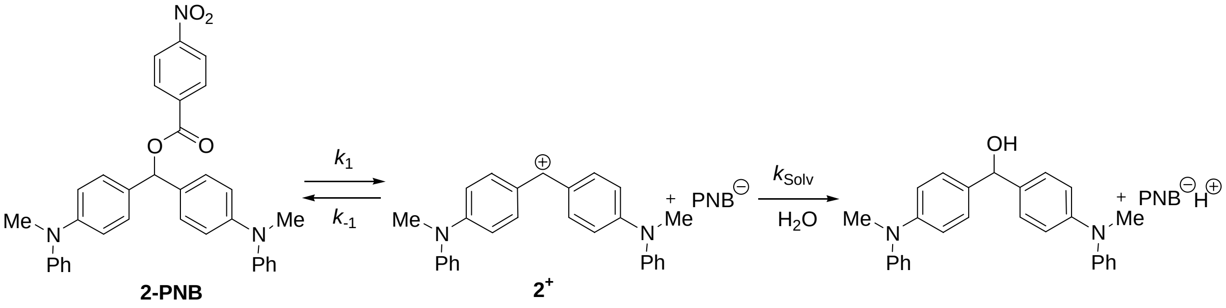
Figure S3.9. Formation and consumption of the blue carbocation **2**$^+$ (monitored at 613 nm, stopped-flow technique, absorptions are converted to concentrations of **2**$^+$) during the heterolysis of **2-PNB** (9.48 × 10^{-6} M) in 20W80A at 25 °C in the presence of different amounts of *n*Bu$_4$N$^+$PNB$^-$.

Table S3.3. Variation of the *p*-nitrobenzoate concentration and effect on the rate constants k_1, k_{-1}, and k_{Solv} (obtained from an analysis of the kinetic curves shown in Figure S3.9 by GEPASI) of the solvolysis reactions of **2-PNB** in 20W80A at 25 °C.

[**2-PNB**]$_0$ [M]	[PNB$^-$]$_0$ [M]	k_1 [s^{-1}]	k_{-1} [M^{-1} s^{-1}]	k_{Solv} [s^{-1}]	*ssq*
9.48 × 10^{-6}	9.33 × 10^{-5}	1.08 ± 0.00	(1.69 ± 0.02) × 10^{4}	1.55 ± 0.00	3.39 × 10^{-13}
9.48 × 10^{-6}	3.67 × 10^{-4}	1.00 ± 0.00	(1.30 ± 0.00) × 10^{4}	1.51 ± 0.00	4.41 × 10^{-14}
9.48 × 10^{-6}	5.55 × 10^{-4}	(9.08 ± 0.04) × 10^{-1}	(1.17 ± 0.06) × 10^{4}	1.53 ± 0.00	2.74 × 10^{-14}
9.48 × 10^{-6}	7.61 × 10^{-4}	(8.47 ± 0.05) × 10^{-1}	(1.04 ± 0.00) × 10^{4}	1.49 ± 0.00	3.12 × 10^{-14}

Photometric Investigation of the Solvolysis Reactions of 2-PNB in 40W60A

The solvolysis reactions of **2-PNB** in 40W60A (at 25 °C) were monitored by stopped-flow UV-Vis-photometry. The increase and subsequent decay of the absorbance at 613 nm (Figure S3.10) was used for the GEPASI analysis of the kinetics of the solvolysis reaction according to Scheme 3.1 (Table S3.4).



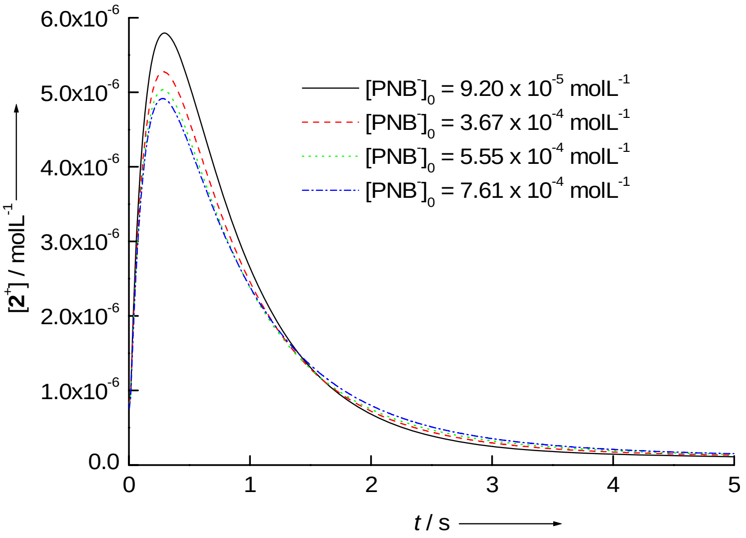


Figure S3.10. Formation and consumption of the blue carbocation **2^+** (monitored at 613 nm, stopped-flow technique, absorptions are converted to concentrations of **2^+**) during the heterolysis of **2-PNB** (9.48×10^{-6} M) in 40W60A at 25 °C in the presence of different amounts of *n*$Bu_4N^+PNB^-$.

Table S3.4. Variation of the *p*-nitrobenzoate concentration and effect on the rate constants k_1, k_{-1}, and k_{Solv} (obtained from an analysis of the kinetic curves shown in Figure S3.10 by GEPASI) of the solvolysis reactions of **2-PNB** in 40W60A at 25 °C.

[**2-PNB**]$_0$ [M]	[PNB$^-$]$_0$ [M]	k_1 [s^{-1}]	k_{-1} [M^{-1} s^{-1}]	k_{Solv} [s^{-1}]	*ssq*
9.48×10^{-6}	9.33×10^{-5}	6.57 ± 0.03	$(5.76 \pm 0.17) \times 10^{3}$	1.51 ± 0.00	2.83×10^{-12}
9.48×10^{-6}	3.67×10^{-4}	6.36 ± 0.04	$(3.96 \pm 0.07) \times 10^{3}$	1.59 ± 0.00	3.66×10^{-12}
9.48×10^{-6}	5.55×10^{-4}	6.30 ± 0.00	$(3.56 \pm 0.06) \times 10^{3}$	1.62 ± 0.00	4.07×10^{-12}
9.48×10^{-6}	7.61×10^{-4}	6.28 ± 0.04	$(3.08 \pm 0.05) \times 10^{3}$	1.60 ± 0.00	4.00×10^{-12}

References

(S1) 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.

(S2) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446–4454.

(S3) a) Mendes, P. *Comput. Appl. Biosci.* **1993**, *9*, 563–571. b) Mendes, P. *Trends Biochem. Sci.* **1997**, *22*, 361–363. c) Mendes, P.; Kell, D. *Bioinformatics* **1998**, *14*, 869–883. d) More information about GEPASI at: www.gepasi.org.

(S4) Loos, R.; Mayr, H. *unpublished results*.

Nucleofugality of Common Leaving Groups in Solvolysis Reactions: An Extension of the Nucleofugality Scale

Introduction

In organic chemistry, the knowledge of leaving group abilities is essential to plan and perform nucleophilic substitution reactions. Nucleophilic and electrophilic reactivity have been a topic of numerous investigations, but nucleofugality and electrofugality, the other side of the coin, have been studied less intensively. Recent publications provide a good survey of leaving groups and their nucleofugalities in organic synthesis (e.g. sulfonates, perfluorated carboxylates),[1] and many theoretical calculations have been carried out to set up nucleofugality scales besides our own attempts for quantifying these parameters.[2]

Recently[3] we constructed the linear free energy relationship (eq 4.1) to predict rate constants of S_N1-type solvolysis reactions, where N_f and s_f are nucleofuge-dependent and E_f is an electrofuge-dependent parameter.

$$\log k_1 = s_f(N_f + E_f) \qquad (4.1)$$

Our last approach to create a general nucleofugality scale as an analog to our comprehensive nucleophilicity scale will now be complemented by determining nucleofugality and electrofugality for numerous nucleofuges and highly stabilized electrofuges.

In order to classify more anionic and neutral leaving groups, we have extended our research on solvolysis reactions. In these solvolysis reactions (Scheme 4.1), the carbocation R^+ is usually 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, determined by analyzing either the time dependant concentrations of the reactants RX or the one of the products ROSolv or HX.

Scheme 4.1.

$$\text{R-X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^+ + \text{X}^- \xrightarrow[\text{HOSolv}]{k_{\text{Solv}}} \text{R-OSolv} + \text{HX}$$

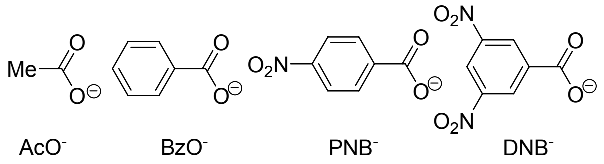
Recently,[3] we have reported the change from the typical S_N1 mechanism (Scheme 1, $k_1 < k_{\text{solv}}$) to the so-called S_N2C^+ mechanism[4] (Scheme 1, $k_1 > k_{\text{solv}}$), where ionization is faster than the subsequent reaction with the solvent. In the latter case, the intermediate carbocation R^+ may accumulate, and if the ionization equilibrium k_1/k_{-1} is favorable, it becomes possible to investigate the ionization step directly. We also reported on the direct UV-Vis spectroscopic observation of the ionization of a series of benzhydryl carboxylates, which ionize to give the colored benzhydrylium ions and undergo subsequent reactions with the solvent within a couple of minutes (“carbocation watching”).[5]

By completing this data set towards benzhydryl carboxylates with less stabilized benzhydrylium ions (which follow the typical S_N1 mechanism and cannot be observed photometrically), we will now be able to construct an electrofugality scale up to highly stabilized benzhydrylium ions which helps us to fix nucleofugality parameters for carboxylates and other important leaving groups. This study focuses on solvolysis reactions of benzhydryl carboxylates with rate constants from $k_1 \approx 1 \times 10^{-1}$ to 1×10^{-4} s^{-1} in order to link the solvolysis rates of benzhydryl chlorides[6] with those of rapidly ionizing benzhydryl carboxylates.[5,7] This link is needed to achieve our objective of a comprehensive electrofugality scale.

Results and Discussion

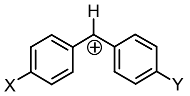
A set of isolable covalent benzhydryl carboxylates has been employed to perform the solvolysis reactions. As nucleofuges various carboxylate ions (Scheme 4.2) have been combined with benzhydrylium ions listed in Table 4.1.

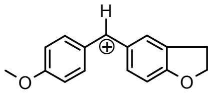
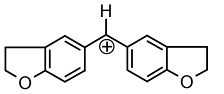
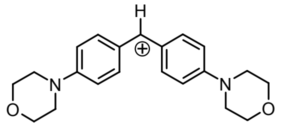
Scheme 4.2. Carboxylate Ions Employed in This Chapter.



As solvents, typical mixtures (v/v) of acetone or acetonitrile with water were employed.

Table 4.1. Benzhydrylium Ions Ar_2CH^+ and Their Electrophilicity Parameters *E*.



Ar_2CH^+	X	Y	E^a
$(ani)_2CH^+$	OCH_3	OCH_3	0.00
$(fur)(ani)CH^+$			–0.56
$(dma)(Ph)CH^+$	$N(CH_3)_2$	H	–[b]
$(fur)_2CH^+$			–1.36
$(pfa)_2CH^+$	$N(Ph)CH_2CF_3$	$N(Ph)CH_2CF_3$	–3.14
$(mfa)_2CH^+$	$N(CH_3)CH_2CF_3$	$N(CH_3)CH_2CF_3$	–3.85
$(dpa)_2CH^+$	NPh_2	NPh_2	–4.72
$(mor)_2CH^+$			–5.53

[a] Electrophilicity parameter as defined in ref [8]. [b] Not determined.

Table 4.2 summarizes the isolated benzhydryl carboxylates and illustrates that *p*-nitrobenzoates and 3,5-dinitrobenzoates of benzhydrylium ions better stabilized than $(fur)_2CH^+$ could not be synthesized.

Table 4.2. Synthesized Covalent Benzhydryl Carboxylates.

	RCO_2^-			
Ar_2CH^+	AcO^-	BzO^-	PNB^-	DNB^-
$(ani)_2CH^+$	×	–[a]	×	×
$(fur)(ani)CH^+$	×	×	×	×
$(dma)(Ph)CH^+$	×	×	–	–
$(fur)_2CH^+$	×	×	×	×
$(pfa)_2CH^+$	×	–[a]	–	–
$(mfa)_2CH^+$	×	×	–	–
$(dpa)_2CH^+$	×	×	–	–
$(mor)_2CH^+$	×	×	–	–

[a] Synthesis is possible but has not been accomplished.

In solvolysis reactions of benzhydryl derivatives the phenomenon of common ion rate depression[9] is often observed. In these cases, the intermediate benzhydrylium ions not only react with the solvent but also undergo ion recombination which results, according to mass law, in a slower overall rate of solvolysis. It was claimed that the appearance of common ion rate depression is a compelling evidence for the existence of free carbocations as intermediates, and grows with the electron donating ability of the cations' substituents.[9,10] Using the steady-state approximation and neglecting the effects of variable ionic strengths, the observed solvolysis rate constant can be defined by eq (4.2), with $\alpha = k_{-1}/k_{\mathrm{Solv}}$ as mass law or selectivity constant which reflects the relative reactivities of the intermediate carbocation toward its former nucleofuge and the solvent. A reduction of k_{obs} by addition of a salt with a common ion can only be observed when the carbocation is sufficiently selective to react with the more nucleophilic leaving group that is present in low concentration and with the less nucleophilic solvent that is present in high concentration. It is generally accepted, that within structurally related substrates α increases with the stability and the lifetime of the intermediate carbocation,[11] and with decreasing nucleophilicity of the solvents.[12]

$$k_{\mathrm{obs}} = \frac{k_1 k_{\mathrm{Solv}}}{k_{\mathrm{Solv}} + k_{-1}[\mathrm{RCO_2^-}]} = \frac{k_1}{1 + \alpha[\mathrm{RCO_2^-}]} \quad (4.2)$$

Some examples of common ion rate depression during solvolysis of benzhydryl carboxylates have been reported. Goering and Levy reported that with carbonyl ^{18}O labelled benzhydryl *p*-nitrobenzoate oxygen scrambling is three times faster than solvolysis at 118.6 °C in 90 % aqueous acetone.[13] Experiments with a chiral substrate showed that under these conditions 72 % of the ion intermediate returned to substrate, 81 % of which gave the original enantiomer while 19 % was converted into the other enantiomer.[14]

The fact that the solvolyses discussed in this chapter are slightly influenced by common ion rate depression is rationalized by Figure 4.1, which shows a plot of the logarithm of the calculated first-order rate constants of the hypothetical reaction of the benzhydrylium ions with either the solvent or the nucleofuge, against the electrophilicity parameter *E* of the carbocations. It is eye-catching that, for *E* < –2, the reaction of the benzhydrylium ion with the acetate ion is faster than the reaction of the carbocation with the solvent. As a consequence k_{obs} of solvolyses of benzhydryl acetates in 20W80AN, which yield benzhydrylium cations which are less electrophilic than $(\text{fur})_2\text{CH}^+$ ($E = -1.36$), can be significantly affected by common ion rate depression at $[\text{AcO}^-] = 5.06 \times 10^{-3}$ M. This is the highest possible concentration of free anion, due to the concentration of the initially deployed benzhydryl carboxylate. By going to less nucleophilic leaving groups, such as benzoate and to more nucleophilic solvents like 60 % aqueous acetone, common ion rate depression decreases and smaller deviations from the first-order rate law were observed.

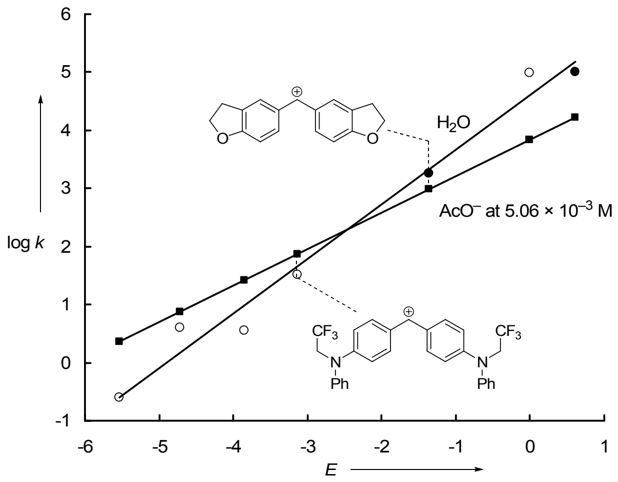
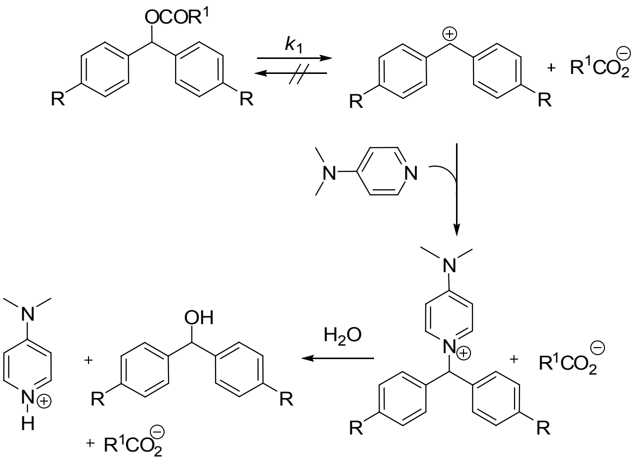


Figure 4.1. Comparison of the calculated first-order rate constant for the reactions of Ar_2CH^+ (characterized by their electrophilicities *E*) with acetate and the first-order rate constants for the reaction with water in 20W80AN (○ from ref [15], ● calculated).

By adding tertiary amines and thus trapping of the free carbocation, we are able to suppress common ion return (Scheme 4.2).[6] Solvolysing $(\text{mfa})_2\text{CH-BzO}$, $(\text{dpa})_2\text{CH-BzO}$, $(\text{mor})_2\text{CH-BzO}$ and $(\text{mor})_2\text{CH-AcO}$ by addition of tertiary amines, clean kinetics according to first-order rate law have been achieved. Queen made the same observation in 1979, which led to the conclusion, that "pyridine must be able to react by a pathway that does not involve free carbocation".[16]

Scheme 4.2. Trapping the Intermediate Carbocations by DMAP.[6]



If both, combination reaction with the carboxylates and reaction with the solvent are slow compared to the heterolysis rate, i.e., when benzhydryl carboxylates with highly stabilized benzhydrylium ions, which have a long lifetime in aqueous solvents and low electrophilicity, are solvolysed, first-order kinetics can be observed even without addition of amine.[7]

Kinetics. Solvolysis rates of benzhydryl carboxylates were monitored by following the increase of the conductivity of the reaction mixtures (conductimeter: Tacussel CD 810, Pt electrode: WTW LTA 1/NS).[17] Freshly prepared solvents (25 mL) were thermostated (± 0.1 °C) at 25 °C for 5 min prior to adding the substrate. Typically, a 0.2 M stock solution of the substrate in CH_2Cl_2 was prepared and 75 – 150 μL were injected into the solvent, and the conductance (*G*) was recorded at given time intervals.

The first order rate constants k_1 (s^{-1}) were obtained by least squares fitting of the conductance data to a single exponential equation $y = A_1\exp(-x/t_1) + y_0$ (with $1/t_1 = k_1$) for the solvolyses of benzhydryl carboxylates in aqueous solvents in the presence of NEt_3, Proton Sponge (N,N,N',N'-tetramethyl-1,8-naphthalene-diamine) or DMAP.

Table 4.3 summarizes the ionization rate constants k_1 for solvolysis reactions of benzhydryl carboxylates which were derived from benzhydrylium ions with $E < 0$. In order to keep the effect of common ion rate depression on the observed rate constant small, some kinetic experiments have only been evaluated up to 60 % conversion. These values are marked in Table 4.3 and should be considered with caution, because single measurements may deviate about 10 %.

Table 4.3. Ionization Rate Constants k_1 of Benzhydryl Derivatives in Different Solvents (25 °C).

