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Original Scientific Article

The Reactivity of Benzoates in Mixtures of Water and Aprotic Solvents†

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Abstract. Nucleofugalities of pentafluorobenzoate (PFB), 2,4,6-trifluorobenzoate (TFB), 2-nitrobenzoate, and 3,5-dinitrobenzoate (DNB) leaving groups have been derived from the solvolysis rate constants of the corresponding X,Y-substituted Z-benzhydryl benzoates in 60 % and 80 % aqueous acetonitrile and 60 % aqueous acetone, by applying the LFER equation: $\log k = s_f(E_f + N_f)$. The experimental barriers ($\Delta G^{\ddagger}_{\mathrm{exp}}$) for solvolyses of 13 dianisylmethyl Z-substituted benzoates in these solvents correlate very well with the $\Delta H^{\ddagger}_{\mathrm{calc}}$ of the model epoxy ring formation (calculated earlier by the B3LYP-PCM quantum-chemical method). Using the $\Delta G^{\ddagger}_{\mathrm{exp}}$ *vs.* $\Delta H^{\ddagger}_{\mathrm{calc}}$ correlation, and taking s_f based on similarity, the nucleofugality parameters for about 70 benzoates have been determined in 60 % and 80 % aqueous acetonitrile and 60 % aqueous acetone. Z-Substituents on the phenyl ring have larger impact on the solvolytic reactivity in the less polar solvent than in the more polar solvent due to the more carbocation-like transition state. (doi: 10.5562/cca2179)

Keywords: nucleofugality, reactivity, substituted benzoate, aprotic solvent

INTRODUCTION

A heterolysis step in S_N1 solvolytic displacement involves generation of a leaving group (nucleofuge) that departs with its bonding electrons, and a carbocation (electrofuge) that departs without an electron pair. It is convenient to express the leaving group effect on reactivity with its nucleofugality (N_f) and the effect of the carbocation structure on reactivity with its electrofugality (E_f). These are kinetic terms developed on the solvolytic behavior of benzhydryl derivatives.[1,2] Since the effect of the leaving group on reactivity depends on solvent, mostly due to its differential solvation, the nucleofugality has been defined for a combination of the leaving group and the solvent. Because of the linear correlation between the logarithms of solvolysis rate constants and electrofugalities of generated benzhydrylium ions, the S_N1 reactivity of any benzhydryl derivative in a given solvent can be estimated semiquantitatively according to the following three-parameter LFER equation:

$$\log k\ (25\ ^\circ\mathrm{C}) = s_f(E_f + N_f) \qquad (1)$$

in which: k is the first-order rate constant for S_N1 reaction, s_f (slope of the $\log k / E_f$ correlation line) and N_f (nucleofugality; negative intercept on the abscissa) are the nucleofuge specific parameters, and E_f is the electrofugality parameter.[2] Predefined parameters are $s_f = 1.00$ for the chloride nucleofuge in pure ethanol and $E_f = 0.00$ for dianisylcarbenium ion. Accordingly, the reactivity of a given nucleofuge in a given solvent is defined with two variables, the slope parameter (s_f) and the nucleofugality (N_f), whose product ($s_f \times N_f$) corresponds to solvolysis $\log k$ of its dianisylmethyl derivative at 25 °C. The nucleofugality parameters (N_f and s_f) for numerous leaving group/solvent combinations have already been defined using Equation (1), constituting a comprehensive nucleofugality scale.[2–4] It should be mentioned that the s_f parameters mostly range from 0.8 to 1.2, so the sole N_f parameter indicates the reactivity of the given leaving group reasonably well.

Benzoates have widely been used as leaving groups in solvolytic reactions because their reactivities can be altered with a variation of the substituents on the phenyl ring. Whereas benzoate anion constitutes a poor leaving group, benzoates with electron-accepting substituents enhance the solvolytic reactivity. Thus, in most solvents *p*-nitrobenzoates solvolyze about one order of magnitude faster than the corresponding benzoates, while 3,5-dinitrobenzoates solvolyze faster for about two orders of magnitude.[2]

We have recently investigated the S_N1 reactivities of substituted benzoates in aqueous alcohols by measuring the heterolysis rates of X,Y-substituted benzhydryl benzoates.[4] We have also presented the method for

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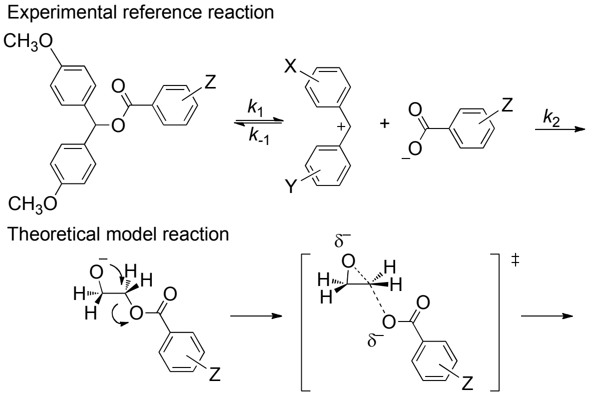


Z = H, penta-F, 2,4,6-tri-F, 2-NO_2, 3-NO_2, 4-NO_2, 3,5-di-NO_2, 4-CN, 2-CF_3, 3,5-di-CF_3, 2-MeO, 3,5-di-Cl, and 2,4,6-tri-Me

Scheme 1.

estimating the nucleofugality of given benzoates by correlating experimental barriers ($\Delta G^{\ddagger}$) for solvolysis of benzhydryl benzoates with enthalpies of activation ($\Delta H^{\ddagger}$) of model reaction, obtained by quantum-chemical calculation.

According to the method, twelve Z-substituted benzoates (Z represents one or more substituents on the phenyl ring) have been chosen for reference leaving groups which are as follows: benzoate (Bz), pentafluorobenzoate (PFB), trifluorobenzoate (TFB), 2-nitrobenzoate, 3-nitrobenzoate, 4-nitrobenzoate (PNB), 3,5-dinitrobenzoate (DNB), 4-cyanobenzoate, 2-trifluoromethylbenzoate, 2-methoxybenzoate, 3,5-dichlorobenzoate and 2,4,6-trimethylbenzoate. For experimental reference data the Gibbs free energies of activation ($\Delta G^{\ddagger}$) for solvolysis of dianisylmethyl derivatives (X = Y = OCH_3 on Scheme 1) of the 12 reference benzoates at 25 °C in 90, 80 and 70 % aqueous ethanol have been taken. For the computed model reaction, the epoxy ring formation starting from 2-oxyethyl Z-benzoate has been chosen (Scheme 1). Geometries of the substrates and the corresponding transition states for the all 12 model reactions have been optimized at the B3LYP/6-311+G(2d,p) level of theory using polarizable continuum (PCM) that mimics water as a solvent. The enthalpies of activation ($\Delta H^{\ddagger}$) obtained have been taken as calculated reference data. The correlation between the experimental $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ calculated by Gaussian 03 turned out excellent (*e.g.* $r = 0.997$ with *rms error* = 0.10 kcal mol^{-1} in 90 % aq. ethanol), enabling extrapolation of $\Delta G^{\ddagger}$ for a heterolysis reaction of any benzoate in a series of aqueous ethanol mixtures. Taking $\Delta H^{\ddagger}$ instead of $\Delta G^{\ddagger}$ is justified with two reasons. Essentially invariant experimental $\Delta S^{\ddagger}$ obtained in solvolyses of numerous benzoates in aqueous solvents indicate that the impact of the entropy of activation on the overall reactivity in these reactions is small and that $\Delta H^{\ddagger}$ is a rate-determining variable. The second reason is that without additional corrections the calculated entropy term included into the calculated Gibbs free energy of activation tends to be quantitatively inaccurate.