Nucleofuge	Solvent	Ar_2CH^+	k_1 [s^{-1}]
AcO^-	20W80AN	$(dpa)_2CH^+$	9.55×10^{-4}
		$(mfa)_2CH^+$	2.60×10^{-2} [a]
		$(pfa)_2CH^+$	1.04×10^{-3} [a,b]
		$(dma)(Ph)CH^+$	5.55×10^{-3} [a,b]
		$(fur)_2CH^+$	1.19×10^{-4}
		$(ani)_2CH^+$	8.83×10^{-6}
	40W60AN	$(mor)_2CH^+$	5.53×10^{-2} [a,b]
		$(dpa)_2CH^+$	2.10×10^{-3} [a,b,c]
		$(mfa)_2CH^+$	8.73×10^{-2} [a,b]
		$(pfa)_2CH^+$	2.37×10^{-3}
		$(dma)(Ph)CH^+$	1.30×10^{-2} [a]
		$(fur)_2CH^+$	4.43×10^{-4}
		$(fur)(ani)CH^+$	1.40×10^{-4}
	20W80A	$(mor)_2CH^+$	1.25×10^{-2} [a,b]
		$(dpa)_2CH^+$	2.80×10^{-4}
		$(mfa)_2CH^+$	1.34×10^{-2} [a,b]
		$(pfa)_2CH^+$	4.01×10^{-4}
		$(dma)(Ph)CH^+$	1.32×10^{-3} [a,b]
		$(fur)_2CH^+$	4.31×10^{-5} [a]
	40W60A	$(mor)_2CH^+$	5.00×10^{-2}
		$(mfa)_2CH^+$	7.25×10^{-2} [a]
		$(pfa)_2CH^+$	1.86×10^{-3}
		$(dma)(Ph)CH^+$	1.32×10^{-2}
		$(fur)_2CH^+$	3.66×10^{-4}
		$(fur)(ani)CH^+$	1.09×10^{-4}

Table 4.3. *Continued.*

Nucleofuge	Solvent	Ar_2CH^+	k_1 [s^{-1}]
BzO^-	20W80AN	$(mor)_2CH^+$	4.96×10^{-2}
		$(dpa)_2CH^+$	2.79×10^{-3}
		$(mfa)_2CH^+$	6.06×10^{-2}
		$(dma)(Ph)CH^+$	7.26×10^{-3} [a]
	40W60AN	$(mor)_2CH^+$	1.32×10^{-1}
		$(mfa)_2CH^+$	1.91×10^{-1}
		$(dma)(Ph)CH^+$	2.56×10^{-2} [a]
		$(fur)_2CH^+$	7.98×10^{-4} [a]
		$(fur)(ani)CH^+$	5.81×10^{-4} [a,b]
	20W80A	$(mor)_2CH^+$	2.52×10^{-2}
		$(dpa)_2CH^+$	6.64×10^{-4}
		$(mfa)_2CH^+$	2.35×10^{-2}
	40W60A	$(mor)_2CH^+$	9.40×10^{-2}
		$(mfa)_2CH^+$	1.28×10^{-1} [a]
		$(dma)(Ph)CH^+$	1.84×10^{-2}
		$(fur)_2CH^+$	4.17×10^{-4} [a]
		$(fur)(ani)CH^+$	2.33×10^{-4} [a]
PNB^-	20W80AN	$(fur)_2CH^+$	4.50×10^{-3}
		$(fur)(ani)CH^+$	2.21×10^{-3} [a]
		$(ani)_2CH^+$	4.11×10^{-4}
	40W60AN	$(fur)_2CH^+$	9.95×10^{-3}
		$(fur)(ani)CH^+$	3.39×10^{-3}
		$(ani)_2CH^+$	1.05×10^{-3}
	10W90A	$(fur)_2CH^+$	6.40×10^{-4} [a]
		$(fur)(ani)CH^+$	2.92×10^{-4} [a]
	20W80A	$(fur)_2CH^+$	1.99×10^{-3}
		$(fur)(ani)CH^+$	6.32×10^{-4}
	40W60A	$(fur)_2CH^+$	9.36×10^{-3}

Table 4.3. *Continued.*

Nucleofuge	Solvent	Ar_2CH^+	k_1 [s^{-1}]
PNB^-	40W60A	$(fur)(ani)CH^+$	3.57×10^{-3}
		$(ani)_2CH^+$	1.07×10^{-3}
DNB^-	20W80AN	$(fur)_2CH^+$	4.55×10^{-2}
		$(fur)(ani)CH^+$	1.82×10^{-2}
		$(ani)_2CH^+$	1.80×10^{-2}
	40W60AN	$(fur)_2CH^+$	1.11×10^{-1}
		$(fur)(ani)CH^+$	3.96×10^{-2}
		$(ani)_2CH^+$	1.02×10^{-2}
	10W90A	$(fur)_2CH^+$	1.61×10^{-2}
		$(fur)(ani)CH^+$	5.11×10^{-3} [a]
	20W80A	$(fur)_2CH^+$	3.47×10^{-2}
		$(fur)(ani)CH^+$	1.12×10^{-2}
	40W60A	$(fur)_2CH^+$	9.03×10^{-2}
		$(fur)(ani)CH^+$	3.68×10^{-2}

[a] First-order kinetics only in the first half-life; only 60 % conversion were used for the evaluation, and deviations between single measurements may be up to 10 %. [b] Deviations between single measurements higher than 10 %. [c] Precipitation of $(dpa)_2CHOH$ during the reaction caused a noisy conductance/time correlation.

Figures 4.2 and 4.3 compare the different ionization rate constants (log k_1) of the solvolyses of benzhydryl carboxylates in aqueous solvents. The plots show the internal consistency of the employed methods, as the higher rate constants (for solvolysis of Ar_2CH-OAc log $k_1 > 1$) have been measured by the direct observation of the ionization step by UV-Vis methods,[5,7] whereas the rate constants (log $k_1 < -1$) have been collected by conductivity measurements.

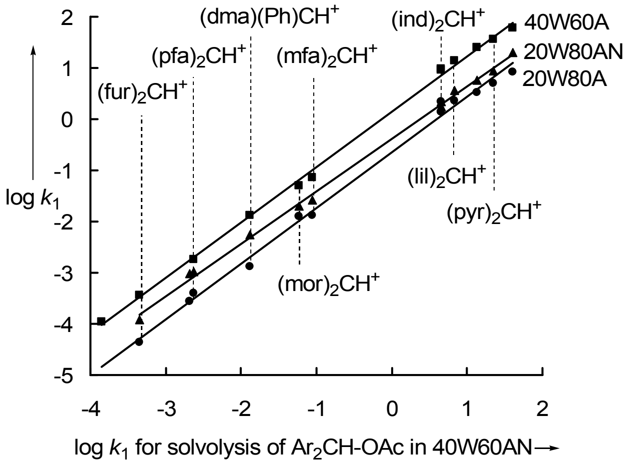


Figure 4.2. Correlation of ionization rate constants of Ar_2CH-OAc in different solvents (given as (v/v); W = water, A = acetone, AN = acetonitrile). Data from Table 2.3 and Table 2.4 in chapter 2.

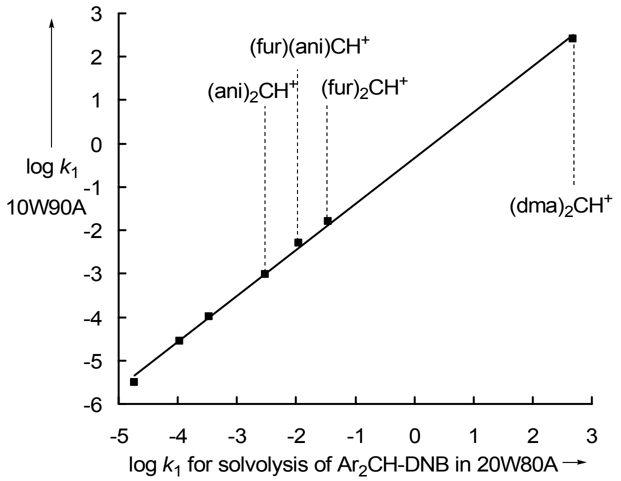


Figure 4.3. Correlation of ionization rate constants of Ar_2CH-DNB in 80 % and 90 % aqueous acetone, including previously determined rate constants (log $k_1 < -3$, log $k_1 > 2$). Data from Table 2.3, Table 2.4 in chapter 2 and Table 1 in ref. [18].

Recent studies have shown that the electrophilic reactivities of benzhydrylium ions toward RCO_2^- increase from $(mor)_2CH^+$ ($E = -5.53$) to $(pfa)_2CH^+$ ($E = -3.14$).[7] Exactly the same order of electrophilicities has previously been observed in reactions of these carbocations with hundreds of other nucleophiles.

However, the relative electrofugalities of benzhydrylium ions, i.e., the ionization rate constants listed in Table 4.3, show a different order. Figures 4.2 and 4.3 show that this order of electrofugality is consistently found for ionizations of various covalent benzhydryl carboxylates in different solvents.

Figure 4.4 shows that log k_1 for the solvolyses of benzhydryl carboxylates increases with Winstein's solvent ionizing power *Y*, which has been derived from *t*-butyl chloride solvolyses.[19] Slopes (*m*) of only 0.40 – 0.50 are found for the ionizations of benzhydryl acetates, benzoates and *p*-nitrobenzoates in aqueous acetone and acetonitrile solutions. This is in line with earlier findings of *m*-values of only 0.35 – 0.54 for the ionization rate constants of benzhydryl carboxylates with better stabilized electrofuges.[7] In contrast, log k_1 for the solvolyses of benzhydryl chlorides in 90% aqueous acetone and 80% aqueous acetone yield an *m*-value of 1.[18] In previous work,[20] we concluded that the rates of the combinations of Ph_2CH^+ and $(p\text{-}MeC_6H_6)_2CH^+$ with Cl^- reflect the diffusion rates, and the transition states correspond to the carbocations. Ionization processes described in this chapter and chapter 2 have transition states which are located between the covalent ester and the ionic species. As the transition states of these ionizations are not longer carbocation-like, small values of *m* ($0.40 \leq m \leq 0.50$) result.

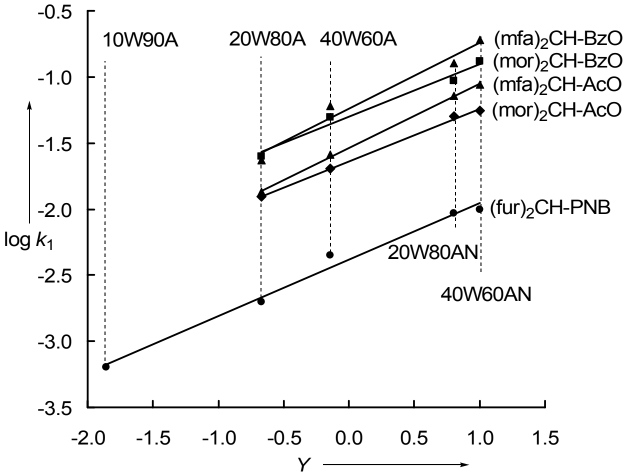


Figure 4.4. Correlation of the rate constants for ionization of some benzhydryl derivatives vs. the solvent ionizing power *Y*.[21] Slopes: (mfa)CH_2–BzO = 0.50, (mor)CH_2–BzO = 0.40, (mfa)CH_2–AcO = 0.49, (mor)CH_2–AcO = 0.40, (fur)CH_2–PNB = 0.43.

Figure 4.5 shows a correlation of the logarithm of ionization rate constants k_1 against the pK_a values of the conjugate carboxylic acid of the nucleofuges in 60 % aqueous acetonitrile. It is apparent (Figure 4.5) that the heterolysis rates increase with decreasing Brønsted basicities of the carboxylate ions.

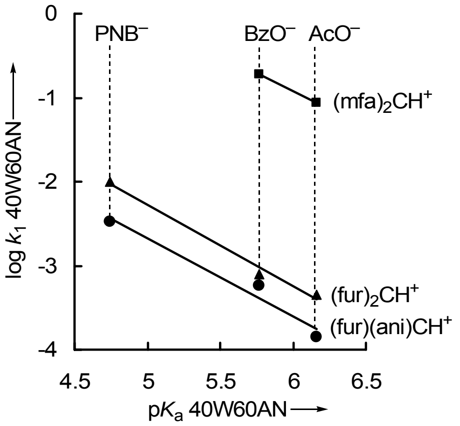


Figure 4.5. Comparison of the ionization rate constants (25 °C) with the pK_a values[22] of the corresponding carboxylic acids in different solvents. pK_a (PNBH) = 4.75; pK_a (BzOH) = 5.77; pK_a (AcOH) = 6.16.

Figure 4.5 compares the affinities of the carboxylate ions AcO^-, BzO^- and PNB^- towards the proton in 60 % aqueous acetonitrile with their leaving group abilities in the same solvent. It is apparent that the *p*-nitrobenzoates, possessing the lowest affinity towards the proton have the best leaving group abilities in 40W60AN. The similarities of the slopes indicate the internal consistency of the ionization constants k_1. However, it should be noted that k_1 of $(fur)_2CH$-BzO and (fur)(ani)CH-BzO may contain errors according to Table 4.3.

Electrofugality. For determining the electrofugality parameters of the stabilized benzhydrylium ions, E_f parameters and solvolysis rate constants of three benzhydryl *p*-nitrobenzoates in 80 % and 90 % aqueous acetone[18] were used to link the ionization rate constants of the benzhydryl carboxylates studied in this work with the previously published data.

The solvolysis rate constants of 14 benzhydryl carboxylates in different solvent systems have been subjected to a least-squares fit according to eq (4.1) by minimizing $\Sigma\Delta^2$, where $\Delta^2 = (\log k_1 - \log k_{1calcd})^2 = (\log k_1 - s_f(N_f + E_f)$, by using the program "What's*Best!* 4.0 Professional" by Lindo Systems. In order to link the new data to published rate constants, N_f and s_f of 3,5-dinitrobenzoate in

10W90A and 20W80A and E_f of the bisanisyl carbenium ion were fixed. The electrofugality parameters now cover a range of approximately 18 orders of magnitude (new E_f parameters listed in Table 4.4). The graphical presentation of some of the linear correlations of log k_1 versus the electrofugality parameter E_f is shown in Figure 4.6, for the sake of clarity only four correlation lines are shown.

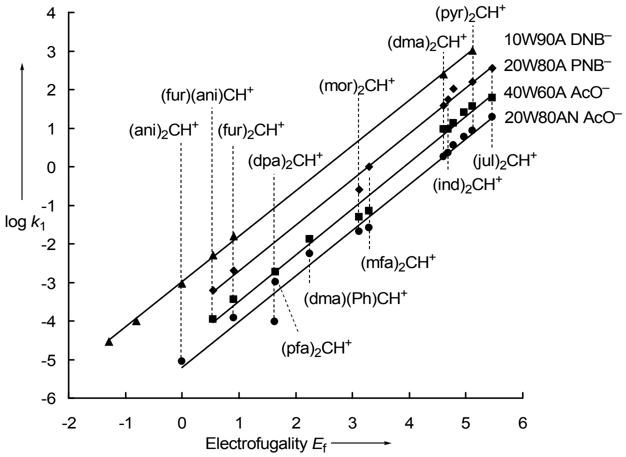
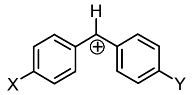
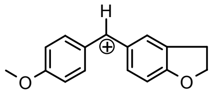
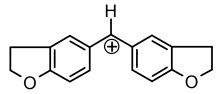
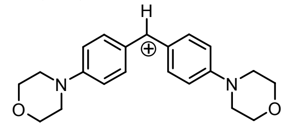
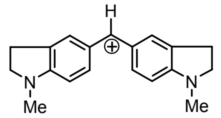
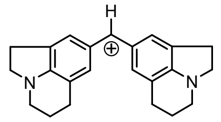
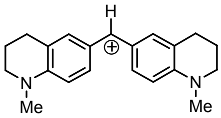
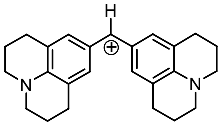


Figure 4.6. Correlation of log k_1 (25 °C) versus the new E_f parameters for highly stabilized benzhydrylium ions.

The resulting E_f parameters for highly stabilized benzhydrylium ions are listed in Table 4.4.

Table 4.4. Electrofugality Parameters (25 °C) of Benzhydrylium Ions in Different Solvents.



Ar_2CH^+	X	Y	E_f
$(ani)_2CH^+$	OCH_3	OCH_3	0^a
$(fur)(ani)CH^+$			0.54
$(fur)_2CH^+$			0.90
$(dpa)_2CH^+$	NPh_2	NPh_2	1.64
$(pfa)_2CH^+$	$N(Ph)CH_2CF_3$	$N(Ph)CH_2CF_3$	1.65
$(dma)(Ph)CH^+$	$N(CH_3)_2$	H	2.24
$(mor)_2CH^+$			3.12
$(mfa)_2CH^+$	$N(CH_3)CH_2CF_3$	$N(CH_3)CH_2CF_3$	3.29
$(dma)_2CH^+$	$N(CH_3)_2$	$N(CH_3)_2$	4.60
$(ind)_2CH^+$			4.68
$(lil)_2CH^+$			4.79
$(thq)_2CH^+$			4.97
$(pyr)_2CH^+$	$N(CH_2)_4$	$N(CH_2)_4$	5.12
$(jul)_2CH^+$			5.46

[a] defined as $E_f = 0$.

A comparison of the electrophilicity parameters E of the benzhydrylium ions (Table 4.1) with the now available electrofugality parameters E_f shows a tremendous aberration from the earlier assumption $E \approx -E_f$.[3] For $E < 0$, this assumption collapses, and the electrofugalities reach a plateau at $E < -7$ (Figure 4.7). It is not yet clear, why a decrease of carbocation reactivity towards nucleophiles is not reflected by an increase of the corresponding carbocation electrofugality. In contrast to earlier assumptions,[23] it cannot generally be assumed that the rates of S_N1 solvolyses always reflect the carbocation stabilities. As pointed out in chapter 2, intrinsic barriers for the heterolyses of benzhydryl carboxylates with the annulated five-membered rings ($(ind)_2CH$-OCOR and $(lil)_2CH$-

OCOR) are significantly higher (≈ 2 kJ mol^{-1}) than their six-membered ring analogues ((thq)$_2$CH-OCOR and (jul)$_2$CH-OCOR). It is obvious that these differences are reflected in the electrofugality parameter E_f and cause the breakdown of the E_f vs. E correlation.

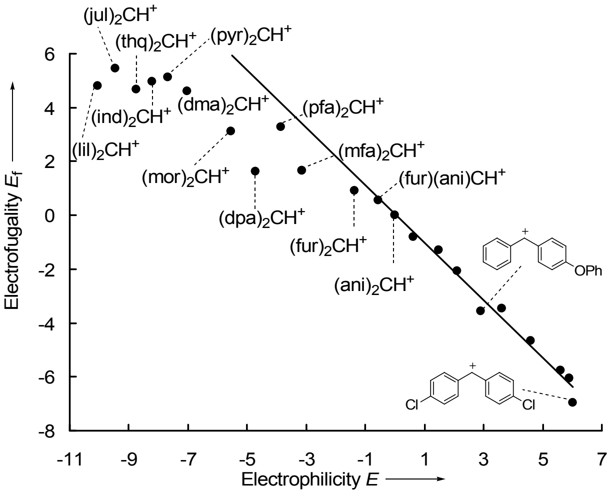


Figure 4.7. Comparison of E and E_f values of several benzhydrylium ions.

The overlap between the different reaction series of benzhydryl halides and benzhydryl carboxylates is very small, i.e., the benzhydryl chlorides and the benzhydryl carboxylates have only three electrofuges in common in only a few solvent systems. This indicates that errors in the solvolysis rates of these systems propagate to the electrofugality parameters E_f of the highly stabilized benzhydrylium ions. If only solvolyses of benzhydryl **chlorides** in non-aqueous and aqueous solvents are employed to estimate E_f parameters for (fur)$_2$CH$^+$and (fur)(ani)CH$^+$,[24] the resulting E_f parameters are somewhat higher (ΔE_f≈ 0.3 – 0.5) than the ones derived in this chapter.

Table 4.5. Comparison of the Ionization Rate Constants k_1 of the Benzhydryl Chlorides and Benzhydryl Carboxylates in Different Solvents.

ratio log k_1	nucleofuge / solvent		
	Cl^- / AN[a]	Cl^- / 10W90A[a]	DNB^- / 20W80A
(fur)$_2$CH$^+$ / (fur)(ani)CH$^+$	5.4	4.2	2.5
(fur)(ani)CH$^+$ / (ani)$_2$CH$^+$	7.2	6.2	3.7

[a] Data taken from ref. 24.

This is due to the differences in relative ionization rates of the benzhydryl chlorides and benzhydryl carboxylates (Table 4.5). The ratio of k_1 of benzhydryl carboxylates in aqueous solvents is significantly smaller than the one of the benzhydryl chlorides, resulting in higher E_f parameters if benzhydryl carboxylates are employed for the derivation. What is the reason for this deviation?

It can be assumed, that the breakdown of the linear correlation is due to a significant change of the transition states of the heterolyses. As E_f values < 0 have been determined by employing heterolyses of benzhydryl derivatives with good nucleofuges as halides and the data of this and the preceding chapter have been derived from solvolyses of benzhydryl carboxylates, the problems may be due to the different transition states, which have been calculated from the combination reactions of the benzhydrylium ions with the leaving groups. Figure 4.8 shows that they can be either diffusion-controlled (in the case of non-aqueous solvents), or have a significant barrier $\Delta G^{\neq}$, as in the case of aqueous solvents.

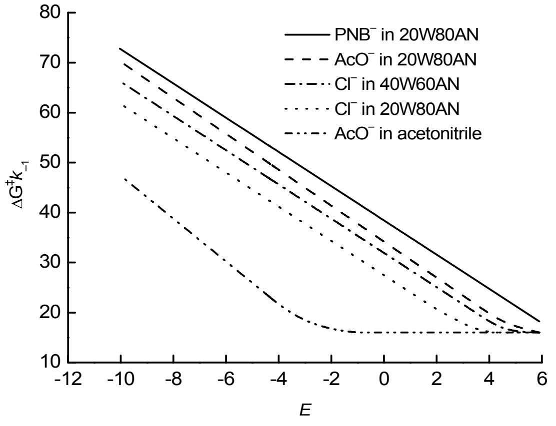


Figure 4.8. Activation Free Enthalpies $\Delta G^{\neq}$ for the combination reactions of benzhydrylium ions with the leaving groups at 25 °C, versus the E parameters of the benzhydrylium ions.

As Figure 4.8 shows for the combination of acetate with benzhydrylium ions in acetonitrile, the reaction is diffusion-controlled for $E > -2$, unlike in aqueous solvents. As chloride is more nucleophilic, we expect the combination for benzhydrylium ions with $E > -2$ with the chloride ion in nonprotic solvents also to be diffusion controlled. The benzhydrylium ions $(\text{fur})_2\text{CH}^+$ and $(\text{fur})(\text{ani})\text{CH}^+$ are located in the region of electrophilic reactivity ($-2 < E < 0$), where the solvolysis rates of this chapter are linked with the previously published ones. So for the heterolyses of benzhydryl chlorides in non-aqueous solvents like acetonitrile, the ion recombination is diffusion controlled in contrast to the recombination in aqueous solvents. The change from a carbocation-like transition state for the solvolyses of benzhydryl chlorides to a transition state between covalent substrate and ions might be the reason for the differences of the E_f parameters derived from the different data sets.

A qualitative rationalization for the deviating E_f values for $(fur)_2CH^+$and $(fur)(ani)CH^+$ might be the different charge distribution in the transition states of the heterolyses of benzhydryl chlorides and benzhydryl carboxylates, where the negative charge is distributed over two (oxygen) atoms instead of only one as in the case of the chlorides. When solvolysis rate constants of benzhydryl carbonates, where the negative charge is distributed over three oxygen atoms are employed,[24] E_f parameters (and ratios $(fur)_2CH\text{-}OCO_2R$ / k_1 (fur)(ani)CH- OCO_2R) are similar to those determined by benzhydryl carboxylates in this chapter.