In this work we have extended our investigation of solvolytic behavior of benzoates further, to mixtures of water and aprotic solvents such are acetone and acetonitrile. Nucleofugalities of various benzoates in these solvents have been determined either experimentally or by applying the above mentioned model. Furthermore, the effects on reactivity of these solvents have been compared with the effects of aqueous ethanol mixtures as well as the effects of the benzoate substituents on reactivity.

EXPERIMENTAL

Substrate Preparation

4,4'-Dimethoxybenzhydryl 3,5-bis(trifluoromethyl)benzoate. A solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.79 g, 2.9 mmol) in anhydrous benzene (10 mL) was added dropwise to the previously prepared solution of 4,4'-dimethoxybenzhydrol (0.50 g, 2.1 mmol) and pyridine (0.45 g, 5.7 mmol) in anhydrous benzene (30 mL). The reaction mixture was stirred over the night under the atmosphere of argon at ambient temperature. Precipitated pyridinium chloride was removed by filtration and the excess of pyridine was removed by 10 % hydrochloric acid. The benzene layer was separated and washed with water. After drying over anhydrous sodium sulfate, benzene was evaporated in vacuo. The crude product was dissolved in diethyl ether (30 mL) and then about 30 mL of concd. aq. NaOH was added. The mixture was stirred for 1 h, and then the organic layer was separated and washed with water. After drying over anhydrous sodium sulfate, the solvent was removed in vacuo to give pale-yellow oil (0.71 g; yield 71.7 %). ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ/ppm = 3.80 (s, 6H, Ar-OCH_3), 6.91 (d, J = 8.8 Hz, 4H; ArH), 7.11 (s, 1H, Ar_2CH), 7.34 (d, J = 8,7 Hz, 4H; ArH), 8.07 (s, 1H, $(CF_3)_2$-ArH), 8.52 (s, 2H; $(CF_3)_2$-ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ/ppm = 55.5 (Ar**O**CH_3), 78.6 (Ar_2**C**H), 114.2, 121.2, 126.6 (F_3C-Ar), 128.8, 129.9, 131.8, 132.2, 132.7, 159.7 (Ar), 163.3 (C=O).

4-Methoxy-, 4-methoxy-4'-methyl- and 4-methoxy-4'-phenoxybenzhydryl 2-nitrobenzoate were prepared according to the procedure described for 4,4'-dimethoxybenzhydryl 2-nitrobenzoate in the Ref. 4.

4-Methoxybenzhydryl 2-nitrobenzoate (4-methoxybenzhydrol (0.50 g; 2.3 mmol), pyridine (0.52 g; 6.5 mmol), 2-nitrobenzoyl chloride (0.61 g; 3.3 mmol); yield 0.60 g, 70.6 %): ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ/ppm = 3.79 (s, 3H, Ar-OCH_3), 6.89 (d, J = 8.7 Hz, 2H; ArH), 7.08 (s, 1H, Ar_2CH), 7.29–7.45 (m, 7H; ArH), 7.58–7.67 (m, 2H, O_2N-ArH), 7.74 (d, J = 6.7 Hz, 1H; O_2N-

ArH), 7.87 (d, J = 6.4 Hz, 1H; O_2N-ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ/ppm = 55.6 ($ArOCH_3$), 79.4 (Ar_2**C**H), 114.3, 121.8, 124.2, 127.4, 128.4, 128.9, 129.3, 130.4, 131.7, 132.3, 133.1, 139.8, 148.6, 159.9 (Ar), 164.7 (C=O).

4-Methoxy-4'-methylbenzhydryl 2-nitrobenzoate (4-methoxy-4'-methylbenzhydrol (0.50 g; 2.2 mmol), pyridine (0.49 g; 6.1 mmol), 2-nitrobenzoyl chloride (0.57 g; 3.1 mmol); yield 0.63 g, 75.9 %): ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ/ppm = 2.34 (s, 3H; Ar-CH_3), 3.79 (s, 3H; Ar-OCH_3), 6.88 (d, J = 7.0 Hz, 2H; ArH), 7.06 (s, 1H, Ar_2CH), 7.17 (d, J = 7.9 Hz, 2H; ArH), 7.18–7.32 (m, 4H; ArH), 7.58–7.67 (m, 2H, O_2N-ArH), 7.74 (d, J = 7.3 Hz, 1H; O_2N-ArH), 7.88 (d, J = 6.9 Hz, 1H; O_2N-ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ/ppm = 21.5 ($ArCH_3$), 55.6 ($ArOCH_3$), 79.4 (Ar_2CH), 114.3, 124.2, 127.4, 127.8, 128.7, 129.2, 129.6, 130.4, 131.9, 132.2, 133.0, 136.8, 138.2, 159.8 (Ar), 164.6 (C=O).

4-Methoxy-4'-phenoxybenzhydryl 2-nitrobenzoate (4-methoxy-4'-phenoxybenzhydrol (0.50 g; 1.6 mmol), pyridine (0.36 g; 4.6 mmol), 2-nitrobenzoyl chloride (0.42 g; 2.3 mmol); yield 0.63 g, 75.9 %): ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ/ppm = 3.81 (s, 3H, Ar-OCH_3), 6.91 (d, J = 8.5 Hz, 2H; ArH), 6.97–7.13 (m, 6H; Ar_2CH + ArH), 7.30–7.37 (m, 6H; ArH), 7.60–7.69 (m, 2H, O_2N-ArH), 7.75 (d, J = 6.9 Hz, 1H; O_2N-ArH), 7.90 (d, J = 6.7 Hz, 1H; O_2N-ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ/ppm = 55.6 ($ArOCH_3$), 79.0 (Ar_2CH), 114.3, 118.9, 119.6, 123.9, 124.2, 127.7, 129.1, 130.1, 130.4, 131.7, 132.3, 133.1, 134.4, 148.6, 157.1, 157.6, 159.9 (Ar), 164.7 (C=O).