It has been shown (open points in Figure 4.9), that the methyl anion affinities (ΔG_{298}) of benzhydrylium ions calculated at the B3LYP/6-31G(d,p) correlate very well with the earlier determined E_f parameters ($E_f \leq 0$).[25,26]

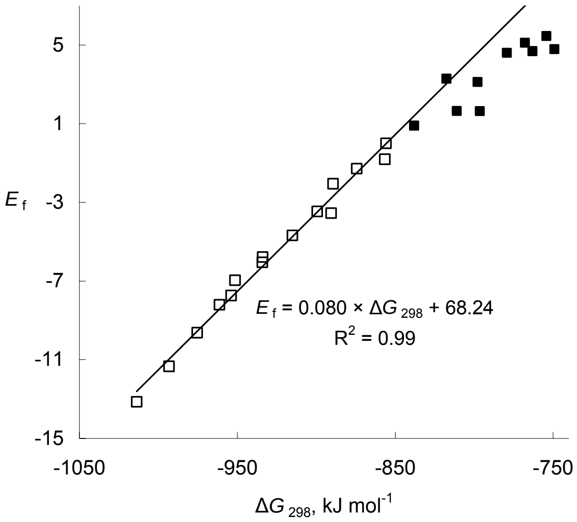


Figure 4.9. Comparison of the methyl anion affinity (ΔG_{298}, kJ mol^{-1})[26] and E_f values of several benzhydrylium ions (□ earlier determined E_f values,[18] ■ this work).

The correlation line gets flatter in the region of $E_f > -3.5$ and it is obvious that ΔG_{298} and E_f only roughly correlate in this range.

This deviation is not surprising, as it has earlier been shown that ΔG_{298} correlates linearly with the electrophilicity for benzhydrylium systems with $E < 0$.[26] Because Figure 4.7 showed that E and E_f correlate only poorly in the range $-10 < E < 0$, a linear correlation of ΔG_{298} and E_f could also not be anticipated in this range.

The same would hold for a correlation of the E_f parameters of the highly stabilized benzhydrylium ions with the recently determined Hammett σ^+ values for different amino groups.[8] These σ^+ values have been established from a correlation with the electrophilicity parameters E of the corresponding benzhydrylium ions and therefore do not linearly correlate with the electrofugality.

Nucleofugality. Nucleofugality parameters N_f and their slope parameters s_f of four carboxylates resulting from the least squares fit are given in Table 4.6.

Table 4.6. Nucleofugality Parameters (N_f/s_f, 25 °C) of Carboxylate Ions in Different Solvents.[a]

Solvent	AcO^-	BzO^-	PNB^-	DNB^-
10W90A	–4.84/0.62[b]	–	–3.30/1.05	–2.57/1.18[c]
20W80A	–4.57/1.19	–4.09/0.96	–3.22/1.18	–2.23/1.13[c]
40W60A	–3.75/1.18	–3.75/1.20	–2.64/1.15	–1.88/1.08
20W80AN	–4.37/1.16	–3.92/1.22	–2.88/1.17	–2.13/1.10
40W60AN	–4.02/1.11	–3.65/1.11	–3.53/0.92	–1.35/1.29

[a] Ionization rates taken from Table 2.4 / chapter 2, Figures 3.1–3.4 / chapter 3 and Table 4.3 / this chapter. [b] Unusual small s_f-parameter due to deviations among the series of ionization rates. [c] As defined in ref [18].

Although there are some deviations among the s_f parameters even within a series of a certain leaving group, a plot of the N_f values of *p*-nitrobenzoate ions and acetate ions against the solvent ionizing power *Y* (Figure 4.10) shows fair correlations. The nucleofugality of the leaving group in a certain solvent mixture rises with the ionizing power of the solvent mixture, whereas the *p*-nitrobenzoate ion is less sensitive against the change of the solvent than the acetate ion. The different slopes may be attributed to the different demand of solvation of the anions. The better the charge is delocalized, the flatter the slope is. Similar results have been found by Bentley and Roberts for 1-adamantyl derivatives.[27]

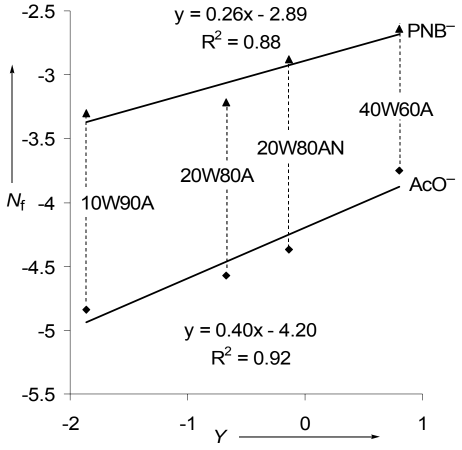


Figure 4.10. Correlation of nucleofuge specific parameters N_f for AcO^- and PNB^- against the ionizing power of the solvent Y[21].

Compared to the recently published nucleofuge-specific parameters for carbonates, e.g. $N_f = 2.19$ and $s_f = 0.96$ for the phenyl carbonate in 20W80A,[28] it is obvious that the carbonates, (which play an important role as protecting groups), are better leaving groups than the carboxylates (slightly better than the 3,5-dinitrobenzoate), but poorer nucleofuges than the halides.

The knowledge of the E_f parameters of highly stabilized benzhydrylium ions now allows us to derive new nucleofugality parameters of interesting nucleofuges, which have been investigated earlier.[29,30] Correlations of the rate constants k_1 with the newly determined E_f parameters of benzhydrylium ions show that the reactions generally follow eq (4.1) (see Experimental Section, exemplarily depicted in Figure 4.11).

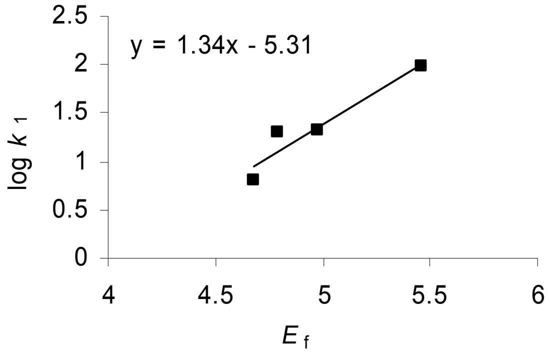


Figure 4.11. Correlation of log k_1 (20 °C) for the ionization of benzhydryl azides in 91 % methanol / 9 % acetonitrile versus the E_f parameters for highly stabilized benzhydrylium ions.[30]

From the correlations one can derive N_f and s_f parameters for several leaving groups in different solvents. The correlations are sometimes of poor quality, but nevertheless they allow a rough estimate of the nucleofuge-specific parameters. Nucleofugality parameters N_f and s_f of some anions are listed in Table 4.7.

Table 4.7. Nucleofugality Parameters (N_f/s_f, 20 °C) of Common Leaving Groups in Different Solvents.

Nucleofuge	CH_3CN	CH_2Cl_2	91E9AN	91M9AN
DMAP	–6.12/0.98	–	–	–
DABCO	3.21/0.52	–	–	–
$P(4\text{-}OMeC_6H_4)_3$	–	–6.00/0.64	–	–
$P(4\text{-}MeC_6H_4)_3$	–	–4.90/0.60	–	–
NO_2^-	–3.59/1.01	–	–	–
N_3^-	–	–	–4.30/1.19	–3.96/1.34

It is now possible to decide on the basis of the nucleofugality scale and by eq (4.1), whether substrates R-X (X = NO_2^-, N_3^-) with anionic leaving groups tolerate certain conditions of workup like column chromatography, recrystallization, or synthetic conversion in given solvents. Furthermore it is possible to qualitatively define neutral leaving groups as DMAP, DABCO or phosphanes, which play an important role in organocatalysis. For organocatalytic reactions the leaving group abilities are essential and the new nucleofugality parameters can help to design effective reactions.

By neglecting the slope parameter one can compare the leaving groups in different solvents qualitatively (Figure 4.12). Note that N_f provides only a rough guide to the relative nucleofuge reactivities of the leaving groups. The small differences in s_f lead to the relative nucleofuge reactivities that are slightly dependent on the nature of the electrofugic reaction partner.

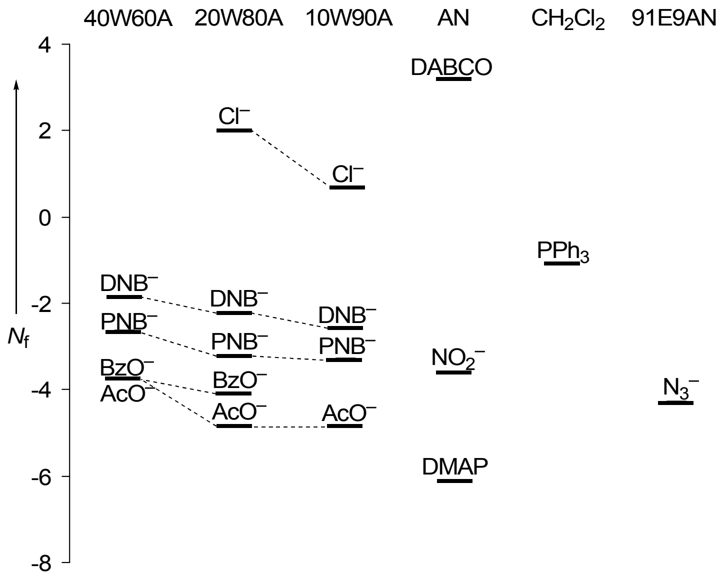


Figure 4.12. Nucleofuge specific parameters N_f for some typical leaving groups.

Figure 4.12 shows, how these leaving groups can be integrated in the nucleofugality scale. For example, it is now possible to quantify the leaving group ability of NO_2^-, which has a comparable nucleofugality in acetonitrile as acetate and benzoate in 60 % aqueous acetone. DMAP in acetonitrile is the poorest leaving group discussed in this work, whereas DABCO in acetonitrile is the best. It is surprising that acetate and benzoate have almost the same N_f parameter in 40W60A, so the differences in solvolysis rates for benzhydryl acetates and –benzoates in 60 % aqueous acetone are only reflected by s_f. However, in acetonitrile/water mixtures and acetone/water mixtures with a higher fraction of acetone, the difference in N_f is ~0.5 units. That means that with a rising amount of water in the solvent, the differences in nucleofugality between acetate and benzoate become less pronounced, which might be due to the good solvatic assistance of the solvent and, therefore, the structural differences of the leaving group play only a minor role.

Conclusion The extension of the electrofugality scale towards highly stabilized benzhydrylium ions has been achieved. As anticipated earlier,[7] electrophilicity E and electrofugality E_f of the benzhydrylium ions are not exclusively reflected by an inverse relationship, so $E \approx -E_f$ does only hold for carbocations which are less stabilized than $(ani)_2CH^+$. Formerly, the rates of solvolysis have been obtained under very different conditions of temperature and solvent, and only extrapolations allowed a moderate comparison with low accuracy. Now, nucleofugality parameters of carboxylates and other anionic and neutral leaving groups have been derived and allow a better comparison.

References

(1) Lepore, S. D.; Mondal, D. *Tetrahedron* **2007**, *63*, 5103-5122.

(2) a) Ayers, P. W.; Anderson, J. S. M.; Rodriguez, J. I.; Jawed, Z. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1918-1925. b) Jaramillo, P.; Domingo, L. R.; Perez, P. *Chem.Phys.Lett.* **2006**, *420*, 95-99. c) Campodonico, P. R.; Aizman, A.; Contreras, R. *Chem. Phys. Lett.* **2006**, *422*, 340-344. d) Bentley, T. W. *Chem. Eur. J.* **2006**, *12*, 6514-6520. e) Campodonico, P. R.; Perez, C.; Aliaga, M.; Gazitua, M.; Contreras, R. *Chem. Phys. Lett.* **2007**, *447*, 375-378.

(3) Denegri, B.; Minegishi, S.; Kronja, O.; Mayr, H. *Angew. Chem.* **2004**, *116*, 2353-2356; *Angew. Chem. Int. Ed.* **2004**, *43*, 2302-2305.

(4) Gelles, E.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1954**, 2918-2929.

(5) Schaller, H. F.; Mayr, H. *Angew. Chem.* **2008**, *120*, 4022-4025; *Angew. Chem. Int. Ed.* **2008**, *47*, 3958-3961.

(6) Streidl, N.; Antipova, A.; Mayr, H., *unpublished results*.

(7) Schaller, H. F.; Tishkov, A. A.; Feng, X.; Mayr, H. *J. Am. Chem. Soc.* **2008**, *130*, 3012-3022.

(8) 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.

(9) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Heck, R.; Robinson, G. C. *J. Am. Chem. Soc.* **1956**, *78*, 328-335.

(10) Winstein, S.; Appel, B.; Baker, R.; Diaz, A. *Chem. Soc. Spec. Publ.* **1965**, *19*, 109-130.

(11) a) Bateman, L. C.; Church, M. G.; Hughes, E. D.; Ingold, C. K.; Taher, N. A. *J. Chem. Soc.* **1940**, 979-1011. b) Bailey, T. H.; Fox, J. R.; Jackson, E.; Kohnstam, G.; Queen, A. *Chem. Commun.* **1966**, *No. 5*, 122-123. c) Ingold, C. K. *Structure and Mechanism in Organic Chemistry, 2nd ed*, Cornell Univ. Press, Ithaca, NY, **1969**.

(12) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. *Ions and Ion Pairs in Organic Reactions*, Vol. 2, Szwarc, M. Ed.; Wiley: New York, 1974. b) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979. c) *Reactive Intermediates, Vol. 3*, 1983 Rappoport, Z. *Reactive Intermediates,* Vol. 3; Abramovitch, R. A., Ed.; Plenum: New York, 1983, p. 427. d) Kitamura, T.; Taniguchi, H.; Tsuno Y.; in *Dicoordinated Carbocations* Stang, P. J.; Rappoport Z., Eds.; Wiley: Chichester, 1997, p. 321.

(13) a) Goering, H. L.; Levy, J. F. *Tetrahedron Lett.* **1961**, 644-647. b) Goering, H. L.; Levy, J. F. *J. Am. Chem. Soc.* **1962**, *84*, 3853-7.

(14) Goering, H. L.; Briody, R. G.; Levy, J. F. *Journal of the American Chemical Society* **1963**, *85*, 3059-3061.

(15) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174-5181.

(16) Queen, A. *Can. J. Chem.* **1979**, *57*, 2646-2651.

(17) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918-6928.

(18) 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..

(19) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770-2777.

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

(21) a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846-854. b) Bentley, T. W.; Dau-Schmidt, J. P.; Llewellyn, G.; Mayr, H. *J. Org. Chem.* **1992**, *57*, 2387-2392. c) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1984**, *49*, 3639-3941. d) Robertson, R. E.; Sugamori, S. E. *Can. J. Chem.* **1972**, *50*, 1353-1360.

(22) a) Niazi, M. S. K.; Ali, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3619-3624 b) Espinosa, S.; Bosch, E.; Roses, M. *Anal. Chem.* **2002**, *74*, 3809-3818.

(23) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522-526.

(24) Streidl, N.; Mayr, H. *unpublished results*.

(25) Streiter, A. *Thesis,* LMU München, **2006**.

(26) Singer, T. *Thesis,* LMU München, **2008**.

(27) Bentley, T. W.; Roberts, K. *J. Chem. Soc. Perkin Trans. II* **1989**, 1055-1060.

(28) Denegri, B.; Kronja, O. *J. Org. Chem.* **2007**, *72*, 8427-8433.

(29) a) Brotzel, F.; Kempf, B.; Singer, T.; Zipse, H.; Mayr, H. *Chem. Eur. J.* **2006**, *13*, 336-345. b) Tishkov, A. A.; Schmidhammer, U.; Roth, S.; Riedle, E.; Mayr, H. *Angew. Chem.* **2005**, *117*, 4699-4703; *Angew. Chem. Int. Ed.* **2005**, *44*, 4623-4626. c) Kempf, B.; Mayr, H. *Chem. Eur. J.* **2005**, *11*, 917-927.

(30) Phan, T. B.; Mayr, H. *J. Phys. Org. Chem.* **2006**, *19*, 706-713.

–Experimental Section–

Nucleofugality of Common Leaving Groups in Solvolysis Reactions: An Extension of the Nucleofugality Scale

General

Materials. Commercially available acetonitrile and water (HPLC-gradient grade, VWR) and acetone (extra dry, Acros) were used without further purification for all experiments.

Mixtures of solvents are given as (v/v) and the solvents are abbreviated: A = acetone, AN = acetonitrile, W = water. For example, the solvent mixture 20W80AN refers to a mixture of water and acetonitrile in a ratio of 20/80 (v/v).

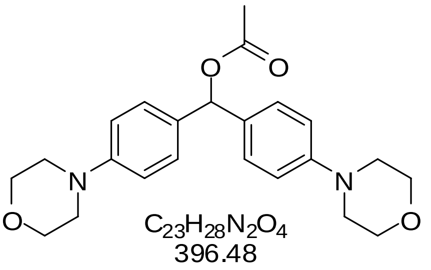
Triethylamine was distilled, N,N,N’,N’-tetramethyl-1,8-naphthalene-diamine (proton sponge, ≥ 99 %, Fluka), quinuclidine (≥ 97 %, Fluka), and 4-(dimethylamino)pyridine (DMAP, > 99 %, Aldrich) were used without further purification.

Spectroscopy. ^{1}H and ^{13}C NMR chemical shifts are expressed in ppm and refer to $CDCl_3$: $\delta_H = 7.26$, $\delta_C = 77.2$.

General Procedure for the Synthesis of Benzhydryl Acetates. A mixture of the substituted benzhydrol (1.0 mmol), DMAP (0.1 equiv, 12 mg, 0.10 mmol), and freshly distilled triethylamine (1.2 equiv, 101 mg, 1.0 mmol) in dry benzene (5 mL) was stirred for 5 min under nitrogen atmosphere before acetic anhydride (1 equiv) was added. Stirring was continued for 8 h at room temperature. Pentane (5 mL) was added, and the reaction mixture was washed quickly with 0.2 M hydrochloric acid (10 mL), saturated aq. $NaHCO_3$ (10 mL), and water. The organic phase was dried ($MgSO_4$) and filtered. Then the solvent was evaporated in vacuo (T < 30 °C). The residue was crystallized from diethyl ether/pentane to give the benzhydryl acetate as a colorless powder.

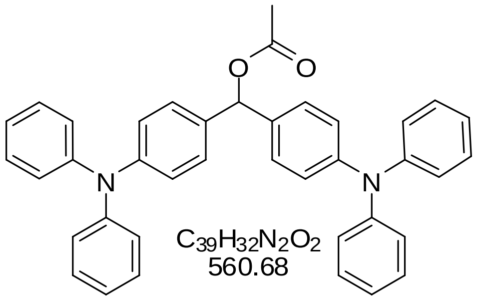
4,4'-Bis(morpholino)benzhydryl acetate was synthesized from 354 mg (1.0 mmol) 4,4'-bis(morpholino)benzhydrol and 102 mg (1.0 mmol) acetic anhydride (yield 65 %, 258 mg).

^{1}H NMR (200 MHz, C_6D_6): δ= 1.73 (s, 3 H, CH_3), 2.65 (t, 8 H, *J* = 3.5 Hz, NCH_2), 3.46 (t, 8 H, *J* = 3.5 Hz, OCH_2), 6.63 (d, 4 H, *J* = 8.7 Hz, ArH), 7.21 (s, 1 H, Ar_2CH), 7.38 ppm (d, 4 H, *J* = 8.7 Hz, ArH); ^{13}C NMR (75.5 MHz, C_6D_6): δ= 21.3 (q, CH_3), 49.6 (t, NCH_2), 67.2 (t, OCH_2), 77.2 (d, Ar_2CH), 116.1 (d, Ar), 129.1 (d, Ar), 132.9 (s, Ar), 151.7 (s, Ar), 169.9 ppm (s, CO_2).



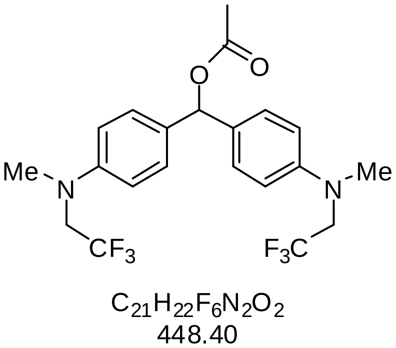
4,4'-Bis(diphenylamino)benzhydryl acetate was synthesized from 517 mg (1.0 mmol) 4,4'- (*p*-diphenyl-amino)methanol and 102 mg (1.0 mmol) acetic anhydride (yield 58 %, 325 mg).

^{1}H NMR (600 MHz, C_6D_6): δ = 1.68 (s, 3 H, CH_3), 6.82 (s, 1 H, Ar_2CH), 6.84-7.26 (m, 28 H, ArH); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 21.1, 77.0, 123.6, 124.3, 125.2, 130.0, 135,5, 148.4, 148.6, 170,2. MS (DEP/EI): *m/z* (%): 558 (16) $[M]^+$, 503 (12), 502 (50), 501 (100) $[M\text{-}CH_3COO]^+$.

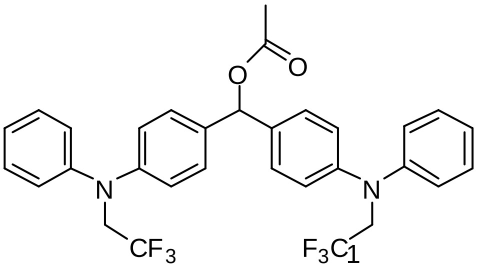


4,4'-Bis (4-methyl(2,2,2-trifluoroethyl)amino) benzhydryl acetate was synthesized from 406 mg (1.0 mmol) 4,4'-Bis (4-methyl(2,2,2-trifluoroethyl)amino) benzhydrol and 102 mg (1.0 mmol) acetic anhydride (yield 55 %, 246 mg).