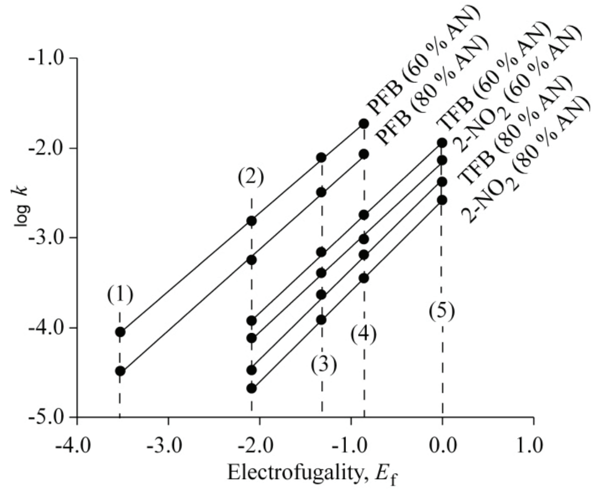


Figure 1. Plots of log k (25 °C) versus E_f for solvolysis of substituted benzhydryl pentafluorobenzoates (PFB), 2,4,6-trifluorobenzoates (TFB), and 2-nitrobenzoates (2-NO_2) in aqueous acetonitrile (volume fractions), (1): X = PhO, Y = H; (2): X = MeO, Y = H; (3): X = MeO, Y = Me; (4): X = MeO, Y = PhO; (5): X = Y = MeO.

4-Methoxy-, 4-methoxy-4'-methyl-, 4-methoxy-4'-phenoxy-, 4,4'-dimethoxybenzhydryl 3,5-dinitrobenzoate and 4,4'-dimethoxy 4-nitrobenzoate were prepared according to the procedure given in the Ref. 1b.

All other substrates were prepared according to the procedure described in the Ref. 4.

Kinetic Methods

Solvolysis rate constants were measured conductometrically. Freshly prepared solvents (30 mL) were thermostated (± 0.1 °C) at a given temperature for several minutes prior to addition of the substrate. Typically, 30–60 mg of substrate were dissolved in 0.10–0.15 mL of dichloromethane and injected into solvent. An increase of the conductivity during solvolysis was monitored automatically by means of a WTW LF 530 conductometer, using the Radiometer 2-pole Conductivity Cell (CDC641T). Individual rate constants were obtained by least-squares fitting of the conductivity data to the first-order kinetic equation for 3–4 half-lives. The rate constants were averaged from at least three measurements. In order to achieve a complete ionization of a liberated acid a proton sponge base [1,8-bis(dimethylamino)naphthalene] was added. The typical molar ratio between the base and the substrate was between 1.5 and 12 depending on a combination of acidity of liberated benzoic acid and an employed solvent. Calibration showed the linear response of conductivity in the presented ranges of concentrations of the proton sponge base and benzoic acids liberated in examined solvolyses.

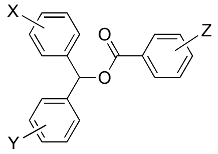
RESULTS AND DISCUSSION

Nucleofugality of Benzoates

X,Y-Substituted benzhydryl Z-benzoates (Scheme 1) have been subjected to kinetic measurements. Solvolysis rates were measured conductometrically in aqueous acetone and aqueous acetonitrile at 25 °C. First-order rate constants are presented in Table 1.

Logarithms of first-order rate constants (at 25 °C) for pentafluorobenzoate (PFB) and trifluorobenzoate (TFB) in 80 % and 60 % acetonitrile, and for 2-nitrobenzoate in 60 % aqueous acetone and 80 % and 60 % acetonitrile have been plotted against the E_f parameters of the benzhydrylium ions.[2] The plots are presented in Figure 1. The nucleofugality parameters have been calculated from the correlation plots. The nucleofuge specific parameters, presented in Table 2, have been obtained with high accuracy due to excellent correlations. It should be mentioned that the order of reactivities of Z-substituted benzoates in the mixtures of aprotic solvents and water are similar as in the series of aqueous ethanol, *i.e.*, it has not been observed significant difference in solvolytic behavior of any Z-benzoate in two solvent systems.

Table 1. Solvolysis Rate Constants of Some Z-substituted Benzoates in Some Mixture of Water and Aprotic Solvents at 25 °C



Z	X, Y	E_f[a]	Solvent[b]	k / s^{-1} [c]
2-NO_2	4-MeO, H	–2.09	80AN20W	$(2.07 \pm 0.06) \times 10^{-5}$
	4-MeO, 4-Me	–1.32		$(1.20 \pm 0.01) \times 10^{-4}$
	4-MeO, 4-PhO	–0.86		$(3.50 \pm 0.05) \times 10^{-4}$
	4-MeO, 4-MeO	0		$(2.60 \pm 0.05) \times 10^{-3}$
	4-MeO, H	–2.09	60AN40W	$(7.55 \pm 0.10) \times 10^{-5}$
	4-MeO, 4-Me	–1.32		$(4.05 \pm 0.02) \times 10^{-4}$
	4-MeO, 4-PhO	–0.86		$(9.67 \pm 0.03) \times 10^{-4}$
	4-MeO, 4-MeO	0		$(7.19 \pm 0.03) \times 10^{-3}$
	4-MeO, H	–2.09	60A40W	$(2.95 \pm 0.02) \times 10^{-5}$
	4-MeO, 4-Me	–1.32		$(1.64 \pm 0.01) \times 10^{-4}$
	4-MeO, 4-PhO	–0.86		$(4.06 \pm 0.06) \times 10^{-4}$
	4-MeO, 4MeO	0		$(3.43 \pm 0.07) \times 10^{-3}$
3,5-di-NO_2	4-MeO, H	–2.09	80AN20W	$(5.13 \pm 0.03) \times 10^{-5}$
	4-MeO, 4-Me	–1.32		$(2.80 \pm 0.03) \times 10^{-4}$
	4-MeO, 4-PhO	–0.86		$(8.07 \pm 0.08) \times 10^{-4}$
	4-MeO, 4-MeO	0		$(5.55 \pm 0.08) \times 10^{-3}$
	4-MeO, H	–2.09	60AN40W	$(1.54 \pm 0.04) \times 10^{-4}$
	4-MeO, 4-Me	–1.32		$(7.27 \pm 0.09) \times 10^{-4}$
	4-MeO, 4-PhO	–0.86		$(1.70 \pm 0.03) \times 10^{-3}$
	4-MeO, 4-MeO	0		$(1.21 \pm 0.03) \times 10^{-2}$
	4-MeO, 4-MeO	0	60A40W	$(1.20 \pm 0.02) \times 10^{-2}$ [g]
2,4,6-tri-F (TFB)	4-MeO, H	–2.09	80AN20W	$(3.35 \pm 0.09) \times 10^{-5}$
	4-MeO, 4-Me	–1.32		$(2.29 \pm 0.03) \times 10^{-4}$
	4-MeO, 4-PhO	–0.86		$(6.40 \pm 0.06) \times 10^{-4}$
	4-MeO, 4-MeO	0		$(4.14 \pm 0.07) \times 10^{-3}$
	4-MeO, H	–2.09	60AN40W	$(1.19 \pm 0.02) \times 10^{-4}$
	4-MeO, 4-Me	–1.32		$(6.79 \pm 0.20) \times 10^{-4}$
	4-MeO, 4-PhO	–0.86		$(1.79 \pm 0.05) \times 10^{-3}$
	4-MeO, 4-MeO	0		$(1.14 \pm 0.03) \times 10^{-2}$
	4-MeO, 4-MeO	0	60A40W	$(6.33 \pm 0.06) \times 10^{-3}$ [h]
penta-F (PFB)	4-PhO, H	–3.52	80AN20W	$(3.25 \pm 0.08) \times 10^{-5}$
	4-MeO, H	–2.09		$(5.61 \pm 0.04) \times 10^{-4}$
	4-MeO, 4-Me	–1.32		$(3.21 \pm 0.05) \times 10^{-3}$
	4-MeO, 4-PhO	–0.86		$(8.45 \pm 0.10) \times 10^{-3}$
	4-MeO, 4-MeO	0		5.00×10^{-2} [f]
	4-PhO, H	–3.52	60AN40W	$(8.92 \pm 0.09) \times 10^{-5}$
	4-MeO, H	–2.09		$(1.51 \pm 0.01) \times 10^{-3}$
	4-MeO, 4-Me	–1.32		$(7.72 \pm 0.07) \times 10^{-3}$
	4-MeO, 4-PhO	–0.86		$(1.84 \pm 0.02) \times 10^{-2}$
	4-MeO, 4-MeO	0		1.06×10^{-1} [f]
	4-MeO, 4-MeO	0	60A40W	8.75×10^{-2} [f][h]