^{1}H NMR (600 MHz, C_6D_6): δ = 1.88 (s, 3 H, CO_2CH_3), 2.54 (s, 6 H, NCH_3), 3.28 (q, 4 H, NCH_2), 6.62 (d , 4 H, J = 3.42, ArH), 7.28 (s, 1 H, Ar_2CH), 7.42 (d, 4 H, *J* = 3.42, ArH); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 21.3, 39.1, 54.2, 77.0, 113.2, 126.6, 129.2, 148.7, 169.9. MS (DEP/EI): *m/z* (%): 448 (11) $[M]^+$, 390 (32), 389 (100) $[M\text{-}CH_3COO]^+$, 388 (14), 321 (16), 305 (19).



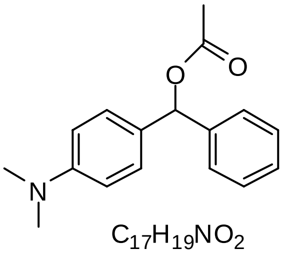
4,4'-Bis (4-phenyl-(2,2,2-trifluoroethyl)amino) benzhydryl acetate was synthesized from 530 mg (1.0 mmol) 4,4'-Bis (4-phenyl-(2,2,2-trifluoroethyl)amino) benzhydrol and 102 mg (1.0 mmol) acetic anhydride (yield 59 %, 338 mg).



$C_{31}H_{26}F_6N_2O_2$
572.54

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 4.27 (q, 4 H, NCH_2), 6.80 (s, 1 H, Ar_2CH), 6.86 – 7.35 (m, 18 H, ArH); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 21.2, 53.7, 75.6, 111.6, 114.2, 114.9, 120.3, 127.7, 128.5, 129.7, 151.3, 153.2, 169.6.

4-Dimethylamino benzhydryl acetate was synthesized from 211 mg (1.0 mmol) *4-dimethylamino benzhydrol* and 102 mg (1.0 mmol) acetic anhydride (yield 65 %, 175 mg).

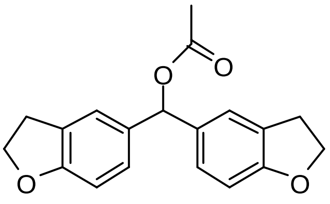


$C_{17}H_{19}NO_2$
269.34

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3 H, CO_2CH_3), 2.85 (s, 6 H, NCH_3), 6.58 (d, 2 H, J = 3.40, ArH), 6.76 (s, 1 H, Ar_2CH), 7.12 (d, 2 H, J = 3.40, ArH), 7.14-7.25 (m, 5 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.8, 40.8, 112.6, 127.1, 127.9, 128.3, 128.7, 141.2, 150.7, 170.6.

MS (DEP/EI): m/z (%): 269 (21) $[M]^+$, 211 (31), 210 (100) $[M-CH_3COO]^+$, 209 (16), 194 (15), 166 (12), 165 (29). EA calcd. (%) $C_{17}H_{19}O_2N$ (269.34): C 75.81, H 7.11, N 5.20; found C 75.22, H 7.22, N 5.07.

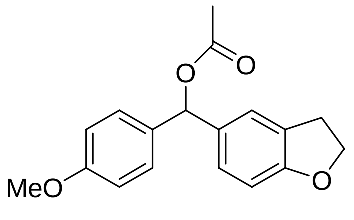
Bis (2,3-dihydrobenzofuran-5-yl)methyl acetate was synthesized from 268 mg (1.0 mmol) Bis-(2,3-dihydrobenzofuran-5-yl)methanol and 102 mg (1.0 mmol) acetic anhydride (yield 91 %, 282 mg).



$C_{19}H_{18}O_4$
310.34

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 3.18 (t, 4 H, J = 8.70,CH_2CH_2O), 4.55 (t, 4 H, J = 8.69, CH_2CH_2O), 6.71 (s, 3 H, Ar_2CH), 6.75 (s, 2 H,ArH), 7.06 – 7.15 (m, 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.8, 30.1, 71.8, 79.8, 109.4, 124.3, 127.7, 128.7, 133.2, 160.2, 170.6. MS (DEP/EI): m/z (%): 310 (12) $[M]^+$, 252 (26), 251 (100) $[M-CH_3COO]^+$, 250 (42), 249 (10).

(2,3-dihydrobenzofuran-5-yl)(4-methoxyphenyl)methyl acetate was synthesized from 256 mg (1.0 mmol) (2,3-dihydrobenzofuran-5-yl)-(4-methoxyphenyl)methanol and 102 mg (1.0 mmol) acetic anhydride (yield 82 %, 245 mg).

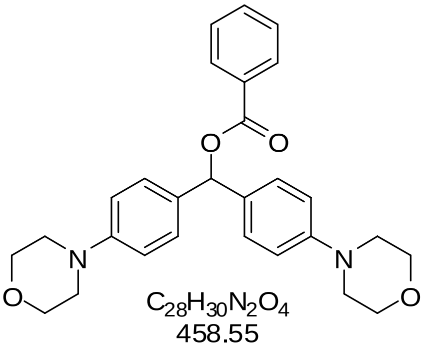


$C_{17}H_{15}O_3$
298.33

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.13$ (s, 3 H, CH_3), 3.17 (t, 2 H, $J = 8.67$, C*H*$_2$CH$_2$O), 3.79 (s, 3 H, OCH_3), 4.56 (t, 2 H, $J = 8.66$, CH$_2$C*H*$_2$O), 6.71 – 6.89 (m, 4 H, ArH, Ar$_2$C*H*), 7.06-7.36 (m, 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 21.1$, 29.0, 55.1, 70.8, 78.2, 111.3, 114.8, 120.8, 128.7, 128.9, 129.7, 133.7, 159.6, 169.7. MS (DEP/EI): *m/z* (%): 298 (27) $[M]^+$, 240 (18), 239 (199) $[M-CH_3COO]^+$, 238 (82), 223 (23).

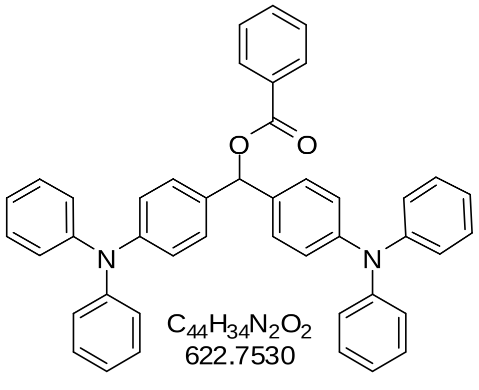
General Procedure for the Synthesis of Benzhydryl Benzoates. A mixture of the substituted benzhydrol (1.0 mmol), DMAP (0.1 equiv, 12 mg, 0.10 mmol), and freshly distilled triethylamine (1.2 equiv, 101 mg, 1.0 mmol) in dry benzene (5 mL) was stirred for 5 min under nitrogen atmosphere before benzoic anhydride (1 equiv) was added stepwise. Stirring was continued for 10 h at room temperature. Pentane (5 mL) was added, and the reaction mixture was washed quickly with 0.2 M hydrochloric acid (10 mL), saturated aq. $NaHCO_3$ (10 mL), and water. The organic phase was dried ($MgSO_4$) and filtered. Then the solvent was evaporated in vacuo (T < 30 °C). The residue was crystallized from diethyl ether/pentane to give the benzhydryl benzoate as a colorless powder.

4,4'-Bis(morpholino)benzhydryl benzoate was synthesized from 354 mg (1.0 mmol) 4,4'-bis(morpholino)benzhydrol and 226 mg (1.0 mmol) benzoic anhydride (yield 44 %, 202 mg).



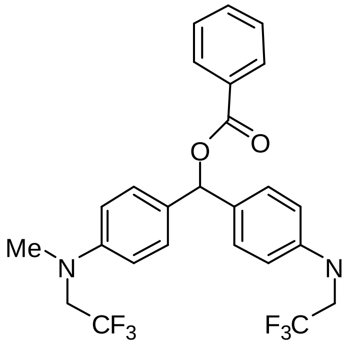
^{1}H NMR (600 MHz, C_6D_6): $\delta = 3.04$ (t, 8 H, $J = 3.46$, NCH_2), 3.74 (t, 8 H, $J = 3.46$, OCH_2), 6.72 – 6.78 (m, 4 H, ArH), 6.93 (s, 1 H, Ar$_2$C*H*), 7.21 - 7.23 (m, 2 H, ArH), 7.31 – 7.35 (m, 3 H, ArH), 8.00 – 8.05 (m, 2 H,); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta =$ 48.9, 66.6, 77.2, 115.1, 129.5, 130.3, 132.7, 133.3, 134.3, 150.5, 165.5.

4,4'-Bis(diphenylamino)benzhydryl benzoate was synthesized from 517 mg (1.0 mmol) 4,4'-bis(diphenylamino)benzhydrol and 226 mg (1.0 mmol) benzoic anhydride (yield 74 %, 463 mg).



^{1}H NMR (200 MHz, C_6D_6): $\delta =$ 6.82 (m, 4 H, Ar$_2$C*H*, ArH), 7.14 – 7.25 (m, 22 H, AH), 7.30 – 7.31 (m, 2 H, ArH), 7.41-7.45 (m, 4 H, ArH), 8.33 – 8.35 (m, 2 H, ArH); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 77.3$, 123.2, 123.7, 124.8, 128.5, 129.6, 130.1, 147.9, 148.1, 165.4.

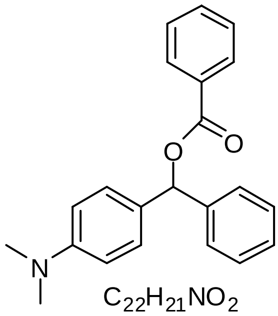
4,4'-Bis (4-methyl(2,2,2-trifluoroethyl)amino) benzhydryl benzoate was synthesized from 406 mg (1.0 mmol) 4,4'-bis (4-methyl(2,2,2-trifluoroethyl)amino) benzhydrol and 226 mg (1.0 mmol) benzoic anhydride (yield 48 %, 246 mg).



$C_{26}H_{24}F_6N_2O_2$
510.47

^{1}H NMR (400 MHz, C_6D_6): δ = 2.34 (s, 6 H, CH_3), 3.10 (q, 4 H, NCH_2), 6.43 (d, 4 H, ArH), 6.89 – 7.06 (m, 4 H, ArH), 7.30 (d, 4 H, ArH), 7.35 (s, 1 H, Ar_2C*H*), 8.02 – 8.23 (m, 2 H, ArH); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 38.7, 53.8, 77.5 (Ar_2CH), 112.9, 121.9, 124.7, 128.6, 128.8, 130.0, 131.0,131.4, 132.9, 148.4, 165.7.

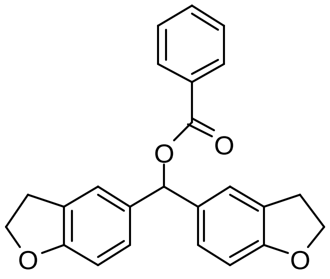
4-Dimethylamino benzhydryl benzoate was synthesized from 211 mg (1.0 mmol) 4-dimethylamino benzhydrol and 226 mg (1.0 mmol) benzoic anhydride (yield 70 %, 232 mg).



$C_{22}H_{21}NO_2$
331.41

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (s, 6 H, NCH_3), 6.71 (d, 2 H, *J* = 3.40, ArH), 7.10 (s, 1 H, Ar_2C*H*), 7.29 – 7.57 (m, 10 H, ArH), 8.15 (d, 2 H, *J* = 3.40, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.8, 77.8, 112.6, 127.2, 127.9, 128.8, 129.1, 129.3, 130.2, 131.0, 132.3, 141.3, 150.7, 166.1. MS (DEP/EI): *m/z* (%): 331 (34) $[M]^+$, 211 (16), 210 (100) $[M\text{-}PhCOO]^+$, 209 (36), 165 (14). EA calcd. (%) $C_{20}H_{21}O_2N$ (331.16): C 79.73, H 6.39, N 4.23; found C 79.39, H 6.23, N 4.05.

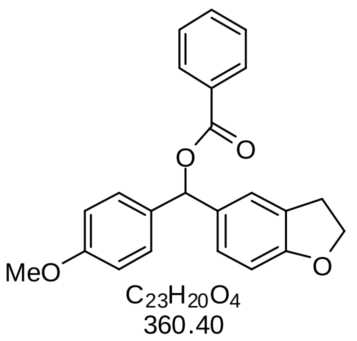
Bis (2,3-dihydrobenzofuran-5-yl)methylbenzoate was synthesized from 268 mg (1.0 mmol) bis-(2,3-dihydrobenzofuran-5-yl)methanol and 226 mg (1.0 mmol) benzoic anhydride (yield 91 %, 340 mg).



$C_{24}H_{20}O_4$
372.41

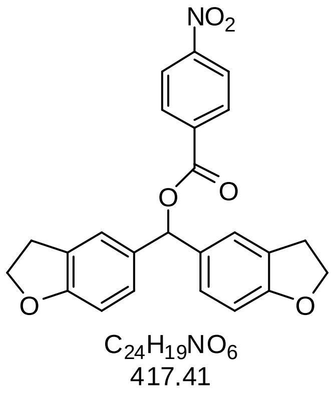
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.19 (t, 4 H, *J* = 8.60, C*H*$_2$CH$_2$O), 4.56 (t, 4 H, *J* = 8.58, CH$_2$C*H*$_2$O), 6.74 (m, 2 H, ArH), 7.01 (s, 1 H, Ar_2C*H*), 7.12 – 7.25 (m, 4 H, ArH), 7.36 – 7.53 (m, 4 H, ArH), 8.10 – 8.15 (m, 2 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.1, 71.7, 79.8, 109.5, 124.2, 127.6, 128.9, 130.2, 130.6, 133.4, 135.5, 159.9, 160.2, 166.1. EA calcd. (%) $C_{24}H_{20}O_4$ (404.42): C 77.40, H 5.41; found C 75.41 H 6.41.

(2,3-dihydrobenzofuran-5-yl)(4-methoxyphenyl)methyl benzoate was synthesized from 256 mg (1.0 mmol) (2,3-dihydrobenzofuran-5-yl)(4-methoxyphenyl)methanol and 226 mg (1.0 mmol) benzoic anhydride (yield 78 %, 281 mg).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.01 (t, 2 H, J = 8.59, C*H*$_2$CH$_2$O), 3.71 (s, 3 H, CH$_3$), 4.45 (t, 2 H, J = 8.61, CH$_2$C*H*$_2$O), 6.79 – 6.82 (m, 2 H, ArH), 6.96 (s, 1 H, Ar$_2$C*H*), 7.15 – 7.41 (m, 7 H, ArH), 8.03 – 8.05 (m, 2 H, ArH); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 30.2, 55.7, 77.8, 79.5, 109.5, 114.3, 124.4, 127.5, 128.8, 129.6, 130.6, 130.8, 133.4, 134.9, 159.2, 159.8, 166.1. MS (DEP/EI): *m/z* (%): 360 (8) [M]$^+$, 239 (11), 238 (63), 237 (100) [M-PhCOO]$^+$; HR-MS (EI): calcd. $C_{23}H_{20}O_4$ 360.1056, found 360.1053 (R = 10000).

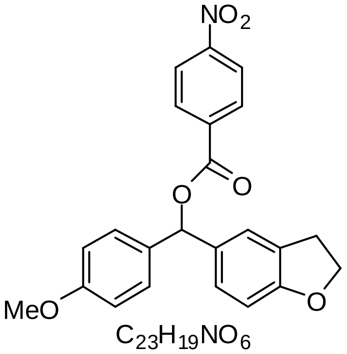


Gerneral Procedure for the Synthesis of Benzhydryl p-*Nitrobenzoates***.** A mixture of the substituted benzhydrol (1.0 mmol) and freshly distilled triethylamine (1.2 equiv, 101 mg, 1.0 mmol) in dry benzene (5 mL) was stirred for 5 min under nitrogen atmosphere before *p*-nitrobenzoyl chloride (1 equiv) was added in portions. Stirring was continued for 20 h at room temperature. Pentane (5 mL) was added, and the reaction mixture was washed quickly with 0.2 M hydrochloric acid (10 mL), saturated aq. NaHCO$_3$ (10 mL), and water. The organic phase was dried (MgSO$_4$) and filtered. Then the solvent was evaporated in vacuo (T < 30 °C). The residue was crystallized from diethyl ether/pentane to give the benzhydryl *p*-nitrobenzoate as a slightly yellow powder.

*Bis-(2,3-dihydrobenzofuran-5-yl)methyl-*p-*nitrobenzoate* was synthesized from 268 mg (1.0 mmol) bis-(2,3-dihydrobenzofuran-5-yl)methanol and 186 mg (1.0 mmol) *p*-nitrobenzoyl chloride (yield 84 %, 351 mg).
^{1}H NMR (600 MHz, CDCl$_3$): δ = 3.14 (t, 4 H, J = 8.70, C*H*$_2$CH$_2$O), 4.57 (t, 4 H, J = 8.70, CH$_2$C*H*$_2$O), 6.76 (d, 2 H, J = 8.06, ArH), 7.03 (s, 1 H, Ar$_2$C*H*), 7.15 – 7.24 (m, 4 H, ArH), 8.28 (s, 4 H, ArH); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 30.5, 72.1, 80.1, 109.7, 124.5, 128.0, 128.2, 132.1, 132.9, 135.8, 151.6, 160.8, 168.4. MS (DEP/EI): *m/z* (%): 417 (6) [M]$^+$, 252 (27), 251 (100) [M-*p*NO$_2$PhCOO]$^+$, 250 (23), 147 (15); HR-EI-MS: calcd. $C_{24}H_{19}$ NO$_6$ 417.1210, found 417.1200 (R = 10000). EA calcd. (%)$C_{24}H_{19}$ NO$_6$ (417.12): C 69.06, H 4.59, N 3.36; found C 68.86 H 5.01, N 3.75.



(2,3-dihydrobenzofuran-5-yl)(4-methoxyphenyl)methyl-p-*nitrobenzoate* was synthesized from 256 mg (1.0 mmol) (2,3-dihydrobenzofuran-5-yl)(4-methoxyphenyl)methanol and 186 mg (1.0 mmol) *p*-nitrobenzoyl chloride (yield 62 %, 251 mg).

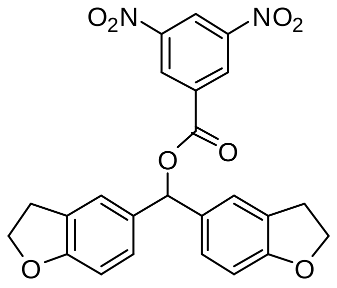


$C_{23}H_{19}NO_6$
405.40

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.19 (t, 2 H, *J* = 8.59, C*H*$_2$CH$_2$O), 3.80 (s, 3 H, CH$_3$), 4.57 (t, 2 H, *J* = 8.61, CH$_2$C*H*$_2$O), 6.69 (d, 1 H, *J* = 8.59, ArH), 6.83 (d, 2 H, *J* = 8.58, ArH), 6.98 (s, 1 H, Ar$_2$C*H*), 7.09 (d, 1 H, *J* = 8.35, ArH), 7.14 (s, 1 H, ArH), 7.26 (d, 2 H, *J* = 8.58, ArH), 8.21 (d, 4 H, *J* = 3.81, ArH); ^{13}C NMR (600 MHz, $CDCl_3$): δ = 31.7, 57.3, 73.5, 80.4, 111.3, 116.3, 125.6, 130.4, 134.1, 133.9, 134.1, 137.9, 152.6, 161.5, 162.2, 165.9. MS (DEP/EI): *m/z* (%): 405 (9) [M]$^+$, 240 (17), 239 (100) [M-*p*NO$_2$PhCOO]$^+$, 238 (66), 223 (119). HR-MS (EI): calcd. $C_{23}H_{19}$ NO_6 405.1199, found 405.1204 (R = 10000). EA calcd. (%)$C_{23}H_{19}$ NO_6 (405.12): C 68.14, H 4.72, N 3.45; found C 68.00, H 4.65, N 3.32.

General Procedure for the Synthesis of Benzhydryl 3,5-Dinitrobenzoates. A mixture of the substituted benzhydrol (1.0 mmol) and freshly distilled triethylamine (1.2 equiv, 101 mg, 1.0 mmol) in dry benzene (5 mL) was stirred for 5 min under nitrogen atmosphere before 3,5-dinitrobenzoyl chloride (1 equiv) was added stepwise. Stirring was continued for 20 h at room temperature. Pentane (5 mL) was added, and the reaction mixture was washed quickly with 0.2 M hydrochloric acid (10 mL), saturated aq. NaHCO$_3$ (10 mL), and water. The organic phase was dried (MgSO$_4$) and filtered. Then the solvent was evaporated in vacuo (T < 30 °C). The residue was crystallized from diethyl ether/pentane to give the benzhydryl *p*-nitrobenzoate as a slightly yellow powder.

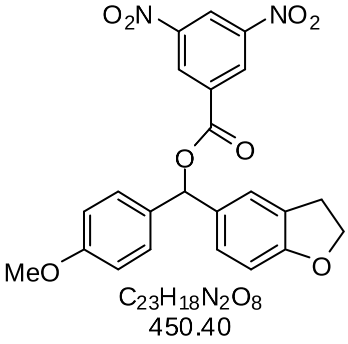
Bis-(2,3-dihydrobenzofuran-5-yl)methyl-3,5-dinitrobenzoate was synthesized from 268 mg (1.0 mmol) bis-(2,3-dihydrobenzofuran-5-yl)methanol and 231 mg (1.0 mmol) 3,5-dinitrobenzoyl chloride (yield 61 %, 283 mg).



$C_{24}H_{18}N_2O_8$
462.41

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.11 (t, 4 H, *J* = 8.70, C*H*$_2$CH$_2$O), 4.52 (t, 4 H, *J* = 8.70, CH$_2$C*H*$_2$O), 6.62 (d, 2 H, *J* = 8.06, ArH), 7.03 (s, 1 H, Ar$_2$C*H*), 7.12 – 7.23 (m, 4 H, ArH), 8.62 (s, 1 H, ArH), 8.91 (s, 2 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.1, 71.8, 80.3, 110.0, 122.8 (), 128.1, 128.2, 132.1, 132.9, 136.2, 148.7, 160.5, 161.3, 162.3. MS (DEP/EI): *m/z* (%): 462 (10) [M]$^+$, 251 (100) [M-(NO$_2$)$_2$PhCOO]$^+$, 250.2 (16). EA calcd. (%) $C_{24}H_{18}$ N_2O_8 (462.42): C 62.34, H 3.92, N 6.06; found C 62.53 H 3.90, N 5.88.

(2,3-dihydrobenzofuran-5-yl)(4-methoxyphenyl)methyl-3,5-dinitrobenzoate was synthesized from 256 mg (1.0 mmol) (2,3-dihydrobenzofuran-5-yl)(4-methoxyphenyl)methanol and 231 mg (1.0 mmol) 3,5-dinitrobenzoyl chloride (yield 67 %, 302 mg).



^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.12 (t, 2 H, J = 8.59, CH_2CH$_2$O), 3.73 (s, 3 H, CH_3), 4.51 (t, 2H, J = 8.62, CH$_2$CH_2O), 6.72 (d, 1 H, J = 8.58, ArH), 6.83 (d, 2 H, J = 8.59, ArH), 6.86 (s, 1 H, Ar$_2$CH), 7.07 (d, 1 H, J = 8.35, ArH), 7.17 (s, 1 H, ArH), 7.29 (d, 2 H, J = 8.58, ArH), 9.13 (s, 1 H, CH(CNO_2)$_2$), 9.15 (s, 2H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.1, 55.7, 71.9, 80.0, 109.7, 114.2, 114.5, 122.8, 124.6, 128.7, 129.1, 133.9, 134.1, 135.9, 149.6, 159.1, 162.2. MS (DEP/EI): *m/z* (%): 450 (21) [M]$^+$, 239 (100) [M-(NO_2)$_2$PhCOO]$^+$, 224 (18); HR-MS (EI): calcd. $C_{23}H_{18}$ N_2O_8 450.1064, found 405.1055 (R = 10000).

Kinetics

Solvolysis Reactions by Conductometry. For the conductometric monitoring of the solvolysis reactions of benzhydryl carboxylates in aqueous acetone and acetonitrile, a WTW LTA 1/NS Pt electrode connected to a Tacussel CD 810 conductometer was used. To freshly prepared aqueous solvent mixtures (25 mL) amine (NEt_3, Proton Sponge (N,N,N',N'-tetramethyl-1,8-naphthalene-diamine) or DMAP) was added and the mixtures were thermostated (25.0 ± 0.1 °C) prior to the injection of a small volume (75–150 µL) of a 0.2 M stock solution of the benzhydryl carboxylates in CH_2Cl_2. The increase of the conductance (G) was then recorded.

The first-order rate constants k_1 (s^{-1}) were obtained by least squares fitting of the conductance/time correlation to a single-exponential equation $G_t = G_0 \exp(-kt) + C$.

The solvolyses were performed at 25 ºC. Slower kinetics of (ani)$_2$CH-OAc were followed at three different higher temperatures, and the rate constant was extrapolated to 25 ºC.

When only a single k_1 value is listed, the evaluated curve was averaged from at least two independent measurements, which deviated less than 5 %.

1.1. Ionization of Benzhydryl Acetates in 20W80AN at 25 ^{o}C

Ionisation of (dpa)$_2$CH-OAc in 20W80AN at 25 ^{o}C

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.50×10^{-3}	3.05×10^{-2}	9.55×10^{-4}

$k_1 = 9.55 \times 10^{-4}$ s^{-1}

Ionisation of (mfa)$_2$CH-OAc in 20W80AN at 25 ^{o}C

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.25×10^{-3}	8.06×10^{-2}	2.31×10^{-2}
2	1.25×10^{-3}	8.06×10^{-2}	2.89×10^{-2}

$k_1 = 2.60 \times 10^{-2}$ s^{-1}

Ionisation of (pfa)$_2$CH-OAc in 20W80AN at 25 ^{o}C

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.06×10^{-3}	3.06×10^{-2}	9.97×10^{-4}
2	5.06×10^{-3}	3.06×10^{-2}	1.09×10^{-3}

$k_1 = 1.04 \times 10^{-3}$ s^{-1}

Ionisation of (dma)(Ph)CH-OAc in 20W80AN at 25 ^{o}C

No.	[Ar$_2$CH-OAc]$_0$, M	[NEt$_3$]$_0$, M	k_{obs}, s^{-1}
1	5.02×10^{-3}	3.04×10^{-2}	5.61×10^{-3}
2	5.02×10^{-3}	3.05×10^{-2}	4.98×10^{-3}
3	5.02×10^{-3}	3.04×10^{-2}	6.05×10^{-3}

$k_1 = 5.55 \times 10^{-3}$ s^{-1}

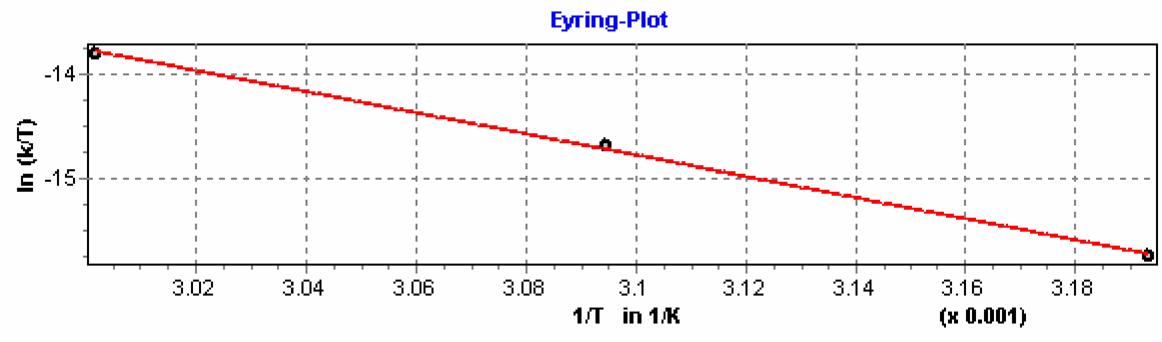
Ionisation of (fur)$_2$CH-OAc in 40W60AN at 25 ^{o}C

No.	[Ar$_2$CH-OAc]$_0$, M	[NEt$_3$]$_0$, M	k_{obs}, s^{-1}
1	5.06×10^{-3}	5.63×10^{-2}	1.19×10^{-4}
2	5.06×10^{-3}	5.63×10^{-2}	1.19×10^{-4}

$k_1 = 1.19 \times 10^{-4}$ s^{-1}

Ionisation of (ani)$_2$CH-OAc in 20W80AN

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}	T, °C
1	5.06×10^{-3}	3.06×10^{-2}	4.58×10^{-5}	40.00
2	5.06×10^{-3}	3.06×10^{-2}	1.35×10^{-4}	50.00
3	5.06×10^{-3}	3.06×10^{-2}	3.44×10^{-4}	60.00



$\Delta H^{\neq}$ = 83.60 kJ mol^{-1} $\Delta S^{\neq}$ = -61.29 kJ mol^{-1}

r^2 = 0.9988

k_1 (25°C) = 8.83 × 10^{-6} s^{-1}

1.2. Ionization of Benzhydryl Acetates in 40W60AN at 25 °C

Ionisation of (mor)$_2$CH-OAc in 40W60AN at 25 °C

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.21 × 10^{-3}	6.64 × 10^{-2}	6.21 × 10^{-2}
2	1.21 × 10^{-3}	6.64 × 10^{-2}	5.49 × 10^{-2}

k_1 = 5.85 × 10^{-2} s^{-1}

Ionisation of (dpa)$_2$CH-OAc in 40W60AN at 25 °C

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.50 × 10^{-3}	3.05 × 10^{-2}	1.67 × 10^{-3}
2	1.50 × 10^{-3}	3.25 × 10^{-2}	2.52 × 10^{-3}

k_1 = 2.10 × 10^{-3} s^{-1}

Ionisation of (mfa)$_2$CH-OAc in 40W60AN at 25 °C

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.25 × 10^{-3}	8.06 × 10^{-2}	9.28 × 10^{-2}
2	1.25 × 10^{-3}	8.06 × 10^{-2}	8.17 × 10^{-2}

k_1 = 8.73 × 10^{-2} s^{-1}

Ionisation of (pfa)$_2$CH-OAc in 40W60AN at 25 °C

No.	[Ar$_2$CH-OAc]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.06 × 10^{-3}	3.06 × 10^{-2}	2.41 × 10^{-3}
2	5.06 × 10^{-3}	3.06 × 10^{-2}	2.32 × 10^{-3}

k_1 = 2.37 × 10^{-3} s^{-1}

Ionisation of (dma)(Ph)CH-OAc in 40W60AN at 25 ^{o}C

No.	$[Ar_2CH\text{-}OAc]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.01×10^{-3}	7.55×10^{-2}	1.24×10^{-2}
2	5.01×10^{-3}	7.55×10^{-2}	1.36×10^{-2}

$k_1 = 1.30 \times 10^{-2}$ s^{-1}

Ionisation of $(fur)_2$CH-OAc in 40W60AN at 25 ^{o}C

No.	$[Ar_2CH\text{-}OAc]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.06×10^{-3}	5.63×10^{-2}	4.45×10^{-4}
2	5.06×10^{-3}	5.63×10^{-2}	4.42×10^{-4}
3	5.06×10^{-3}	5.63×10^{-2}	4.42×10^{-4}

$k_1 = 4.43 \times 10^{-4}$ s^{-1}

Ionisation of (fur)(ani)CH-OAc in 40W60AN at 25 ^{o}C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.07×10^{-3}	3.00×10^{-2}	1.38×10^{-4}
2	5.07×10^{-3}	3.00×10^{-2}	1.42×10^{-4}

$k_1 = 1.40 \times 10^{-4}$ s^{-1}

1.3. Ionization of Benzhydryl Acetates in 20W80A at 25 ^{o}C

Ionisation of $(mor)_2$CH-OAc in 20W80A at 25 ^{o}C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.21×10^{-3}	6.64×10^{-2}	1.49×10^{-2}
2	1.21×10^{-3}	6.64×10^{-2}	1.01×10^{-2}

$k_1 = 1.25 \times 10^{-2}$ s^{-1}

Ionisation of $(dpa)_2$CH-OAc in 20W80A at 25 ^{o}C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.50×10^{-3}	3.05×10^{-2}	2.80×10^{-4}

$k_1 = 2.80 \times 10^{-4}$ s^{-1}

Ionisation of $(mfa)_2$CH-OAc in 20W80A at 25 ^{o}C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.25×10^{-3}	8.06×10^{-2}	1.13×10^{-2}
2	1.25×10^{-3}	8.06×10^{-2}	1.55×10^{-2}

$k_1 = 1.34 \times 10^{-2}$ s^{-1}

Ionisation of $(pfa)_2$CH-OAc in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.06×10^{-3}	3.06×10^{-2}	4.01×10^{-4}

$k_1 = 4.01 \times 10^{-4}$ s^{-1}

Ionisation of (dma)(Ph)CH-OAc in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.21×10^{-3}	6.64×10^{-2}	1.15×10^{-3}
2	1.21×10^{-3}	6.64×10^{-2}	1.48×10^{-3}

$k_1 = 1.32 \times 10^{-3}$ s^{-1}

Ionisation of $(fur)_2$CH-OAc in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.21×10^{-3}	6.67×10^{-2}	4.33×10^{-5}
2	1.21×10^{-3}	6.67×10^{-2}	4.29×10^{-5}

$k_1 = 4.31 \times 10^{-5}$ s^{-1}

1.4. Ionization of Benzhydryl Acetates in 40W60A at 25 °C

Ionisation of $(mor)_2$CH-OAc in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.21×10^{-3}	6.64×10^{-2}	5.00×10^{-2}

$k_1 = 5.00 \times 10^{-2}$ s^{-1}

Ionisation of $(mfa)_2$CH-OAc in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	1.50×10^{-3}	3.05×10^{-2}	7.07×10^{-2}
2	1.50×10^{-3}	3.05×10^{-2}	7.43×10^{-2}

$k_1 = 7.25 \times 10^{-2}$ s^{-1}

Ionisation of $(pfa)_2$CH-OAc in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OAc]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.06×10^{-3}	3.06×10^{-2}	1.83×10^{-3}
2	5.06×10^{-3}	3.06×10^{-2}	1.89×10^{-3}

$k_1 = 1.86 \times 10^{-3}$ s^{-1}

Ionisation of (dma)(Ph)CH-OAc in 40W60A at 25 °C

No.	$[\mathrm{Ar_2CH\text{-}OAc}]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.01×10^{-3}	3.99×10^{-2}	1.34×10^{-2}
2	5.01×10^{-3}	3.99×10^{-2}	1.32×10^{-2}
3	5.01×10^{-3}	3.99×10^{-2}	1.29×10^{-2}

$k_1 = 1.32 \times 10^{-2}\ \mathrm{s}^{-1}$

Ionisation of $\mathrm{(fur)_2CH\text{-}OAc}$ in 40W60A at 25 °C

No.	$[\mathrm{Ar_2CH\text{-}OAc}]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.02×10^{-3}	3.65×10^{-2}	4.05×10^{-4}
2	5.02×10^{-3}	3.65×10^{-2}	3.44×10^{-4}
3	5.02×10^{-3}	3.69×10^{-2}	3.48×10^{-4}

$k_1 = 3.66 \times 10^{-4}\ \mathrm{s}^{-1}$

Ionisation of (fur)(ani)CH-OAc in 40W60A at 25 °C

No.	$[\mathrm{Ar_2CH\text{-}OAc}]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.01×10^{-3}	3.23×10^{-2}	1.09×10^{-4}
2	5.01×10^{-3}	3.23×10^{-2}	1.08×10^{-4}

$k_1 = 1.09 \times 10^{-4}\ \mathrm{s}^{-1}$

2.1. Ionization of Benzhydryl Benzoates in 20W80AN at 25 °C

Ionisation of $\mathrm{(mor)_2CH\text{-}OBz}$ in 20W80AN at 25 °C

No.	$[\mathrm{Ar_2CH\text{-}OBz}]_0$, M	[DMAP]$_0$, M	k_{obs}, s^{-1}
1	9.48×10^{-4}	4.91×10^{-3}	4.87×10^{-2}
2	9.48×10^{-4}	4.91×10^{-3}	5.03×10^{-2}
3	9.48×10^{-4}	4.91×10^{-3}	4.98×10^{-2}

$k_1 = 4.96 \times 10^{-2}\ \mathrm{s}^{-1}$

Ionisation of $\mathrm{(dpa)_2CH\text{-}OBz}$ in 20W80AN at 25 °C

No.	$[\mathrm{Ar_2CH\text{-}OBz}]_0$, M	[DMAP]$_0$, M	k_{obs}, s^{-1}
1	9.00×10^{-4}	4.91×10^{-3}	2.71×10^{-3}
2	9.00×10^{-4}	4.91×10^{-3}	2.71×10^{-3}
3	9.00×10^{-4}	4.91×10^{-3}	2.94×10^{-3}

$k_1 = 2.79 \times 10^{-3}\ \mathrm{s}^{-1}$

Ionisation of $\mathrm{(mfa)_2CH\text{-}OBz}$ in 20W80AN at 25 °C

No.	$[\mathrm{Ar_2CH\text{-}OBz}]_0$, M	[DMAP]$_0$, M	k_{obs}, s^{-1}
1	1.00×10^{-3}	4.91×10^{-3}	6.05×10^{-2}
2	1.00×10^{-3}	4.91×10^{-3}	6.06×10^{-2}

$k_1 = 6.06 \times 10^{-2}\ \mathrm{s}^{-1}$

Ionisation of (dma)(Ph)CH-OBz in 20W80AN at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.01×10^{-3}	3.00×10^{-2}	6.81×10^{-3}
2	5.02×10^{-3}	3.00×10^{-2}	8.24×10^{-3}

$k_1 = 7.53 \times 10^{-3}$ s^{-1}

2.2. Ionization of Benzhydryl Benzoates in 40W60AN at 25 °C

Ionisation of $(mor)_2$CH-OBz in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[DMAP]_0$, M	k_{obs}, s^{-1}
1	9.48×10^{-4}	4.91×10^{-3}	1.31×10^{-1}
2	9.48×10^{-4}	4.91×10^{-3}	1.33×10^{-1}

$k_1 = 1.32 \times 10^{-1}$ s^{-1}

Ionisation of $(mfa)_2$CH-OBz in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[DMAP]_0$, M	k_{obs}, s^{-1}
1	6.68×10^{-4}	4.91×10^{-3}	1.81×10^{-1}
2	6.68×10^{-4}	4.91×10^{-3}	2.01×10^{-1}

$k_1 = 1.91 \times 10^{-1}$ s^{-1}

Ionisation of (dma)(Ph)CH-OBz in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.01×10^{-3}	3.02×10^{-2}	2.65×10^{-2}
2	5.01×10^{-3}	3.02×10^{-2}	2.59×10^{-2}
3	5.01×10^{-3}	3.02×10^{-2}	2.43×10^{-2}

$k_1 = 2.56 \times 10^{-2}$ s^{-1}

Ionisation of $(fur)_2$CH-OBz in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.05×10^{-3}	3.53×10^{-2}	8.31×10^{-4}
2	5.05×10^{-3}	3.53×10^{-2}	7.63×10^{-4}
3	5.05×10^{-3}	3.53×10^{-2}	8.00×10^{-4}

$k_1 = 7.98 \times 10^{-4}$ s^{-1}

Ionisation of (fur)(ani)CH-OBz in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.01×10^{-3}	3.05×10^{-2}	5.25×10^{-4}
2	5.01×10^{-3}	3.05×10^{-2}	6.36×10^{-4}

$k_1 = 5.81 \times 10^{-4}$ s^{-1}

2.3. Ionization of Benzhydryl Benzoates in 20W80A at 25 °C

Ionisation of $(mor)_2CH$-OBz in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[DMAP]_0$, M	k_{obs}, s^{-1}
1	4.74×10^{-4}	4.91×10^{-3}	2.63×10^{-2}
2	4.74×10^{-4}	4.91×10^{-3}	2.41×10^{-2}

$k_1 = 2.52 \times 10^{-2}\ s^{-1}$

Ionisation of $(dpa)_2CH$-OBz in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[DMAP]_0$, M	k_{obs}, s^{-1}
1	4.50×10^{-4}	4.91×10^{-3}	6.46×10^{-4}
2	4.50×10^{-4}	4.91×10^{-3}	6.48×10^{-4}
3	4.50×10^{-4}	4.91×10^{-3}	6.98×10^{-4}

$k_1 = 6.64 \times 10^{-4}\ s^{-1}$

Ionisation of $(mfa)_2CH$-OBz in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[DMAP]_0$, M	k_{obs}, s^{-1}
1	6.68×10^{-4}	4.91×10^{-3}	2.36×10^{-2}
2	6.68×10^{-4}	4.91×10^{-3}	2.33×10^{-2}

$k_1 = 2.35 \times 10^{-2}\ s^{-1}$

2.4. Ionization of Benzhydryl Benzoates in 40W60A at 25 °C

Ionisation of $(mor)_2CH$-OBz in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[DMAP]_0$, M	k_{obs}, s^{-1}
1	4.74×10^{-4}	4.91×10^{-3}	9.17×10^{-2}
2	4.74×10^{-4}	4.91×10^{-3}	9.62×10^{-2}

$k_1 = 9.40 \times 10^{-2}\ s^{-1}$

Ionisation of $(mfa)_2CH$-OBz in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	$[DMAP]_0$, M	k_{obs}, s^{-1}
1	6.68×10^{-4}	4.91×10^{-3}	1.31×10^{-1}
2	6.68×10^{-4}	4.91×10^{-3}	1.25×10^{-1}

$k_1 = 1.28 \times 10^{-1}\ s^{-1}$

Ionisation of (dma)(Ph)CH-OBz in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.01×10^{-3}	3.06×10^{-2}	1.88×10^{-2}
2	5.01×10^{-3}	3.06×10^{-2}	1.86×10^{-2}
3	5.01×10^{-3}	3.06×10^{-2}	1.76×10^{-2}

$k_1 = 1.84 \times 10^{-2}$ s^{-1}

Ionisation of (fur)$_2$CH-OBz in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.09×10^{-3}	3.65×10^{-2}	4.28×10^{-4}
2	5.09×10^{-3}	3.65×10^{-2}	3.93×10^{-4}
3	5.09×10^{-3}	3.65×10^{-2}	4.31×10^{-4}

$k_1 = 4.17 \times 10^{-4}$ s^{-1}

Ionisation of (fur)(ani)CH-OBz in 40W60A at 25 °C

No.	$[Ar_2CH\text{-}OBz]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.10×10^{-3}	3.12×10^{-2}	2.41×10^{-4}
2	5.05×10^{-3}	3.12×10^{-2}	2.25×10^{-4}

$k_1 = 2.33 \times 10^{-4}$ s^{-1}

3.1. Ionization of Benzhydryl *p*-Nitrobenzoates in 20W80AN at 25 °C

Ionisation of (fur)$_2$CH-PNB in 20W80AN at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.11×10^{-3}	3.02×10^{-2}	4.50×10^{-3}

$k_1 = 4.50 \times 10^{-3}$ s^{-1}

Ionisation of (fur)(ani)CH-PNB in 20W80AN at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.00×10^{-3}	3.15×10^{-2}	2.29×10^{-3}
2	5.00×10^{-3}	3.15×10^{-2}	2.13×10^{-3}

$k_1 = 2.21\times 10^{-3}$ s^{-1}

Ionisation of (ani)$_2$CH-PNB in 20W80AN at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.46×10^{-3}	4.69×10^{-2}	4.09×10^{-4}
2	5.46×10^{-3}	4.69×10^{-2}	4.13×10^{-4}