Table 1. Continued

Z	X, Y	E_f (a)	Solvent (b)	k / s^{-1} (c)
H(Bz)	4-MeO, 4-MeO	0	80AN20W	2.55×10^{-5} (d)
			60AN40W	$(6.77 \pm 0.05) \times 10^{-5}$
			60A40W	3.36×10^{-5} (e)(f)
3-NO$_2$	4-MeO, 4MeO	0	80AN20W	$(4.16 \pm 0.06) \times 10^{-4}$
			60AN40W	$(1.13 \pm 0.03) \times 10^{-3}$
			60A40W	$(9.66 \pm 0.17) \times 10^{-4}$
4-NO$_2$	4-MeO, 4-MeO	0	80AN20W	$(4.15 \pm 0.06) \times 10^{-4}$
			60AN40W	$(1.17 \pm 0.02) \times 10^{-3}$
			60A40W	$(1.07 \pm 0.01) \times 10^{-3}$ (e)
4-CN	4-MeO, 4-MeO	0	80AN20W	$(2.84 \pm 0.06) \times 10^{-4}$
			60AN40W	$(8.59 \pm 0.10) \times 10^{-4}$
			60A40W	$(7.26 \pm 0.07) \times 10^{-4}$
2-CF$_3$	4-MeO, 4-MeO	0	80AN20W	$(5.42 \pm 0.03) \times 10^{-4}$
			60AN40W	$(1.66 \pm 0.04) \times 10^{-3}$
			60A40W	$(6.79 \pm 0.14) \times 10^{-4}$
3,5-di-CF$_3$	4-MeO, 4-MeO	0	80AN20W	$(1.02 \pm 0.01) \times 10^{-3}$
			60AN40W	$(2.29 \pm 0.03) \times 10^{-3}$
			60A40W	$(2.63 \pm 0.04) \times 10^{-3}$
3,5-di-Cl	4-MeO, 4-MeO	0	80AN20W	$(4.20 \pm 0.08) \times 10^{-4}$
			60AN40W	$(1.06 \pm 0.03) \times 10^{-3}$
			60A40W	$(9.98 \pm 0.20) \times 10^{-4}$
2-MeO	4-MeO, 4-MeO	0	80AN20W	$(2.90 \pm 0.10) \times 10^{-5}$
			60AN40W	$(1.23 \pm 0.03) \times 10^{-4}$
			60A40W	$(3.92 \pm 0.02) \times 10^{-5}$
2,4,6-tri-Me	4-MeO, 4-MeO	0	80AN20W	$(5.18 \pm 0.07) \times 10^{-5}$
			60AN40W	$(2.14 \pm 0.03) \times 10^{-4}$
			60A40W	$(7.12 \pm 0.10) \times 10^{-5}$

(a) Electrofugality parameters are taken from Ref. 2.
(b) Binary solvents are expressed as volume fractions at 25 °C: AN =acetonitrile, A = acetone, W = water.
(c) Average rate constants from at least two runs performed at 25 °C unless otherwise noted. Errors shown are standard deviations.
(d) Extrapolated from data at higher temperatures by using the Eyring equation.
(e) Rate constants were taken from Ref. 2.
(f) Calculated from equation $\log k = s_f(E_f + N_f)$.
(g) Rate constant was taken from Ref. 3c.
(h) Rate constants were taken from Ref. 4.

As mentioned above, the correlations of the experimental $\Delta G^{\ddagger}$ for solvolysis of reference dianisylmethyl benzoates and the calculated $\Delta H^{\ddagger}$ for the epoxy ring formation starting from 2-oxyethyl benzoates enabled interpolating the reaction rates of a vast number of benzoates in aqueous ethanol mixtures.[4] To assess the experimental barriers of the reference benzoates, we have determined the rates of some more dianisylmethyl Z-benzoates in 60 % and 80 % aqueous acetonitrile and 60 % aqueous acetone. The first-order rate constants are presented in the bottom half of Table 1. The experimental solvolytic barriers in a given solvent for 13 reference benzoates have been correlated with the calculated $\Delta H^{\ddagger}$ values for the model reaction in water (data taken from Ref. 4). The correlations turned out very good in all three solvents used (r = 0.999 in 80 % *aq*. acetonitrile, r = 0.998 in 60 % *aq*. acetonitrile, and r = 0.988 in 60 % *aq*. acetone). The correlation in 80 % *aq*. acetonitrile is presented on Figure 2.