$k_1 = 4.11\times 10^{-4}$ s^{-1}

3.2. Ionization of Benzhydryl *p*-Nitrobenzoates in 40W60AN at 25 °C

Ionisation of $(fur)_2CH$-PNB in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.07×10^{-3}	3.00×10^{-2}	9.79×10^{-3}
2	5.07×10^{-3}	3.00×10^{-2}	9.88×10^{-3}
3	5.07×10^{-3}	3.00×10^{-2}	1.02×10^{-2}

$k_1 = 9.95 \times 10^{-3}\ s^{-1}$

Ionisation of (fur)(ani)CH-PNB in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	4.81×10^{-3}	2.79×10^{-2}	3.33×10^{-3}
2	4.81×10^{-3}	2.79×10^{-2}	3.44×10^{-3}

$k_1 = 3.39 \times 10^{-3}\ s^{-1}$

Ionisation of $(ani)_2CH$-PNB in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.46×10^{-3}	4.69×10^{-2}	1.04×10^{-3}
2	5.46×10^{-3}	4.69×10^{-2}	1.05×10^{-3}

$k_1 = 1.05\times 10^{-3}\ s^{-1}$

3.3. Ionization of Benzhydryl *p*-Nitrobenzoates in 10W90A at 25 °C

Ionisation of $(fur)_2CH$-PNB in 10W90A at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.02×10^{-3}	6.32×10^{-2}	6.40×10^{-4}

$k_1 = 6.40 \times 10^{-4}\ s^{-1}$

Ionisation of (fur)(ani)CH-PNB in 10W90A at 25 °C

No.	$[Ar_2CH\text{-}PNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	6.51×10^{-3}	4.12×10^{-2}	2.92×10^{-4}

$k_1 = 2.92 \times 10^{-4}\ s^{-1}$

3.4. Ionization of Benzhydryl *p*-Nitrobenzoates in 20W80A at 25 °C

Ionisation of (fur)$_2$CH-PNB in 20W80A at 25 °C

No.	[Ar$_2$CH-PNB]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.11×10^{-3}	3.02×10^{-2}	2.08×10^{-3}
2	5.11×10^{-3}	3.02×10^{-2}	2.04×10^{-3}
3	5.11×10^{-3}	3.02×10^{-2}	1.86×10^{-3}

$k_1 = 1.99 \times 10^{-3}$ s^{-1}

Ionisation of (fur)(ani)CH-PNB in 20W80A at 25 °C

No.	[Ar$_2$CH-PNB]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.00×10^{-3}	3.15×10^{-2}	6.31×10^{-4}
2	5.00×10^{-3}	3.15×10^{-2}	6.31×10^{-4}
3	5.02×10^{-3}	3.15×10^{-2}	6.33×10^{-4}

$k_1 = 6.32\times 10^{-4}$ s^{-1}

3.5. Ionization of Benzhydryl *p*-Nitrobenzoates in 40W60A at 25 °C

Ionisation of (fur)$_2$CH-PNB in 40W60A at 25 °C

No.	[Ar$_2$CH-PNB]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.11×10^{-3}	3.02×10^{-2}	9.36×10^{-3}

$k_1 = 9.36 \times 10^{-3}$ s^{-1}

Ionisation of (fur)(ani)CH-PNB in 40W60A at 25 °C

No.	[Ar$_2$CH-PNB]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.00×10^{-3}	3.15×10^{-2}	3.57×10^{-3}

$k_1 = 3.57\times 10^{-3}$ s^{-1}

Ionisation of (ani)$_2$CH-PNB in 40W60A at 25 °C

No.	[Ar$_2$CH-PNB]$_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.46×10^{-3}	4.69×10^{-2}	1.06×10^{-3}
2	5.46×10^{-3}	4.69×10^{-2}	1.08×10^{-3}

$k_1 = 1.07\times 10^{-3}$ s^{-1}

4.1. Ionization of Benzhydryl Dinitrobenzoates in 20W80AN at 25 °C

Ionisation of $(fur)_2CH$-DNB in 20W80AN at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.05×10^{-3}	3.21×10^{-2}	4.55×10^{-2}

$k_1 = 4.55 \times 10^{-2}$ s^{-1}

Ionisation of (fur)(ani)CH-DNB in 20W80AN at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.27×10^{-3}	2.70×10^{-2}	1.83×10^{-2}
3	5.27×10^{-3}	2.70×10^{-2}	1.80×10^{-2}

$k_1 = 1.82 \times 10^{-2}$ s^{-1}

Ionisation of $(ani)_2CH$-DNB in 20W80AN at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	4.24×10^{-3}	3.21×10^{-2}	1.80×10^{-2}

$k_1 = 1.80 \times 10^{-2}$ s^{-1}

4.2. Ionization of Benzhydryl Dinitrobenzoates in 40W60AN at 25 °C

Ionisation of $(fur)_2CH$-DNB in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.05×10^{-3}	3.21×10^{-2}	1.12×10^{-1}
2	5.05×10^{-3}	3.21×10^{-2}	1.10×10^{-1}

$k_1 = 1.11 \times 10^{-1}$ s^{-1}

Ionisation of (fur)(ani)CH-DNB in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	$[NEt_3]_0$, M	k_{obs}, s^{-1}
1	5.27×10^{-3}	2.70×10^{-2}	4.04×10^{-2}
2	5.27×10^{-3}	2.70×10^{-2}	4.00×10^{-2}
3	5.27×10^{-3}	2.70×10^{-2}	3.94×10^{-2}

$k_1 = 3.96 \times 10^{-2}$ s^{-1}

Ionisation of $(ani)_2CH$-DNB in 40W60AN at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	4.24×10^{-3}	3.21×10^{-2}	1.01×10^{-2}
2	4.24×10^{-3}	3.21×10^{-2}	9.97×10^{-3}
3	4.24×10^{-3}	3.21×10^{-2}	1.04×10^{-2}

$k_1 = 1.02 \times 10^{-2}$ s^{-1}

4.3. Ionization of Benzhydryl Dinitrobenzoates in 10W90A at 25 °C

Ionisation of $(fur)_2CH$-DNB in 10W90A at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.05×10^{-3}	3.21×10^{-2}	1.61×10^{-2}

$k_1 = 1.61 \times 10^{-2}$ s^{-1}

Ionisation of (fur)(ani)CH-DNB in 10W90A at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.27×10^{-3}	2.70×10^{-2}	5.11×10^{-3}

$k_1 = 5.11 \times 10^{-3}$ s^{-1}

4.4. Ionization of Benzhydryl Dinitrobenzoates in 20W80A at 25 °C

Ionisation of $(fur)_2CH$-DNB in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.05×10^{-3}	3.21×10^{-2}	3.52×10^{-2}
2	5.05×10^{-3}	3.21×10^{-2}	3.48×10^{-2}
3	5.05×10^{-3}	3.21×10^{-2}	3.40×10^{-2}

$k_1 = 3.47 \times 10^{-2}$ s^{-1}

Ionisation of (fur)(ani)CH-DNB in 20W80A at 25 °C

No.	$[Ar_2CH\text{-}DNB]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.27×10^{-3}	2.70×10^{-2}	1.16×10^{-2}
2	5.27×10^{-3}	2.70×10^{-2}	1.07×10^{-2}
3	5.27×10^{-3}	2.70×10^{-2}	1.14×10^{-2}

$k_1 = 1.12 \times 10^{-2}$ s^{-1}

4.5. Ionization of Benzhydryl Dinitrobenzoates in 40W60A at 25 °C

Ionisation of $(fur)_2CH$-DNB in 40W60A at 25 °C

No.	$[Ar_2CH\text{-DNB}]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.05×10^{-3}	3.21×10^{-2}	9.03×10^{-2}

$k_1 = 9.03 \times 10^{-2}$ s^{-1}

Ionisation of (fur)(ani)CH-DNB in 40W60A at 25 °C

No.	$[Ar_2CH\text{-DNB}]_0$, M	[proton sponge]$_0$, M	k_{obs}, s^{-1}
1	5.27×10^{-3}	2.70×10^{-2}	3.68×10^{-2}

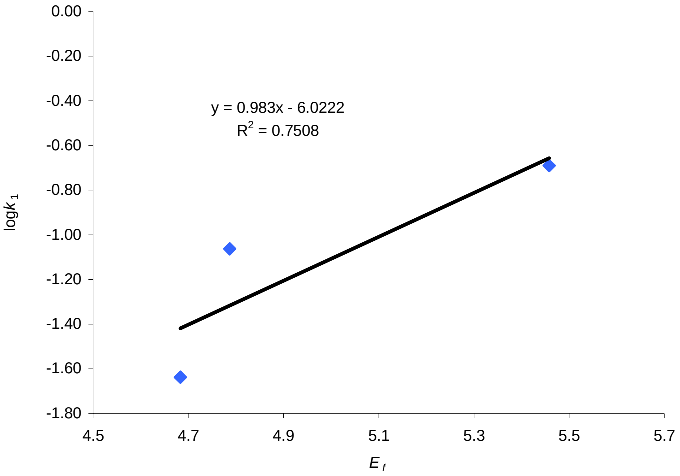
$k_1 = 3.68 \times 10^{-2}$ s^{-1}

5. Determination of Nucleofugality Parameters for Common Leaving Groups.

5.1 Nucleofugality parameter of DMAP in acetonitrile

Ar_2CH^+	E_f	k_1, M^{-1} s^{-1}	$\lg k_1$
$(lil)_2CH^+$	4.79	8.71×10^{-2} [a]	-1.06
$(jul)_2CH^+$	5.46	2.04×10^{-1} [a]	-0.69
$(ind)_2CH^+$	4.68	2.29×10^{-1} [a]	-1.64

[a] from M. Baidya, S. Kobayashi, F. Brotzel, U. Schmidhammer, E. Riedle, H. Mayr, *Angew. Chem.* **2007**, *119*, 6288-6292; *Angew. Chem. Int. Ed.* **2007**, *46*, 6176-6179.

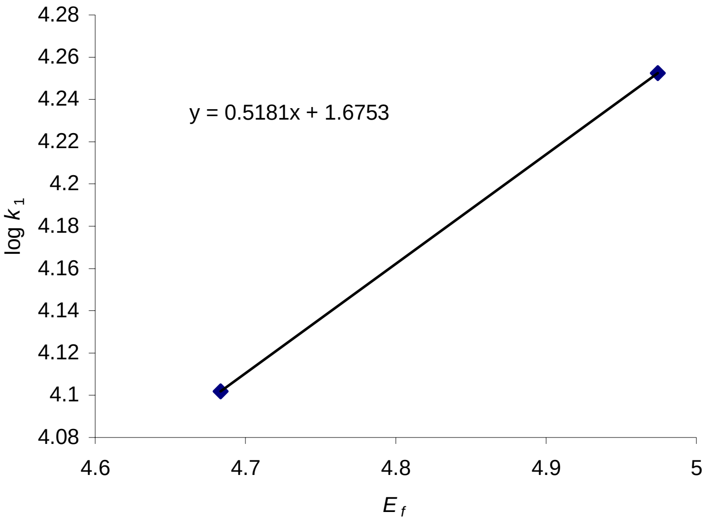


N_f = -6.12
s_f= 0.98

5.2 Nucleofugality parameter of DABCO in acetonitrile

Ar_2CH^+	E_f	k_1, $M^{-1} s^{-1}$	lgk_1
$(ind)_2CH^+$	4.68	1.26×10^4 [a]	4.10
$(thq)_2CH^+$	4.97	1.78×10^4 [a]	4.25

[a] from M. Baidya, S. Kobayashi, F. Brotzel, U. Schmidhammer, E. Riedle, H. Mayr, *Angew. Chem.* **2007**, *119*, 6288-6292; *Angew. Chem. Int. Ed.* **2007**, *46*, 6176-6179.

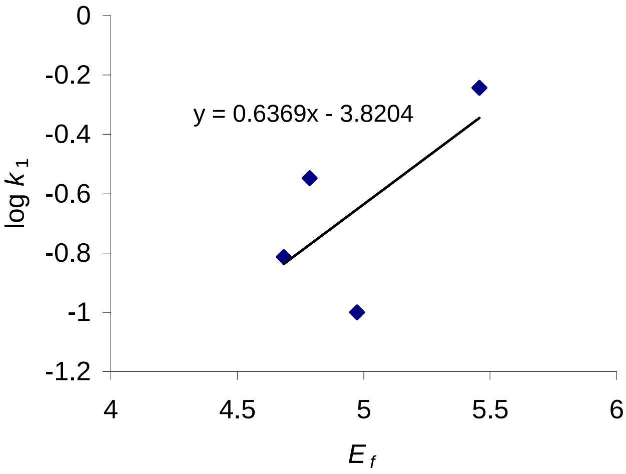


N_f = 3.21
s_f= 0.52

5.3 Nucleofugality parameter of $P(4\text{-}OMeC_6H_4)_3$ in CH_2Cl_2

Ar_2CH^+	E_f	k_1, $M^{-1} s^{-1}$	lgk_1
$(lil)_2CH^+$	4.79	2.82×10^{-1} [a]	-0.55
$(jul)_2CH^+$	5.46	5.75×10^{-1} [a]	-0.24
$(ind)_2CH^+$	4.68	1.55×10^{-1} [a]	-0.81
$(thq)_2CH^+$	4.97	1.00×10^{-1} [a]	-1

[a] from B. Kempf, H. Mayr, *Chem. Eur. J.* **2005**, *11*, 917-927.

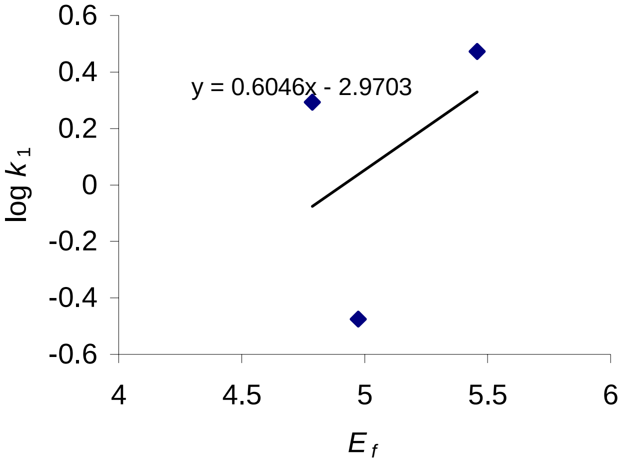


N_f = -6.00
s_f = 0.64

5.4 Nucleofugality parameter of $P(4\text{-}MeC_6H_4)_3$ in CH_2Cl_2

Ar_2CH^+	E_f	k_1, M^{-1} s^{-1}	$\lg k_1$
$(lil)_2CH^+$	4.79	1.95 [a]	0.29
$(jul)_2CH^+$	5.46	2.95 [a]	0.47
$(thq)_2CH^+$	4.97	0.33 [a]	-0.48

[a] from B. Kempf, H. Mayr, *Chem. Eur. J.* **2005**, *11*, 917-927.

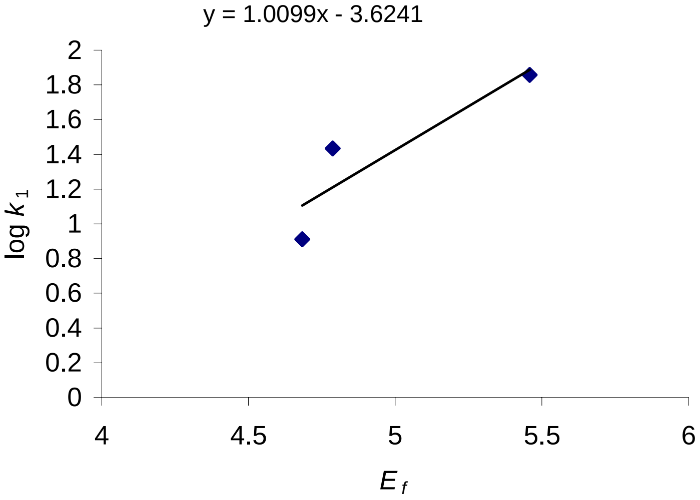


N_f = -4.90
s_f = 0.60

5.5 Nucleofugality parameter of NO_2^- in acetonitrile

Ar_2CH^+	E_f	k_1, M^{-1} s^{-1}	$\lg k_1$
$(lil)_2CH^+$	4.79	2.75×10^1 [a]	1.44
$(jul)_2CH^+$	5.46	7.24×10^1 [a]	1.86
$(ind)_2CH^+$	4.68	8.13 [a]	0.91

[a] from A. A. Tishkov, U. Schmidhammer, S. Roth, E. Riedle, H. Mayr, *Angew. Chem.* **2005**, *117*, 4699-4703; *Angew. Chem. Int. Ed.* **2005**, *44*, 4623-4626.

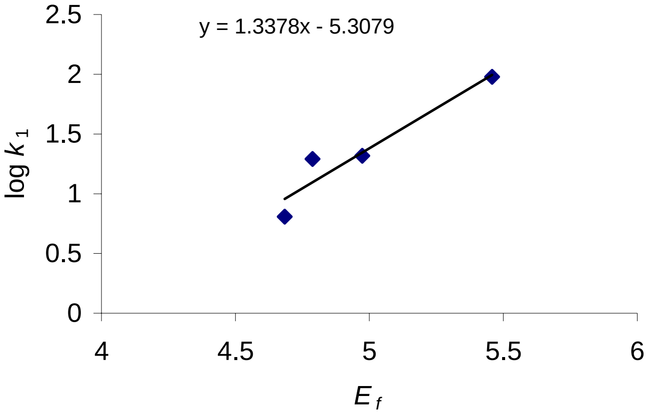


N_f = -3.59
s_f = 1.01

5.6 Nucleofugality parameter of N_3^- in 91M9AN

Ar_2CH^+	E_f	k_1, M^{-1} s^{-1}	$\lg k_1$
$(lil)_2CH^+$	4.79	1.95×10^{1} [a]	1.29
$(jul)_2CH^+$	5.46	9.55×10^{1} [a]	1.98
$(ind)_2CH^+$	4.68	6.46 [a]	0.81
$(thq)_2CH^+$	4.97	2.09×10^{1} [a]	1.32

[a] from T. B. Phan, H. Mayr, *J. Phys. Org. Chem.* **2006**, *19*, 706-713.

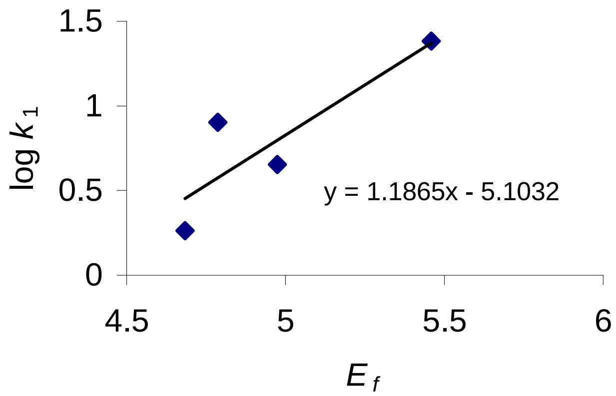


N_f = -3.96
s_f = 1.34

5.7 Nucleofugality parameter of N_3^- in 91E9AN

Ar_2CH^+	E_f	k_1, M^{-1} s^{-1}	$\lg k_1$
$(lil)_2CH^+$	4.79	7.94 [a]	0.90
$(jul)_2CH^+$	5.46	2.40×10^{1} [a]	1.38
$(ind)_2CH^+$	4.68	1.82 [a]	0.26
$(thq)_2CH^+$	4.97	4.47 [a]	0.65

[a] from T. B. Phan, H. Mayr, *J. Phys. Org. Chem.* **2006**, *19*, 706-713.



N_f = -4.30
s_f = 1.19

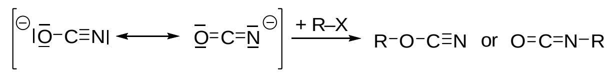
Ambident Reactivity of the Cyanate Anion

Schaller, H. F.; Schmidhammer, U.; Riedle, E.; Mayr, H. *Chem. Eur. J.* **2008**, *14*, 3866-3868.

Introduction

The cyanate anion is an ambident nucleophile, which may react with electrophiles either at the oxygen terminus to yield alkyl cyanates or at the nitrogen terminus to yield isocyanates (Scheme 5.1).[1]

Scheme 5.1. Ambident reactions of the cyanate anion.



Because the charge density is higher at the more electronegative oxygen center while the larger HOMO coefficient is at nitrogen,[2] the concept of charge and orbital control[3] predicts hard electrophiles to attack at the oxygen side and soft electrophiles to attack at the nitrogen. It was, therefore, expected that alkyl cyanates should be formed in nucleophilic substitution reactions with S_N1 character while alkyl isocyanates should be formed in nucleophilic substitution reactions with S_N2 character.[4]

In line with early work of Wurtz on the alkylation of potassium cyanate with diethyl sulfate,[5] Slotta and Lorenz reported that the reaction of dialkyl sulfates with alkali metal cyanates is the best method for synthesizing alkyl isocyanates (eq 5.1).[6]

$$\mathrm{KOCN} + (\mathrm{RO})_2\mathrm{SO}_2 \rightarrow \mathrm{R\text{-}NCO} + \mathrm{ROSO_3K} \qquad (5.1)$$

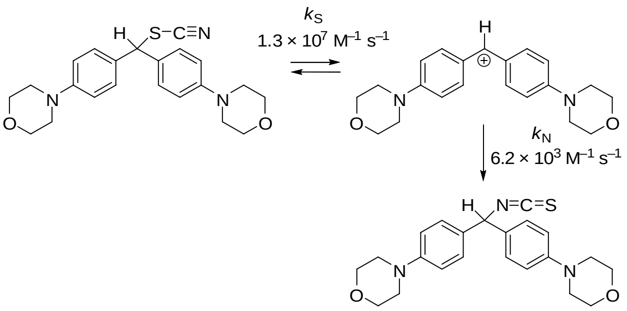
It cannot be excluded, however, that the selective formation of alkyl isocyanates under these conditions is due to a cyanate ion catalyzed isomerization of an initially formed alkyl cyanate into its thermodynamically more stable isomer (eq 5.2).[7]

$$\mathrm{R\text{-}OCN} + \mathrm{NCO}^- \rightarrow \mathrm{R\text{-}NCO} + \mathrm{NCO}^- \qquad (5.2)$$

Subsequent isomerization of the initial products may also be responsible for the selective formation of alkyl isocyanates by the reaction of silver cyanate with primary alkyl halides and trityl chloride. On the other hand, almost equal amounts of alkyl cyanates and isocyanates were obtained when secondary iodoalkanes were treated with silver cyanate, and the formation of *tert*-butyl isocyanate together with 2-methylpropene and cyanic acid was also considered as an indication for concomitant O- and N-attack.[4]

In previous work,[8] kinetic investigations were employed to demonstrate the change of regioselectivity in reactions of the thiocyanate ion with benzhydrylium ions of variable electrophilicity. A biexponential decay of the benzhydrylium absorbances, a fast reversible attack at the sulfur terminus, and the slow irreversible attack at nitrogen side was observed when morpholino-substituted benzhydrylium ions were photolytically generated in the presence of SCN^- ions (Scheme 5.2).

Scheme 5.2. Ambident reaction of the thiocyanate anion (20 °C, acetonitrile).[8]

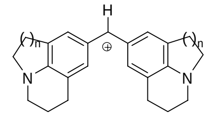
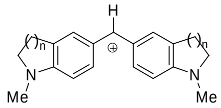
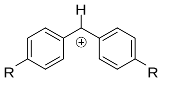
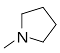
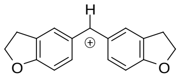
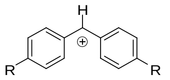


When more electrophilic carbocations were employed, the k_S/k_N ratio decreased because both reactions approach diffusion control.

Results and Discussion

We now set out to examine whether reactions with benzhydrylium ions (Table 5.1) can also be employed to elucidate the ambident reactivity of cyanate ions.

Table 5.1. Second-order rate constants of the reactions of cyanate ions with the benzhydrylium ions **1** (20 °C, acetonitrile)

Benzhydrylium Ions			E [a]	k_2 [M^{-1} s^{-1}]
	n = 1	**1a**	–10.04	1.11×10^{3}
	n = 2	**1b**	–9.45	2.53×10^{3}
	n = 1	**1c**	–8.76	1.33×10^{4}
	n = 2	**1d**	–8.22	3.47×10^{4}
	R = 	**1e**	–7.69	1.09×10^{5}
	R = NMe_2	**1f**	–7.02	3.21×10^{5}
	R = NMePh	**1g**	–5.89	2.88×10^{6}
	R = $N(Ph)_2$	**1h**	–4.72	3.48×10^{7}
	R = $NMe(CH_2CF_3)$	**1i**	–3.85	1.60×10^{8}
		**1j**	–1.36	1.06×10^{10}
	R = OMe	**1k**	0.00	– [b]
	R = Me	**1l**	3.63	2.47×10^{10}
	R = Cl	**1m**	6.02	– [b]

[a] Electrophilicity parameters as defined previously.[9,10] [b] Only used for product studies.

Exclusive formation of benzhydrylium isocyanates was observed when benzhydrylium tetrafluoroborate **1h**-BF_4 or chloro-bis(4-methoxyphenyl)methane **1k**-Cl was treated with tetraethylammonium cyanate in acetonitrile (for product identification see Experimental Section). As in the examples quoted above, it was not clear whether the isolated products resulted from kinetic or thermodynamic control.

The kinetics of the reactions of the less electrophilic benzhydrylium ions were followed photometrically by combining acetonitrile solutions of (**1a–f**)-BF_4 with solutions of $Et_4N^+OCN^-$ in a stopped-flow instrument and monitoring the decay of the absorbance at the absorption maxima[8,11] in the visible as described previously.[9] The experiments were carried out with an excess of $Et_4N^+OCN^-$ under first-order conditions, resulting in an exponential decay of the absorbances of the benzhydrylium ions, from which the first-order rate constants k_{obs} were derived.

The reactions of the carbocations **1g**–**j** and **1l** were too fast to be determined in this way. Therefore, the corresponding diarylisocyanatomethanes, which were obtained by mixing the benzhydrylium tetrafluoroborates (**1g**–**i**)-BF_4 or the chlorodiarylmethanes (**1j**,**l**)-Cl with an excess of $Et_4N^+OCN^-$, were irradiated by laser pulses (<1 ps, approx. 1 μJ, center wavelengths between 265 and 300 nm matched to the absorption maxima) to yield the benzhydrylium ions **1g**–**j** and **1l** as described previously.[12,13] The generated benzhydrylium ions then reacted with the cyanate anion, and the change of absorbance due to the reaction of the benzhydrylium ions with the cyanate anions was monitored at appropriate timescales. As in the stopped-flow experiments, these reactions were also performed under first-order conditions.

As depicted in the Experimental Section, plots of the first-order rate constants k_{obs} vs. [OCN^-] were linear, and the resulting slopes gave the second-order rate constants k_2 listed in Table 5.1.

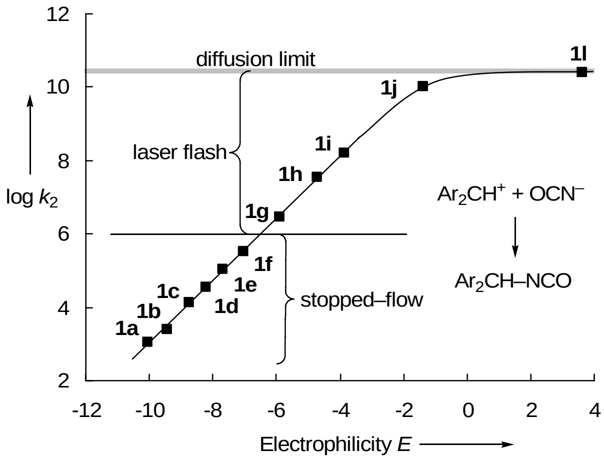


Figure 5.1. Plot of log k_2 for the reactions of the cyanate ion with benzhydrylium ions **1a**–**j**,**l** in acetonitrile at 20 °C versus their electrophilicity parameters E.

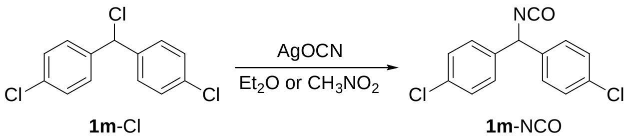
Figure 5.1 shows that the second-order rate constants k_2 for **1a**–**i** correlate linearly with the electrophilicity parameters E of the benzhydrylium ions as required by eq 5.3, where E is the electrophilicity parameter, N is the nucleophilicity parameter and s is the nucleophile-specific slope parameter.

$$\log k_2 = s(N + E) \qquad (5.3)$$

The flattening of the curve at log $k_2 > 10$ is due to diffusion control, which is in the same order of magnitude as for other reactions of benzhydrylium ions with anions in acetonitrile.[12,14] The fact that the rate constants determined by the stopped-flow and the Laser flash technique are on the same correlation line shows the internal consistency of our kinetic measurements, and from the linear part of this graph we can derive $N = 13.60$ and $s = 0.84$ for OCN^{-} in acetontrile.

Can all observed second-order rate constants be assigned to N-attack as suggested by the product studies? The smooth correlation line shown in Figure 5.1 indicates that the rate-determining step does not change throughout this reaction series. If N-attack would be accompanied by a fast and reversible O-attack, one should be able to observe a biexponential decay as in the previous studies with SCN^{-}.[8] From the fact that all kinetics investigated in this work show monoexponential decays, one can derive that the equilibrium constants for O-attack – if it occurs at all – must be so small that the low concentrations of the intermediate benzhydryl cyanates are kinetically irrelevant. This argument does not hold when N- and O-attack proceed with comparable rates, which may occur in the diffusion-controlled range. One can assume that highly electrophilic carbocations which do not meet a barrier when approaching OCN^{-} from either side will give mixtures of R-NCO and R-OCN. However, when the benzhydryl chloride **1m**-Cl was treated with AgOCN in diethyl ether or nitromethane following a procedure reported by Holm and Wentrup,[4] the corresponding benzhydryl isocyanate **1m**-NCO was isolated exclusively (Scheme 5.3). Therefore, we cannot specify whether the isocyanate **1m**-NCO is the result of kinetic or thermodynamic control because even primary alkyl cyanates have been reported to rearrange into alkyl isocyanates under mild conditions.[7]

Scheme 5.3.



The fact that NCO^- reacts quantitatively even with **1a** and **1b**, i.e., with carbocations of low Lewis acidity, while the ionization equilibrium is on the side of the ions for (**1a**–**f**)-NCS[8] indicates that NCO^- is a much stronger Lewis base towards carbocations than NCS^-. A direct comparison of the N-nucleophilicities of NCO^- and NCS^- can be derived from their reactions with the benzhydrylium ions **1g** and **1i**: The nitrogen of NCO^- is 500–1000 times more reactive than the nitrogen of NCS^-.

Conclusion

We finally want to come back to the question of charge and orbital control: Do S_N1 reactions of cyanates proceed with charge control to give alkyl cyanates? Figure 5.1 shows that carbocations with electrophilicity parameters $E > -1$, i. e., carbocations which are less stabilized than the dianisylcarbenium ion **1k** or the tritylium ion undergo diffusion-controlled reactions with NCO^-. Those types of carbocations which are typically generated as intermediates of S_N1 reactions will therefore undergo barrier-less reactions with the cyanate anion without passing through a transition state, and reactivity concepts which are based on relative activation energies cannot be employed. Because similar situations have recently been reported for the reactions of carbocations with SCN^-,[8] CN^-,[15] and NO_2^-,[12] cyanate anions are the fourth example of prototype ambident anions, the behavior of which cannot be explained by the HSAB concept or the concept of charge and orbital control. Other cases can be expected to follow.

References

(1) a) *The Chemistry of Cyanates and Their Thio Derivatives,* Part 1; Patai, S. Ed.; Wiley: New York, **1977**. b) *The Chemistry of Cyanates and Their Thio Derivatives,* Part 2; Patai S. Ed.; Wiley: New York, **1977**. c) *Ambident Anions*; Reutov, O. A., Beletskaya, I. P., Kurts, A. L. Eds.; Consultants Bureau, New York, **1983**.

(2) Schädler, H. D.; Köhler, H. *Z. Chem.* **1990**, *30*, 67.

(3) *Chemical Reactivity and Reaction Paths*;: Klopman, G. Ed., Wiley, New York, **1974**.

(4) Holm, A.; Wentrup, C. *Acta Chem. Scand.* **1966**, *20*, 2123-2127.

(5) Wurtz, A. v.; *Liebigs Ann. Chem.* **1849**, *71*, 326-342.

(6) Slotta, K. H. L. Lorenz, *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 1320-1323.

(7) a) Jensen, K. A.; Holm, A. *Acta Chem. Scand.* **1964**, *18*, 826-828. b) Jensen, K. A.; Due, M.; Holm, A.; *Acta Chem. Scand.* **1965**, *19*, 438-442. c) Martin, D.; Niclas, H. J.; Habisch, D. *Liebigs Ann. Chem.* **1969**, *727*, 10-21. d) Pasinszki, T.; Havasi, B.; Kovács, A. *J. Phys. Chem. A* **2003**, *107*, 1720-1726.

(8) Loos, R.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 14126-14132.

(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) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66-77.

(11) Schaller, H. F.; Tishkov, A. A.; Feng, X.; Mayr, H. *J. Am. Chem. Soc.* **2008**, *130*, 3012-3022.

(12) Tishkov, A. A.; Schmidhammer, U.; Roth, S.; Riedle, E.; Mayr, H. *Angew. Chem.* **2005**, *117*, 4699-4703; *Angew. Chem. Int. Ed.* **2005**, *44*, 4623-4626.

(13) Schmidhammer, U.; Roth, S.; Riedle, E.; Tishkov, A. A.; Mayr, H. *Rev. Sci. Instrum.* **2005**, *76*, 093111.

(14) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710-7716.

(15) Tishkov, A. A.; Mayr, H. *Angew. Chem.* **2005**, *117*, 145-148; *Angew. Chem. Int. Ed.* **2005**, *44*, 142-145.

- Experimental Section -

Ambident Reactivity of the Cyanate Anion

Schaller, H. F.; Schmidhammer, U.; Riedle, E.; Mayr, H. *Chem. Eur. J.* **2008**, *14*, 3866-3868.

General

Materials. Commercially available acetonitrile (extra dry, Acros) was used without further purification for all experiments.The benzhydrylium tetrafluoroborates $Ar_2CH^+ BF_4^-$ and benzhydryl chlorides Ar_2CH-Cl were prepared as described before.[S1,S2] Tetraethylammonium cyanate was synthesized from $Et_4N^+ BF_4^-$ and KOCN in ethanol according to literature.[S3]

Spectroscopy. ^1H and ^{13}C NMR chemical shifts are expressed in ppm and refer to $CDCl_3$: δ_H = 7.26, δ_C = 77.2. An IR-Spectrometer (Spectrum BX from Perkin Elmer) with an ATR unit (attenuated total reflection; Dura Sampler Diamond ATR from Smiths Detection) was used to record the IR spectra.

Kinetics

Determination of the Rates of the Combinations of Benzhydrylium Ions with the Cyanate Anion. Reactions of cyanate ions with the colored benzhydrylium ions gave colorless products. The reactions of (**1a–l**)-BF_4 with $Et_4N^+OCN^-$ were followed photometrically at the absorption maxima of Ar_2CH^+ (460–645 nm) by UV-Vis spectroscopy. All experiments were performed under first-order conditions (excess of $Et_4N^+OCN^-$) at 20 °C in acetonitrile. First-order rate constants k_{obs} were obtained by least-squares fitting of the decay absorbances to the mono-exponential curve $A_t = A_0 \exp(-k_{obs}t)$.

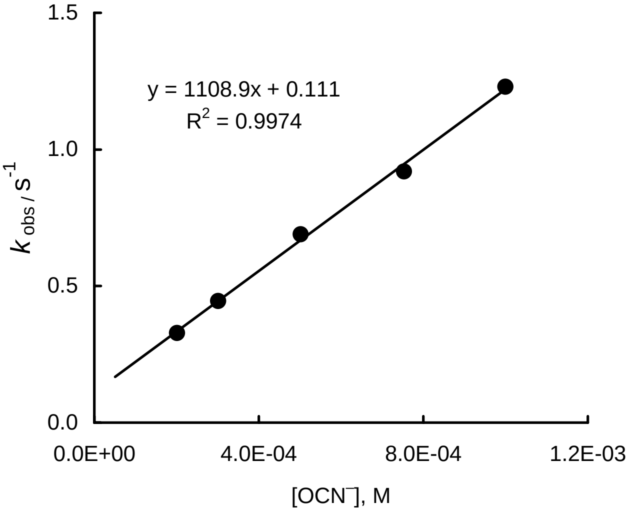
For electrophiles **1a-f** a stopped-flow instrument (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software) was used in single-mode by mixing equal volumes of a **(1a–f)**-BF_4 and a $Et_4N^+ OCN^-$ solution as reported previously.[S1]

As described in the main text of chapter 5, the less stabilized benzhydrylium ions ($E \geq -6$) were generated from suitable precursors [**1g–i** from (**1g–i**)-NCO, **1j** from **1j**-Cl, **1l** from **1l**-Cl] by laser flash photolysis.[S4, S5] Initial concentrations of the cation precursors are given in the tables below. The actual carbocation concentrations are much lower than the initial precursor concentrations because each laser pulse converts only 1–4 % of the precursor molecules into the corresponding carbocations. Due to the high molar exctinction coefficient of the carbocations and the low one of the precursors, still an excellent detectivity results. Care was taken to exchange the sample between laser shots to avoid accumulative effects. At the same time the sample was kept long enough in the observation region to allow the recording of the full decay curve.

Combination Reaction of the Cyanate Anion with 1a in Acetonitrile

(20 °C, Stopped-Flow Technique, Monitored at 632 nm)

No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	9.92×10^{-6}	2.01×10^{-4}	3.28×10^{-1}
2	9.92×10^{-6}	3.01×10^{-4}	4.45×10^{-1}
3	9.92×10^{-6}	5.02×10^{-4}	6.90×10^{-1}
4	9.92×10^{-6}	7.53×10^{-4}	9.19×10^{-1}
5	9.92×10^{-6}	1.00×10^{-3}	1.23

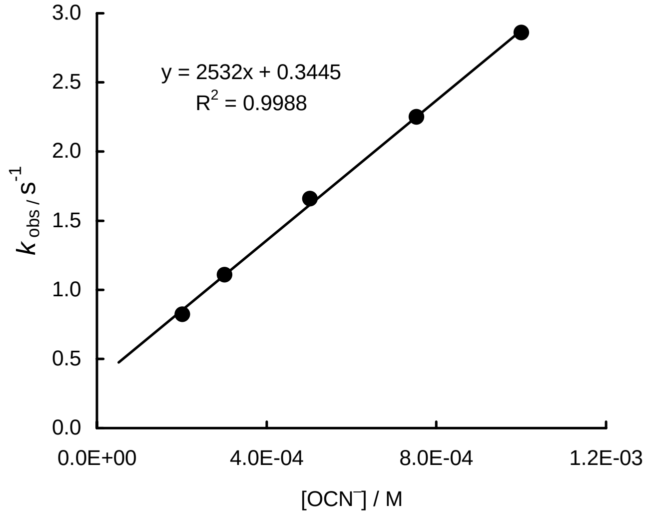


$\boldsymbol{k_2 = 1.11 \times 10^3\ M^{-1}\ s^{-1}}$

Combination Reaction of the Cyanate Anion with 1b in Acetonitrile

(20 °C, Stopped-Flow Technique, Monitored at 635 nm)

No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	8.49×10^{-6}	2.01×10^{-4}	8.23×10^{-1}
2	8.49×10^{-6}	3.01×10^{-4}	1.11
3	8.49×10^{-6}	5.02×10^{-4}	1.66
4	8.49×10^{-6}	7.53×10^{-4}	2.25
5	8.49×10^{-6}	1.00×10^{-3}	2.86

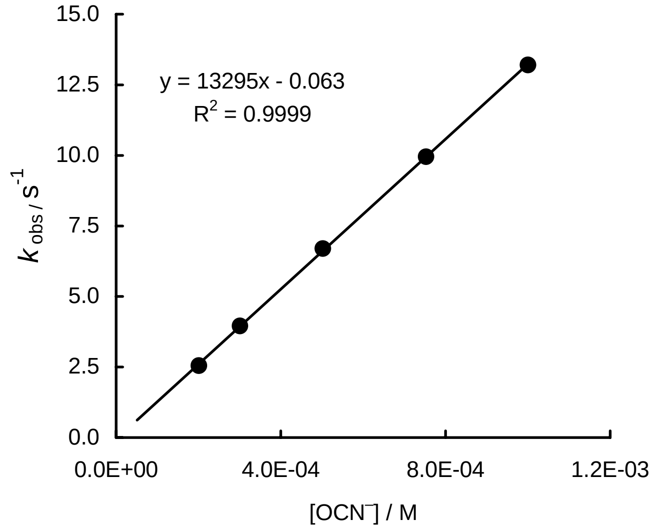


$k_2 = 2.53 \times 10^3$ M^{-1} s^{-1}

Combination Reaction of the Cyanate Anion with 1c in Acetonitrile

(20 °C, Stopped-Flow Technique, Monitored at 616 nm)

No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	9.91×10^{-6}	2.01×10^{-4}	2.55
2	9.91×10^{-6}	3.01×10^{-4}	3.95
3	9.91×10^{-6}	5.02×10^{-4}	6.69
4	9.91×10^{-6}	7.53×10^{-4}	9.95
5	9.91×10^{-6}	1.00×10^{-3}	1.32×10^{1}

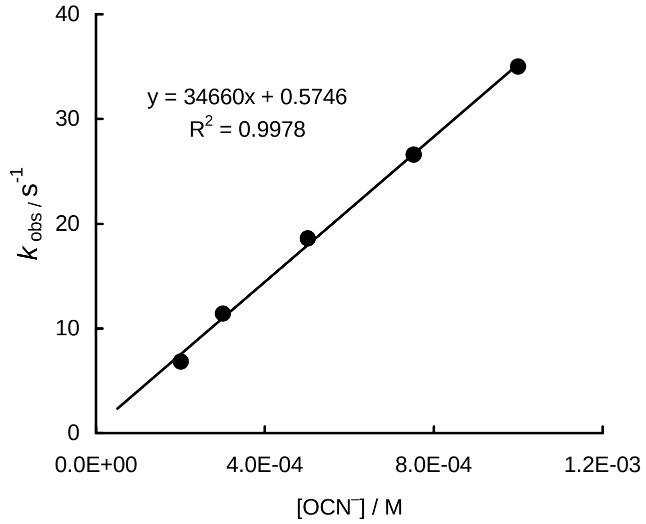


$k_2 = 1.33 \times 10^4$ M^{-1} s^{-1}

Combination Reaction of the Cyanate Anion with 1d in Acetonitrile

(20 °C, Stopped-Flow Technique, Monitored at 620 nm)

No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	1.00×10^{-5}	2.01×10^{-4}	6.83
2	1.00×10^{-5}	3.01×10^{-4}	1.14×10^{1}
3	1.00×10^{-5}	5.02×10^{-4}	1.86×10^{1}
4	1.00×10^{-5}	7.53×10^{-4}	2.66×10^{1}
5	1.00×10^{-5}	1.00×10^{-3}	3.50×10^{1}