To justify the method, we extrapolated the rate constants of the 13 reference dianisylmethyl benzoates in aqueous acetone and acetonitrile from $\Delta H^{\ddagger}$ of model 2-oxyethyl benzoates using the $\Delta G^{\ddagger}_{\mathrm{exp}}$ *vs.* $\Delta H^{\ddagger}_{\mathrm{calc}}$ correlation lines and calculated deviations from the experimental data (Table 3). We also calculated the corresponding nucleofugalities by Equation (1) for the reference benzoate nucleofuges in given solvents, taking the experimental s_f where available, or the s_f values of benzoates having similar structure (see below). Data presented in Table 3 illustrate high accuracy of the

Table 2. Nucleofugality parameters N_f and s_f for some Z-substituted benzoates in 60 and 80 % aqueous acetonitrile and 60 % aqueous acetone

Z		Solvent[(a)(b)]		
		80AN20W	60AN40W	60A40W
2-NO$_2$	N_f	–2.58 ± 0.02	–2.30 ± 0.08	–2.53 ± 0.11
	s_f	1.01 ± 0.01	0.94 ± 0.02	0.98 ± 0.03
3,5-di-NO$_2$	N_f	–2.31 ± 0.02	–2.16 ± 0.10	–2.20 ± 0.18[(c)]
	s_f	0.98 ± 0.01	0.90 ± 0.03	0.90 ± 0.05[(c)]
TFB	N_f	–2.36 ± 0.10	–2.05 ± 0.03	–2.30 ± 0.07[(d)]
	s_f	1.00 ± 0.03	0.95 ± 0.01	0.97 ± 0.02[(d)]
PFB	N_f	–1.43 ± 0.07	–1.12 ± 0.03	–1.15 ± 0.07[(d)]
	s_f	0.91 ± 0.02	0.87 ± 0.01	0.92 ± 0.02[(d)]

[(a)] Binary solvents are expressed as volume fractions at 25 °C: AN = acetonitrile, A = acetone, W = water.
[(b)] Errors shown are standard errors.
[(c)] Taken from Ref. 2.
[(d)] Taken from Ref. 4.

model, indicating that most deviations between the calculated and experimental rate constants for solvolysis of dianisylmethyl benzoates, as well as between corresponding calculated N_f values and the experimental N_f values, are in the limits of the experimental error.

Our further aim was to estimate the barriers and the rate constants for solvolysis of a vast number of variously substituted benzoates in aqueous acetonitrile and acetone based on the correlation presented in Figure 2, and to extract the corresponding nucleofugality parameters. To define the reactivity of benzoates for which experimental reactivities are not available, we used the computed $\Delta H^\ddagger$ values for the epoxy ring formation[4] starting from 66 different 2-oxyethyl Z-benzoates in which substituents on the benzoate moiety have systematically been varied. The barriers and the corresponding rates for the solvolytic displacement reactions in the three aqueous solvents of 66 dianisylmethyl benzoates have been calculated from the $\Delta G^\ddagger_{exp}$ *vs.* $\Delta H^\ddagger_{calc}$ correlation lines. The estimated reaction rates of various dianisylmethyl benzoates in 60 %, and 80 % aqueous acetonitrile and in 60 % aqueous acetone are given in Table 4. The empirical observation that similarly substituted benzoates produce $\log k$ *vs.* E_f lines with similar slopes,[4,5] enables an approximation of the s_f parameters for benzoates whose experimental data are not available. The nucleofugalities (N_f) of various benzoate leaving groups have been calculated from equation $\log k = s_f\ N_f$ ($E_f = 0$ for dianisylmethyl electrofuge; Table 4).

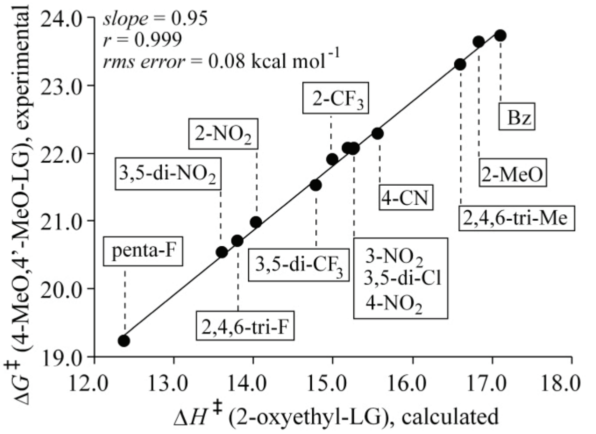


Figure 2. Correlation of experimental activation free energies (kcal mol^{-1}) for solvolysis of dianisylmethyl Z-benzoates in 80 % acetonitrile at 25 °C against PCM-B3LYP/6-311+G(2d,p) calculated activation enthalpies for heterolyses of 2-oxyethyl Z-benzoates.

In summary, the nucleofugalities (experimental and calculated) are now available for the spectrum of about 80 substituted benzoates in aqueous ethanol,[4] acetone and acetonitrile, which covers the reactivity range of seven orders of magnitude. The most reactive benzoate leaving group examined here is pentacyanobenzoate, while the least reactive is 3,4,5-triaminobenzoate. Taking the earlier published electrofugality parameters,[2,6] numerous N_f data available now ultimately enable predicting solvolytic reaction rates of large variety of aryl and alkyl benzoates according to Equation (1).

The reliability of the results obtained with the above-presented model is illustrated with the Hammett diagram by two aspects. Plotting the calculated rate constants for heterolysis of dianisylmethyl Z-benzoates against the sum of the Hammett σ parameters (Figure 3) produces lines with excellent correlation. Secondly, the ρ values obtained (ρ = 1.72 in 80 % *aq.* acetonitrile, ρ = 1.59 in 60 % *aq.* acetonitrile, and ρ = 1.77 in 60 % *aq.* acetone) are in accordance with the ρ values obtained earlier for the heterolysis reactions that solvolyze via S_N1 pathway.[7]

Table 3. Calculated Solvolysis Rate Constants, Deviations from the Experimental data for Reference Dianisylmethyl Z-Benzoates and Related Calculated Nucleofugalities at 25 °C

Solvent(a)	Z(b)	k^{calc} (25 °C) / s^{-1} (c)	s_{f} (d)	$N_{\mathrm{f}}^{\mathrm{calc}}$ (e)
80 % AN(f)	H	2.02×10^{-5} (–26 %)	1.12(i)	–4.19 (±0.00)
	2-NO$_2$	2.77×10^{-3} (+6 %)	1.01	–2.53 (+0.05)
	3-NO$_2$	3.87×10^{-4} (–8 %)	0.98(i)	–3.48
	4-NO$_2$ (PNB)	4.40×10^{-4} (+6 %)	0.98(i)	–3.43 (–0.02)
	3,5-di-NO$_2$ (DNB)	5.57×10^{-3} (±0 %)	0.98	–2.30 (+0.01)
	4-CN	2.45×10^{-4} (–16 %)	0.98(i)	–3.68
	2-CF$_3$	6.04×10^{-4} (+10 %)	1.01	–3.19
	3,5-di-CF$_3$	8.36×10^{-4} (–22 %)	0.98	–3.14
	3,5-di-Cl	4.02×10^{-4} (–4 %)	0.98	–3.47
	2,4,6-tri-F (TFB)	4.09×10^{-3} (–1 %)	1.00	–2.39 (–0.03)
	penta-F (PFB)	4.09×10^{-2} (–22 %)	0.91	–1.53 (–0.10)
	2-MeO	3.14×10^{-5} (+8 %)	1.01	–4.46
	2,4,6-tri-Me	4.57×10^{-5} (–13 %)	1.00	–4.34
60 % AN(g)	H (Bz)	8.18×10^{-5} (+17 %)	1.02(i)	–4.01 (–0.09)
	2-NO$_2$	7.79×10^{-3} (+8 %)	0.94	–2.24 (+0.06)
	3-NO$_2$	1.26×10^{-3} (+10 %)	0.91(i)	–3.19
	4-NO$_2$ (PNB)	1.42×10^{-3} (+18 %)	0.91(i)	–3.13 (+0.17)
	3,5-di-NO$_2$ (DNB)	1.49×10^{-2} (+19 %)	0.90	–2.03 (+0.13)
	4-CN	8.24×10^{-4} (–4 %)	0.91(i)	–3.39
	2-CF$_3$	1.90×10^{-3} (+13 %)	0.94	–2.89
	3,5-di-CF$_3$	2.57×10^{-3} (+11 %)	0.90	–2.88
	3,5-di-Cl	1.30×10^{-3} (+18 %)	0.90	–3.21
	2,4,6-tri-F (TFB)	1.12×10^{-2} (–2 %)	0.95	–2.05 (±0.00)
	penta-F (PFB)	9.44×10^{-2} (–12 %)	0.87	–1.18 (–0.06)
	2-MeO	1.23×10^{-4} (±0 %)	0.94	–4.16
	2,4,6-tri-Me	1.74×10^{-4} (–23 %)	0.95	–3.96
60 % A(h)	H (Bz)	3.02×10^{-5} (–11 %)	1.15(i)	–3.93 (–0.04)
	2-NO$_2$	4.82×10^{-3} (+29 %)	0.98	–2.36 (+0.17)
	3-NO$_2$	6.33×10^{-4} (–53 %)	1.11(i)	–2.88
	4-NO$_2$ (PNB)	7.23×10^{-4} (–48 %)	1.11(i)	–2.83 (–0.04)
	3,5-di-NO$_2$ (DNB)	9.92×10^{-3} (–21 %)	0.90(i)	–2.23 (–0.03)
	4-CN	3.95×10^{-4} (–84 %)	1.11(i)	–3.07
	2-CF$_3$	1.00×10^{-3} (+32 %)	0.98	–3.06
	3,5-di-CF$_3$	1.40×10^{-3} (–88 %)	0.90(i)	–3.17
	3,5-di-Cl	6.59×10^{-4} (–51 %)	0.90(i)	–3.53
	2,4,6-tri-F (TFB)	7.21×10^{-3} (+12 %)	0.97(i)	–2.21 (+0.09)
	penta-F (PFB)	7.75×10^{-2} (–13 %)	0.92(i)	–1.21 (–0.06)
	2-MeO	4.74×10^{-5} (+17 %)	0.98	–4.41
	2,4,6-tri-Me	7.00×10^{-5} (–2 %)	0.97(i)	–4.28

(a) Aqueous binary solvents are expressed as volume fractions at 25 °C: AN = acetonitrile, A = acetone.

(b) Z represents one or more substituents on the phenyl ring.

(c) Calculated from $\Delta G^{\ddagger}$ (dianisylmethyl Z-benzoate) / $\Delta H^{\ddagger}$ (2-oxyethyl Z-benzoate) correlation. Deviations (in %) from experimental values are given in parentheses $[(k^{\mathrm{calc}} - k^{\mathrm{exp}}) / k^{\mathrm{calc}} \times 100]$.

(d) Experimental s_{f} values employed for calculating N_{f} values.

(e) Calculated from k^{calc} and related s_{f} using Equation (1).

(f) Slope = 0.95 ± 0.02, intercept = 7.60 ± 0.24 (r = 0.999; *root mean square error* = 0.08 kcal mol^{-1}).

(g) Slope = 0.88 ± 0.02, intercept = 7.97 ± 0.26 (r = 0.998; *root mean square error* = 0.09 kcal mol^{-1}).

(h) Slope = 0.97 ± 0.05, intercept = 6.85 ± 0.68 (r = 0.988; *root mean square error* = 0.21 kcal mol^{-1}).

(i) Taken from Refs. 2 and 4.

Table 4. Calculated Solvolysis Rate Constants at 25 °C for Dianisylmethyl Z-Benzoates and Related Calculated Nucleofugalities