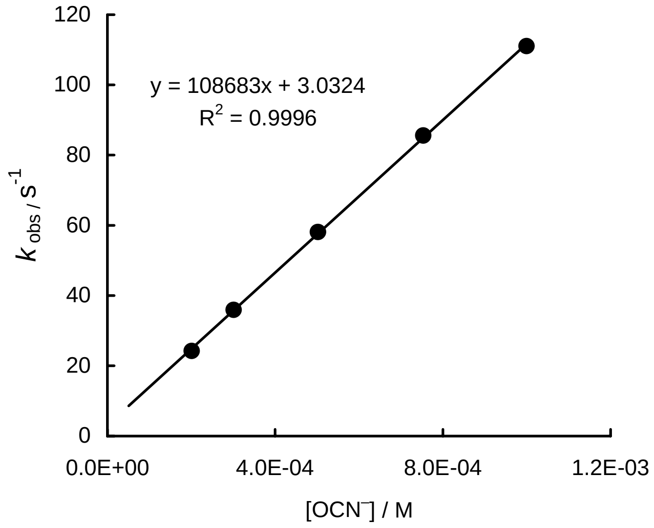


$k_2 = 3.47 \times 10^4$ M^{-1} s^{-1}

Combination Reaction of the Cyanate Anion with 1e in Acetonitrile

(20 °C, Stopped-Flow Technique, Monitored at 612 nm)

No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	9.99×10^{-6}	2.01×10^{-4}	2.42×10^{1}
2	9.99×10^{-6}	3.01×10^{-4}	3.59×10^{1}
3	9.99×10^{-6}	5.02×10^{-4}	5.81×10^{1}
4	9.99×10^{-6}	7.53×10^{-4}	8.56×10^{1}
5	9.99×10^{-6}	1.00×10^{-3}	1.11×10^{2}

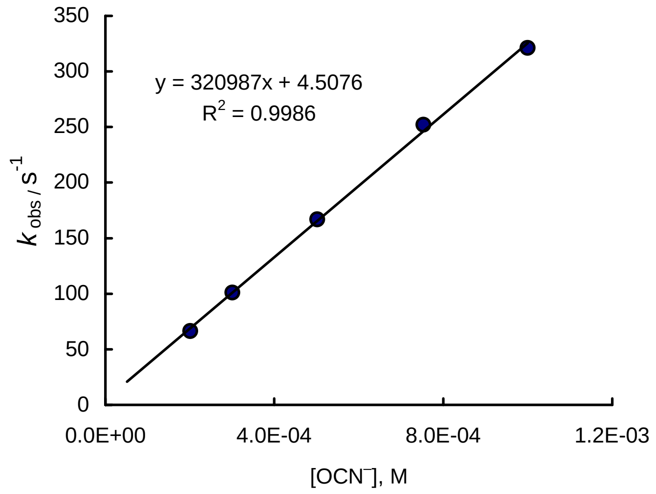


$k_2 = 1.09 \times 10^5$ M^{-1} s^{-1}

Combination Reaction of the Cyanate Anion with 1f in Acetonitrile

(20 °C, Stopped-Flow Technique, Monitored at 605 nm)

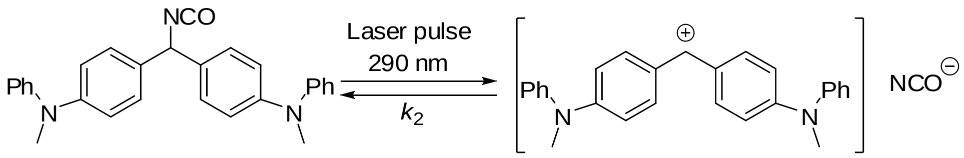
No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	1.01×10^{-5}	2.01×10^{-4}	6.65×10^{1}
2	1.01×10^{-5}	3.01×10^{-4}	1.01×10^{2}
3	1.01×10^{-5}	5.02×10^{-4}	1.67×10^{2}
4	1.01×10^{-5}	7.53×10^{-4}	2.52×10^{2}
5	1.01×10^{-5}	1.00×10^{-3}	3.21×10^{2}



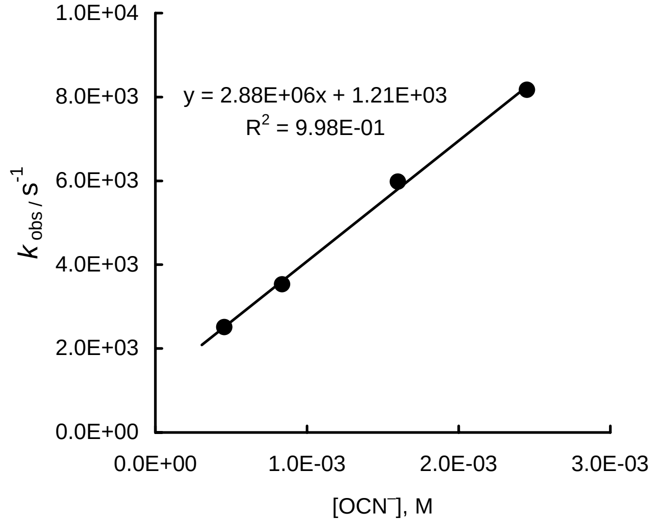
$k_2 = 3.21 \times 10^5$ M^{-1} s^{-1}

Combination Reaction of the Cyanate Anion with 1g in Acetonitrile

(20 °C, Laser-Flash Technique, Monitored at 613 nm)



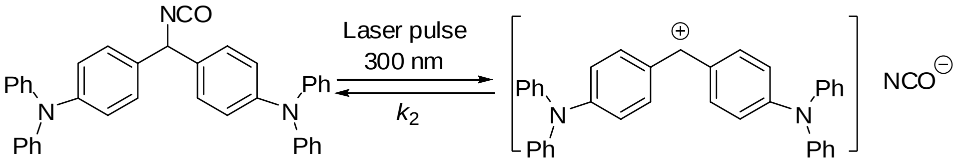
No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	4.01×10^{-4}	4.56×10^{-4}	2.51×10^{3}
2	4.01×10^{-4}	8.36×10^{-4}	3.53×10^{3}
3	4.01×10^{-4}	1.60×10^{-3}	5.98×10^{3}
4	4.01×10^{-4}	2.45×10^{-3}	8.17×10^{3}



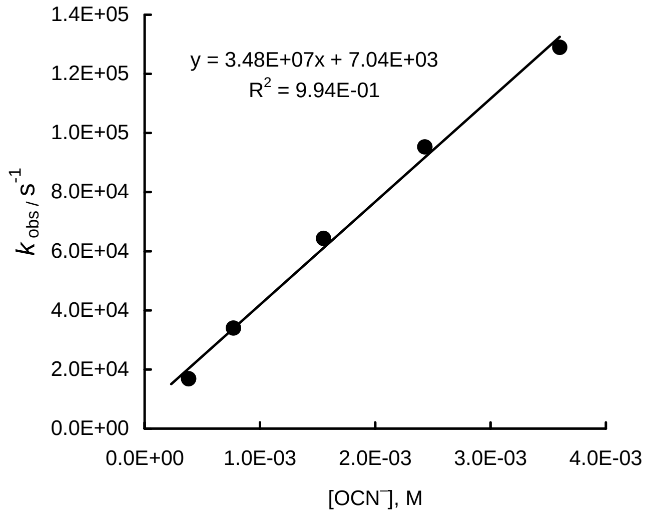
$k_2 = 2.88 \times 10^6$ M^{-1} s^{-1}

Combination Reaction of the Cyanate Anion with 1h in Acetonitrile

(20 °C, Laser-Flash Technique, Monitored at 645 nm)



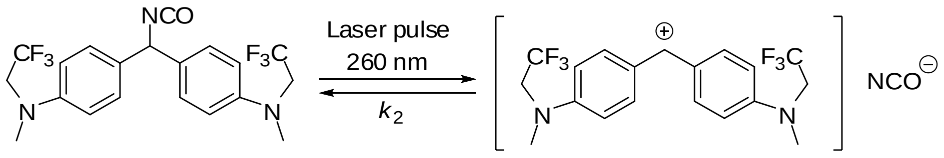
No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	4.00×10^{-4}	5.80×10^{-4}	1.68×10^{4}
2	4.00×10^{-4}	9.70×10^{-4}	3.40×10^{4}
3	4.00×10^{-4}	1.75×10^{-3}	6.43×10^{4}
4	4.00×10^{-4}	2.63×10^{-3}	9.53×10^{4}
5	4.00×10^{-4}	3.80×10^{-3}	1.29×10^{5}



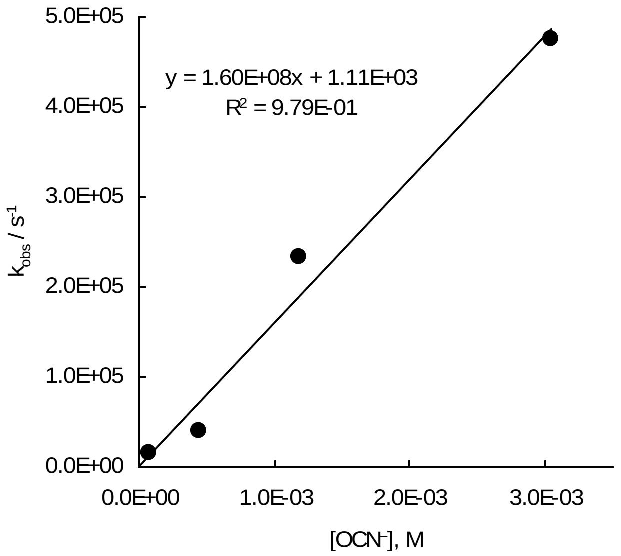
$k_2 = 3.48 \times 10^7$ M^{-1} s^{-1}

Combination Reaction of the Cyanate Anion with 1i in Acetonitrile

(20 °C, Laser-Flash Technique, Monitored at 585 nm)



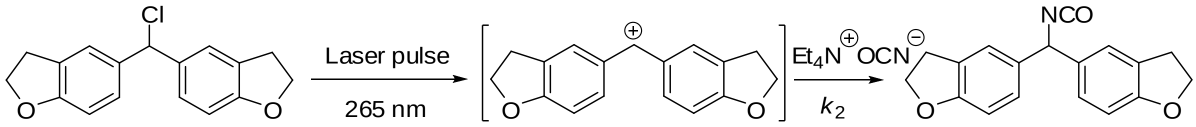
No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	4.00×10^{-4}	7.30×10^{-5}	1.53×10^{4}
2	4.00×10^{-4}	4.44×10^{-4}	3.95×10^{4}
3	4.00×10^{-4}	1.19×10^{-3}	2.33×10^{5}
4	4.00×10^{-4}	3.05×10^{-3}	4.76×10^{5}



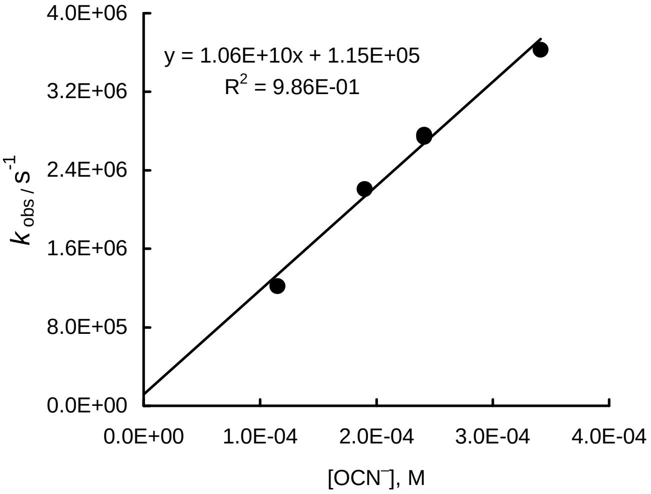
k_2 = 1.60 × 10^8 $M^{–1}$ $s^{–1}$

Combination Reaction of the Cyanate Anion with 1j in Acetonitrile

(20 °C, Laser-Flash Technique, Monitored at 525 nm)



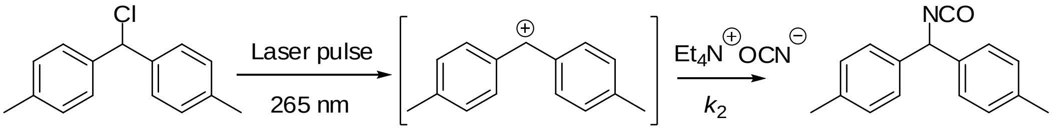
No.	$[Ar_2CH^+]_0$, M	$[OCN^–]_0$, M	k_{obs}, $s^{–1}$
1	$6.07 \times 10^{–4}$	$1.15 \times 10^{–4}$	1.22×10^6
2	$6.07 \times 10^{–4}$	$1.90 \times 10^{–4}$	2.21×10^6
3	$6.07 \times 10^{–4}$	$2.41 \times 10^{–4}$	2.74×10^6
4	$6.07 \times 10^{–4}$	$2.41 \times 10^{–4}$	2.76×10^6
5	$6.07 \times 10^{–4}$	$3.41 \times 10^{–4}$	3.63×10^6



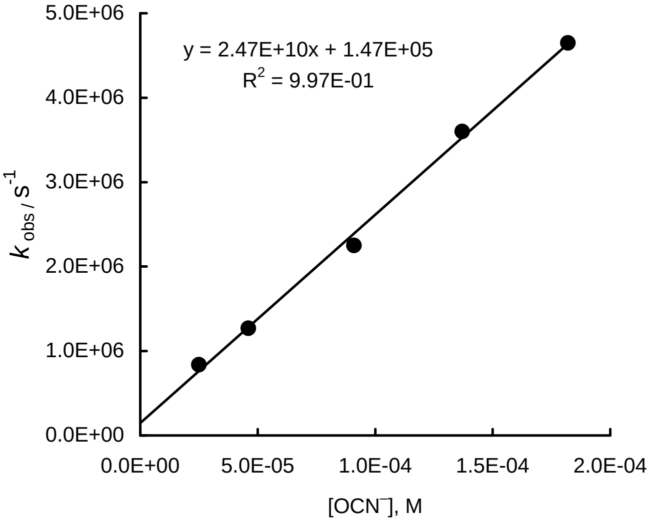
k_2 = 1.06 × 10^{10} $M^{–1}$ $s^{–1}$

Combination Reaction of the Cyanate Anion with 1l in Acetonitrile

(20 °C, Laser-Flash Technique, Monitored at 460 nm)



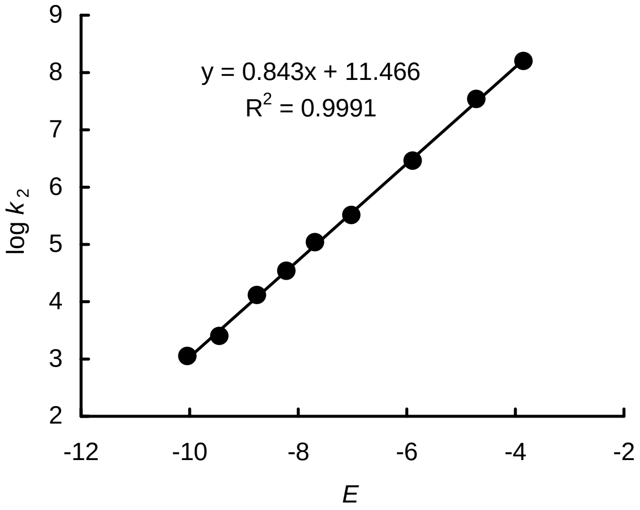
No.	$[Ar_2CH^+]_0$, M	$[OCN^-]_0$, M	k_{obs}, s^{-1}
1	3.76×10^{-3}	2.50×10^{-5}	8.38×10^{5}
2	3.76×10^{-3}	4.60×10^{-5}	1.27×10^{6}
3	3.76×10^{-3}	9.10×10^{-5}	2.25×10^{6}
4	3.76×10^{-3}	1.37×10^{-4}	3.60×10^{6}
5	3.76×10^{-3}	1.82×10^{-4}	4.65×10^{6}



$k_2 = 2.47 \times 10^{10}\ M^{-1}\ s^{-1}$

Determination of the Nucleophilicity Parameters *N* and *s* for the Cyanate Anion in Acetonitrile (at 20 °C)

Ar_2CH^+	E	k_2, $M^{-1}\ s^{-1}$	$\lg k_2$
1a	–10.04	1.11×10^{3}	3.05
1b	–9.45	2.53×10^{3}	3.40
1c	–8.76	1.33×10^{4}	4.12
1d	–8.22	3.47×10^{4}	4.54
1e	–7.69	1.09×10^{5}	5.04
1f	–7.02	3.21×10^{5}	5.51
1g	–5.89	2.88×10^{6}	6.46
1h	–4.72	3.48×10^{7}	7.54
1i	–3.85	1.60×10^{8}	8.20

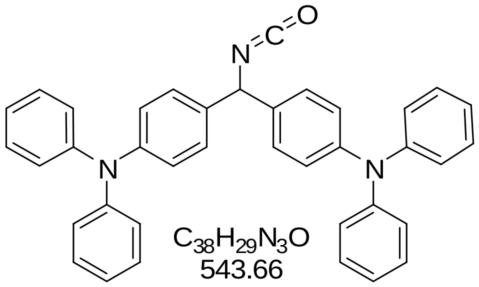


***N* = 13.60**
***s* = 0.84**

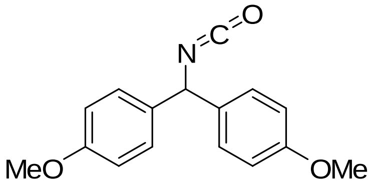
The second-order rate constants $k_2 > 1 \times 10^{10}$ M^{-1} s^{-1} for the reactions of the cyanate anion with electrophiles **1j,l** were excluded because they are affected by the diffusion limit.

Product Characterization

1h-NCO. To a solution of **1h**-BF_4 (1.00 mmol, 588 mg) in dry acetonitrile (10 mL) tetraethylammonium cyanate (1.10 mmol, 189 mg) was added under nitrogen atmosphere. Instantly, the deeply green colored solution turned colorless. After evaporation of ca. 8 mL of the acetonitrile, Et_2O (5 mL) was added to the residue. The resulting suspension was treated for 10 min with ultrasound and then filtered through glass wool. The solvents were evaporated under reduced pressure: **1h**-NCO (391 mg, 72 %), slightly yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.75 (s, 1 H, *H*CNCO), 7.03–7.29 ppm (m, 28 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 61.5 (d, H*C*NCO), 123.3, 123.4, 124.7, 124.4, 124.7, 127.5, 129.4, 135.1, 147.7 ppm. MS (EI): *m/z* (%): 543 (13) [M]$^+$, 503 (19), 502 (77), 501 (100) [M-NCO]$^+$; HR-MS (EI): calcd. for $C_{38}H_{29}N_3O$ 543.2311, found 543.2325.

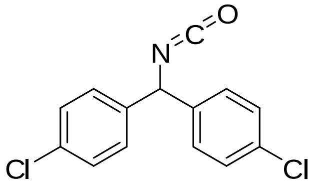


1k-NCO. To a solution of **1k**-Cl (1.00 mmol, 263 mg) in dry acetonitrile (10 mL) tetraethylammonium cyanate (1.10 mmol, 189 mg) was added under nitrogen atmosphere. The solution was stirred at 40 °C for 4 h. After evaporation of ca. 8 mL of the acetonitrile, Et_2O (5 mL) was added to the residue. The resulting suspension was treated for 10 min with ultrasound and then filtered through glass wool. The solvents were evaporated under reduced pressure to give a viscous liquid residue that was purified by column chromatography (silica gel, CH_2Cl_2, $R_f = 0.85$): **1k**-NCO (166 mg, 62 %), colorless solid. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 3.77$ (s, 6 H, OC*H*$_3$), 5.75 (s, 1 H, *H*CNCO) 6.87 (d, *J* = 8.7 Hz, 4 H, ArH), 7.21 ppm (d, *J* = 8.7 Hz, 4 H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 55.4$ (q, OMe), 61.3 (d, *C*HNCO), 114.2 (d, Ar), 127.82 (d, Ar), 128.57 (s, N*C*O), 134.0 (s, *C*-CHNCO), 159.3 ppm (*C*-OMe). MS (EI): *m/z* (%): 269 (21) $[M]^+$, 228 (22), 227 (100) $[M\text{-}NCO]^+$, 212 (7), 197 (7); HR-MS (EI): calcd for $C_{16}H_{15}NO_3$ 269.1052, found 269.1031.



$C_{16}H_{15}NO_3$
269.30

1m-NCO. A mixture of **1m**-Cl (1.00 mmol, 272 mg) and silver cyanate (1.20 mmol, 180 mg) in diethyl ether (15 mL) was stirred for 1 h at room temperature in the dark. The suspension was filtered, and the solvent was evaporated: **1m**-NCO (264 mg, 95 %), colorless oil.



$C_{14}H_9Cl_2NO$
278.13

When **1m**-Cl (1.00 mmol) and silver cyanate (1.20 mmol) reacted in nitromethane (15 mL), 255 mg (92 %) **1m**-NCO was obtained. ^1H NMR (600 MHz, $CDCl_3$): δ = 5.80 (s, 1 H, C*H*NCO), 7.22 (d, *J* = 8.6 Hz, 4 H, ArH), 7.33 ppm (d, *J* = 8.6 Hz, 4 H, ArH); a crosspeak for ^1H (δ = 5.80 ppm) and ^{15}N (δ = 46.25 ppm) is observed in a gHMBC experiment (400 MHz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 60.8 (d, *C*HNCO), 124.8 (s, N*C*O), 127.8 (d, Ar), 129.1 (d, Ar), 134.1 (s, *C*-CHNCO), 139.3 (s, Ar); IR (ATR, cm^{-1}): 2244 (s, –N=C=O), 1498 (m), 1409 (w), 1089 (m), 1013 (m), 814 (m), 785 (m).

References

(S1) 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.

(S2) 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.

(S3) Kobler, H.; Munz, R.; Al Gasser, G.; Simchen, G. *Liebigs Ann. Chem.* **1978**, 1937-1945.

(S4) Schmidhammer, U.; Roth, S.; Riedle, E.; Tishkov, A. A.; Mayr, H. *Rev. Sci. Instrum.* **2005**, *76*, 093111.

(S5) Tishkov, A. A.; Schmidhammer, U. Roth, S.; Riedle, E.; Mayr, H. *Angew. Chem.* **2005**, *117*, 4699-4703; *Angew. Chem. Int. Ed.* **2005**, *44*, 4623-4626.

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