Z(a)	60 % *aq*. acetonitrile(b)		80 % *aq*. acetonitrile(b)		60 % *aq*. acetone(b)	
	k^{calc} / s^{-1} (c)	N_f^{calc} (s_f)(d)(e)	k^{calc} / s^{-1} (c)	N_f^{calc} (s_f)(d)(e)	k^{calc} / s^{-1} (c)	N_f^{calc} (s_f)(d)(e)
2,4-di-NO_2	5.35×10^{-2}	–1.30 (0.98)	1.21×10^{-1}	–1.02 (0.90)	1.02×10^{-1}	–1.10 (0.90)
2,6-di-NO_2	4.72×10^{-2}	–1.35 (0.98)	1.08×10^{-1}	–1.07 (0.90)	8.99×10^{-2}	–1.16 (0.90)
3,4-di-NO_2	4.40×10^{-3}	–2.40 (0.98)	1.20×10^{-2}	–2.14 (0.90)	7.78×10^{-3}	–2.34 (0.90)
3,4,5-tri-NO_2	3.32×10^{-2}	–1.48 (1.00)	7.78×10^{-2}	–1.17 (0.95)	6.25×10^{-2}	–1.24 (0.97)
2,4,6-tri-NO_2	6.38×10^{-1}	–0.20 (1.00)	1.20	0.08 (0.95)	1.32	0.12 (0.97)
2-CN	5.28×10^{-4}	–3.24 (1.00)	1.68×10^{-3}	–2.95 (0.94)	8.73×10^{-4}	–3.12 (0.98)
3-CN	2.38×10^{-4}	–3.70 (0.98)	8.02×10^{-4}	–3.40 (0.91)	3.83×10^{-4}	–3.08 (1.11)
2,4-di-CN	5.22×10^{-3}	–2.33 (0.98)	1.40×10^{-2}	–2.06 (0.90)	9.27×10^{-3}	–2.26 (0.90)
2,6-di-CN	6.16×10^{-2}	–1.24 (0.98)	1.38×10^{-1}	–0.96 (0.90)	1.18×10^{-1}	–1.03 (0.90)
3,5-di-CN	2.47×10^{-3}	–2.66 (0.98)	7.01×10^{-3}	–2.39 (0.90)	4.29×10^{-3}	–2.63 (0.90)
3,4-di-CN	2.31×10^{-3}	–2.69 (0.98)	6.60×10^{-3}	–2.42 (0.90)	4.00×10^{-3}	–2.66 (0.90)
3,4,5-tri-CN	1.75×10^{-2}	–1.76 (1.00)	4.30×10^{-2}	–1.44 (0.95)	3.23×10^{-2}	–1.54 (0.97)
2,4,6-tri-CN	5.57×10^{-1}	–0.25 (1.00)	1.06	0.03 (0.95)	1.15	0.06 (0.97)
penta-CN	1.35×10^{1}	1.24 (0.91)	2.03×10^{1}	1.50 (0.87)	3.07×10^{1}	1.62 (0.92)
3-CHO	1.44×10^{-4}	–3.92 (0.98)	5.05×10^{-4}	–3.62 (0.91)	2.29×10^{-4}	–3.28 (1.11)
4-CHO	1.50×10^{-4}	–3.90 (0.98)	5.23×10^{-4}	–3.61 (0.91)	2.38×10^{-4}	–3.26 (1.11)
3,5-di-CHO	5.23×10^{-4}	–3.35 (0.98)	1.66×10^{-3}	–3.09 (0.90)	8.63×10^{-4}	–3.40 (0.90)
3-CF_3	1.23×10^{-4}	–3.99 (0.98)	4.35×10^{-4}	–3.69 (0.91)	1.94×10^{-4}	–3.34 (1.11)
4-CF_3	1.22×10^{-4}	–3.99 (0.98)	4.32×10^{-4}	–3.70 (0.91)	1.92×10^{-4}	–3.35 (1.11)
2,4-di-CF_3	4.14×10^{-3}	–2.43 (0.98)	1.13×10^{-2}	–2.16 (0.90)	7.31×10^{-3}	–2.37 (0.90)
2,6-di-CF_3	8.00×10^{-3}	–2.14 (0.98)	2.08×10^{-2}	–1.87 (0.90)	1.44×10^{-2}	–2.05 (0.90)
3,4-di-CF_3	7.54×10^{-4}	–3.19 (0.98)	2.34×10^{-3}	–2.92 (0.90)	1.26×10^{-3}	–3.22 (0.90)
3,4,5-tri-CF_3	3.87×10^{-3}	–2.41 (1.00)	1.06×10^{-2}	–2.08 (0.95)	6.81×10^{-3}	–2.23 (0.97)
2,4,6-tri-CF_3	5.63×10^{-2}	–1.25 (1.00)	1.27×10^{-1}	–0.94 (0.95)	1.08×10^{-1}	–1.00 (0.97)
penta-CF_3	6.06×10^{-1}	–0.24 (0.91)	1.15	0.07 (0.87)	1.25	0.11 (0.92)
2-Cl	4.10×10^{-4}	–3.35 (1.01)	1.33×10^{-3}	–3.06 (0.94)	6.73×10^{-4}	–3.24 (0.98)
3-Cl	9.19×10^{-5}	–4.12 (0.98)	3.33×10^{-4}	–3.82 (0.91)	1.44×10^{-4}	–3.46 (1.11)
4-Cl	5.21×10^{-5}	–4.37 (0.98)	1.96×10^{-4}	–4.07 (0.91)	8.00×10^{-5}	–3.69 (1.11)
2,4-di-Cl	6.78×10^{-4}	–3.23 (0.98)	2.12×10^{-3}	–2.97 (0.90)	1.13×10^{-3}	–3.27 (0.90)
2,6-di-Cl	6.31×10^{-3}	–2.24 (0.98)	1.67×10^{-2}	–1.97 (0.90)	1.13×10^{-2}	–2.16 (0.90)
3,4-di-Cl	1.91×10^{-4}	–3.79 (0.98)	6.56×10^{-4}	–3.54 (0.90)	3.06×10^{-4}	–3.90 (0.90)
3,4,5-tri-Cl	6.32×10^{-4}	–3.20 (1.00)	1.98×10^{-3}	–2.84 (0.95)	1.05×10^{-3}	–3.07 (0.97)
2,4,6-tri-Cl	1.39×10^{-2}	–1.86 (1.00)	3.47×10^{-2}	–1.54 (0.95)	2.54×10^{-2}	–1.64 (0.97)
penta-Cl	5.68×10^{-2}	–1.37 (0.91)	1.28×10^{-1}	–1.03 (0.87)	1.09×10^{-1}	–1.05 (0.92)
3-F	7.19×10^{-5}	–4.23 (0.98)	2.65×10^{-4}	–3.93 (0.91)	1.12×10^{-4}	–3.56 (1.11)
4-F	3.28×10^{-5}	–4.57 (0.98)	1.28×10^{-4}	–4.28 (0.91)	4.97×10^{-5}	–3.88 (1.11)
2,4-di-F	1.44×10^{-4}	–3.92 (0.98)	5.04×10^{-4}	–3.66 (0.90)	2.28×10^{-4}	–4.05 (0.90)
2,6-di-F	4.04×10^{-3}	–2.44 (0.98)	1.11×10^{-2}	–2.17 (0.90)	7.12×10^{-3}	–2.39 (0.90)
3,5-di-F	2.81×10^{-4}	–3.62 (0.98)	9.37×10^{-4}	–3.36 (0.90)	4.56×10^{-4}	–3.71 (0.90)
3,4-di-F	1.22×10^{-4}	–4.00 (0.98)	4.31×10^{-4}	–3.74 (0.90)	1.92×10^{-4}	–4.13 (0.90)

Table 4. Continued

Z[(a)]	60 % *aq*. acetonitrile[(b)]		80 % *aq*. acetonitrile[(b)]		60 % *aq*. acetone[(b)]	
	k^{calc} / s^{-1} [(c)]	$N_{\text{f}}^{\text{calc}}$ (s_{f})[(d)(e)]	k^{calc} / s^{-1} [(c)]	$N_{\text{f}}^{\text{calc}}$ (s_{f})[(d)(e)]	k^{calc} / s^{-1} [(c)]	$N_{\text{f}}^{\text{calc}}$ (s_{f})[(d)(e)]
3,4,5-tri-F	4.27×10^{-4}	−3.37 (1.00)	1.38×10^{-3}	−3.01 (0.95)	7.01×10^{-4}	−3.25 (0.97)
2-Ph	4.70×10^{-5}	−4.28 (1.01)	1.79×10^{-4}	−3.99 (0.94)	7.20×10^{-5}	−4.23 (0.98)
3-Ph	2.45×10^{-5}	−4.71 (0.98)	9.76×10^{-5}	−4.41 (0.91)	3.67×10^{-5}	−4.00 (1.11)
4-Ph	1.71×10^{-5}	−4.86 (0.98)	7.02×10^{-5}	−4.56 (0.91)	2.54×10^{-5}	−4.14 (1.11)
3,5-di-Ph	2.84×10^{-5}	−4.64 (0.98)	1.12×10^{-4}	−4.39 (0.90)	4.27×10^{-5}	−4.85 (0.90)
3-MeO	1.96×10^{-5}	−4.80 (0.98)	7.95×10^{-5}	−4.50 (0.91)	2.92×10^{-5}	−4.08 (1.11)
4-MeO	5.61×10^{-6}	−5.36 (0.98)	2.50×10^{-5}	−5.06 (0.91)	8.04×10^{-6}	−4.59 (1.11)
2,4-di-MeO	3.89×10^{-6}	−5.52 (0.98)	1.78×10^{-5}	−5.28 (0.90)	5.50×10^{-6}	−5.84 (0.90)
2,6-di-MeO	6.87×10^{-5}	−4.25 (0.98)	2.54×10^{-4}	−3.99 (0.90)	1.06×10^{-4}	−4.41 (0.90)
3,5-di-MeO	2.19×10^{-5}	−4.75 (0.98)	8.81×10^{-5}	−4.51 (0.90)	3.27×10^{-5}	−4.98 (0.90)
3,4-di-MeO	6.15×10^{-6}	−5.32 (0.98)	2.71×10^{-5}	−5.07 (0.90)	8.82×10^{-6}	−5.62 (0.90)
3,4,5-tri-MeO	1.66×10^{-5}	−4.78 (1.00)	6.83×10^{-5}	−4.39 (0.95)	2.47×10^{-5}	−4.75 (0.97)
2,4,6-tri-MeO	3.06×10^{-5}	−4.51 (1.00)	1.20×10^{-4}	−4.13 (0.95)	4.61×10^{-5}	−4.47 (0.97)
2-Me	1.08×10^{-5}	−4.92 (1.01)	4.57×10^{-5}	−4.62 (0.94)	1.58×10^{-5}	−4.90 (0.98)
3-Me	1.22×10^{-5}	−5.02 (0.98)	5.10×10^{-5}	−4.72 (0.91)	1.78×10^{-5}	−4.28 (1.11)
4-Me	9.89×10^{-6}	−5.11 (0.98)	4.22×10^{-5}	−4.81 (0.91)	1.44×10^{-5}	−4.36 (1.11)
2,4-di-Me	4.98×10^{-6}	−5.41 (0.98)	2.23×10^{-5}	−5.17 (0.90)	7.10×10^{-6}	−5.72 (0.90)
2,6-di-Me	8.41×10^{-5}	−4.16 (0.98)	3.06×10^{-4}	−3.90 (0.90)	1.31×10^{-4}	−4.31 (0.90)
3,5-di-Me	9.54×10^{-6}	−5.12 (0.98)	4.08×10^{-5}	−4.88 (0.90)	1.39×10^{-5}	−5.40 (0.90)
3,4-di-Me	6.98×10^{-6}	−5.26 (0.98)	3.05×10^{-5}	−5.02 (0.90)	1.01×10^{-5}	−5.55 (0.90)
3,4,5-tri-Me	4.89×10^{-6}	−5.31 (1.00)	2.20×10^{-5}	−4.90 (0.95)	6.97×10^{-6}	−5.32 (0.97)
penta-Me	2.74×10^{-5}	−5.01 (0.91)	1.08×10^{-4}	−4.56 (0.87)	4.13×10^{-5}	−4.77 (0.92)
3-NH_2	1.00×10^{-5}	−5.10 (0.98)	4.27×10^{-5}	−4.80 (0.91)	1.46×10^{-5}	−4.36 (1.11)
4-NH_2	1.67×10^{-6}	−5.89 (0.98)	8.12×10^{-6}	−5.59 (0.91)	2.30×10^{-6}	−5.08 (1.11)
3,5-di-NH_2	6.02×10^{-6}	−5.33 (0.98)	2.66×10^{-5}	−5.08 (0.90)	8.64×10^{-6}	−5.63 (0.90)
3,4,5-tri-NH_2	1.24×10^{-6}	−5.91 (1.00)	6.17×10^{-6}	−5.48 (0.95)	1.70×10^{-6}	−5.95 (0.90)

[(a)] Z represents one or more substituents on the phenyl ring.

[(b)] Aqueous binary solvents are expressed as volume fractions at 25 °C: AN = acetonitrile, A = acetone.

[(c)] Calculated from $\Delta G^{\ddagger}$ (dianisylmethyl Z-benzoate) / $\Delta H^{\ddagger}$ (2-oxyethyl Z-benzoate) correlation.

[(d)] $N_{\text{f}}^{\text{calc}}$ is calculated from k^{calc} and related s_{f} (given in parentheses) using Equation (1). E_{f} value for dianisylmethyl electrofuge is 0.00.

[(e)] s_{f} values not obtained in this work are taken from Refs. 2 and 4.

Effects of Z-Substituents on the Reactivity of Benzoates

The $\Delta G^{\ddagger}_{\text{exp}}$ *vs.* $\Delta H^{\ddagger}_{\text{calc}}$ correlation lines obtained in various solvents are not parallel, indicating that the Z-substituents in different solvents influence the reaction barriers of the heterolysis reactions of benzhydryl benzoates differently. Slopes of the plots depend on solvent polarity in a way that they decrease as the fraction of water in a given solvent series increases. Thus, while the slope in 80 % *aq*. acetonitrile is 0.95, it is 0.88 in 60 % *aq*, acetonitrile. Similar results have been obtained in a series of aqueous ethanol mixtures (slopes are: 0.97 in 90 % *aq*. ethanol, 0.93 in 80 % *aq*. ethanol, and 0.91 in 70 % *aq*. ethanol, respectively).[4]

This observation can be rationalized if the degree of charge separation in TS of the heterolysis step is considered. In a less polar solvent a reaction is slower, hence the charge is more separated in the later transition state, *i.e.* the TS is more carbocation-like than in a more polar solvent. The effects of the Z-substituents on reactivity come from more or less polar interactions (field effect and inductive effect) with the generated negative charge in TS. Therefore in the less polar solvent, where the charge in TS is separated more, the impact of the Z-substituent on the barrier is more important than in the more polar solvent, and the Z-substituents cause more pronounced change of the reaction barriers for the heterolysis of benzhydryl benzoates than in the more polar solvent.

Assumption that the above results could be rationalized in terms of more or less carbocation-like transition states can be verified with the Hammett ρ parameters (Figure 3) obtained by plotting the calculated rate constants for solvolyses of benzhydryl benzoates against the σ values of the Z-substituents. The reaction that proceed *via* TS in which the charge is more separated produce steeper Hammett plots due to more pronounced interactions of the Z-substituent with the generating negative charge. The results obtained in aqueous acetonitrile (see above) and aqueous ethanol (the ρ values are 1.75, 1.68 and 1.65 in 90 %, 80 % and 70 % aqueous ethanol, respectively)[4] support the above premises.

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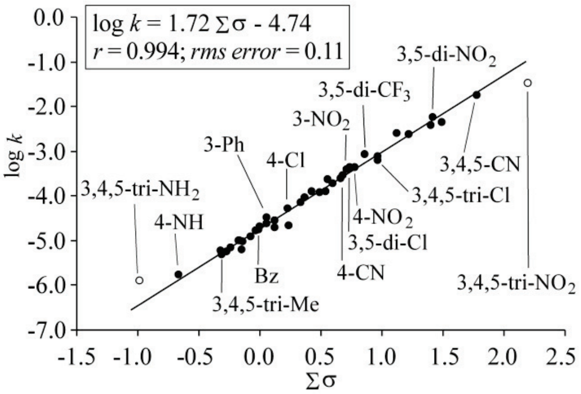

Figure 3. Hammett plot of calculated rate constants for solvolysis of dianisylmethyl benzoates in 80 % acetonitrile at 25 °C. The deviating points represented with open circles are not included in the correlation.[8]

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