



## Supporting Information

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# S<sub>N</sub>1 Reactions with Inverse Rate Profiles

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## 1. Kinetics of solvolysis reactions

Solvolysis rates of benzhydrylium derivatives were followed conductimetrically by means of a WTW LF530 conductimeter using a Pt electrode LTA 1/NS. Freshly prepared solvents (30 mL) were thermostated ( $\pm 0.1$  °C) at the given temperature for 5 min prior to addition of the substrate. Typically, 20 to 70 mg of the substrate was dissolved in 100–150  $\mu$ L of dichloromethane and injected into the solvent, and the conductance (G) was recorded at given time intervals. The increase of the conductance was sufficient when benzhydrylium chlorides or bromides were used, but in case of 3,5-dinitrobenzoates and trifluoroacetates, 2,6-lutidine was added to ionize the weak acid produced by solvolysis.

The first-order rate constants  $k$  ( $s^{-1}$ ) were obtained by least squares fitting of the conductance data to a single-exponential equation  $G_t = G_0 \exp(-kt) + c$ . Each rate constant is averaged from at least three kinetic runs.

Most solvolyses were performed at 25 °C. Reactions too slow to be followed at 25 °C were followed at three different higher temperatures to obtain the corresponding Eyring activation parameters (see footnotes in Table S1). The rate constants at 25 °C were then calculated by using the Eyring activation parameters.

Calibrations showed linear relationships between conductance and the concentrations of HCl, HBr, and 2,6-lutidinium trifluoroacetate in all four solvents. Linearity was also observed with 2,6-lutidinium 3,5-dinitrobenzoate in 80E20W.<sup>[S27]</sup> Because of non-linear relationships between conductance and the concentration of 2,6-lutidinium 3,5-dinitrobenzoate in 90A10W,

80A20W, and 100E,<sup>[S27]</sup> polynomial dependences of conductance on the concentration of 2,6-lutidinium 3,5-dinitrobenzoate were determined and applied to the conductance data for each kinetic run.

## 2. Nucleofugality and electrofugality parameters

Table S1 lists all rate constants of benzhydryl bromides, chlorides, trifluoroacetates, and 3,5-dinitrobenzoates that were available in at least two of the solvents 90% aqueous acetone (90A10W), 80% aqueous acetone (80A20W), 100% ethanol (100E), and 80% aqueous ethanol (80E20W).<sup>[S27]</sup> Thus, only rate constants were used for the correlations which have been confirmed by the consistency of two or more experiments.

All rate constants listed in Table S1 have then been subjected to a least squares analysis according to Equation (3), that is,  $\Sigma \Delta^2$ , where  $\Delta^2 = (\log k_1 - \log k_1^{\text{calc}})^2 = (\log k_1 - s_f(N_f + E_f))^2$  was minimized using the commercial software “*What’sBest!*”.<sup>[14]</sup>

In order to link Eq. (3) to Eq. (2), the electrofugality parameter  $E_f$  for the bis(4-methoxyphenyl)methyl cation (**1**) was set to 0, and  $s_f = 1$  was selected for the nucleofuge system Cl<sup>-</sup>/100E. Optimization of all other parameters yielded the parameters  $E_f$ ,  $s_f$ , and  $N_f$ , which were then used to calculate solvolysis rate constants by Eq. (3). In thirteen cases (marked by (\*) in Table S1), the deviation between calculated and experimental rate constants was larger than  $|\log k_1 - \log k_1^{\text{calc}}| > 0.13$ . These deviations may either be due to experimental error or due to the nonapplicability of Eq. (3) to these systems. Since eight of the strongly deviating systems refer to the 4-CH<sub>3</sub>,4'-NO<sub>2</sub> substituted benzhydrylium system, a failure of Eq. (3) to describe these solvolyses appears to be likely. The 3-CF<sub>3</sub> substituted benzhydrylium system, represented with three entries, shows similar behaviour. The entries marked by (\*) were then cancelled, and a new correlation analysis was performed to yield a revised set of  $E_f$ ,  $N_f$ , and  $s_f$ .

For several solvolysis reactions, more than one experimental rate constant is given in Table S1. In these cases, those which differed more from the value calculated by Eq. (3) were cancelled; only when  $|\log k_1 - \log k_1^{\text{calc}}| < 0.05$  for rate constants including one of our own work, we continued optimization with the value from our own laboratory.

In this way, the values marked by (\*\*) in Table S1 were cancelled, and the remaining rate constants were again subjected to a least squares optimization to yield the parameters  $E_f$ ,  $N_f$ , and  $s_f$  listed in Tables 1 and 2.

**Table S1.** First-order rate constants (25 °C) for solvolysis of benzydrylium derivatives in different solvents.<sup>[S27]</sup>

Leaving group	Substituent(s)	$10^5 k_1 / \text{s}^{-1}$	$10^5 k_1^{\text{calc}} / \text{s}^{-1}$	Reference
<b>90A10W</b>				
Chloride	H,H	0.46	(**)	[S9, S10]
		0.507	0.500	[S11]
		0.554	(**)	[S12]
	4-F	0.978 <sup>a</sup>	0.956	this work
	4-CH <sub>3</sub>	11.1	11.8	this work
	4-OCH <sub>3</sub>	4540	4470	this work
	4-OC <sub>6</sub> H <sub>5</sub>	200	188	this work
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	183	194	this work
		143	(**)	[S11]
		4-CH <sub>3</sub> ,4'-NO <sub>2</sub>	0.3	(*)
Bromide	H,H	18.8	(**)	[S4]
		16.4	(**)	[S13]
		18	(**)	[S14]
		18.7	18.4	this work
	4-F	36.0	34.9	this work
	4-Cl	6.45 <sup>b</sup>	6.66	this work
	4-CH <sub>3</sub>	408	416	this work
	4-OC <sub>6</sub> H <sub>5</sub>	6860	6440	this work
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	6240	6640	this work
	4-CH <sub>3</sub> ,4'-NO <sub>2</sub>	7.448	(*)	[S3]
3,5-Dinitrobenzoate	4-OCH <sub>3</sub>	0.316 <sup>c</sup>	0.319	this work
	4-OCH <sub>3</sub> ,4'-CH <sub>3</sub>	2.3 <sup>d</sup>	2.15	this work
	4-OCH <sub>3</sub> ,4'-OCH <sub>3</sub>	42.2	41.2	this work
	4-OCH <sub>3</sub> ,4'-OC <sub>6</sub> H <sub>5</sub>	6.05	6.55	this work
Trifluoroacetate	4-CH <sub>3</sub>	4.95 <sup>e</sup>	5.01	this work
	4-OCH <sub>3</sub>	1440	1580	this work
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	79.7	75.6	this work
	4-OCH <sub>3</sub> ,4'-CH <sub>3</sub>	10200	9690	this work
<b>80A20W</b>				
Chloride	H,H	7.27	(**)	[S15]
		6.07	(**)	[S11]
		7.25	(**)	[S16]
		7.25	(**)	[S9]
		7.3	(**)	[S8]
		7.17	(**)	[S6]
		6.82 <sup>f</sup>	6.51	this work
	4-CH <sub>3</sub>	157	(**)	[S17]
		164	(**)	[S6]
		176	164	this work
	4-OC <sub>6</sub> H <sub>5</sub>	2640	2780	this work
	4-F	13.4	12.6	this work
	4-Cl	1.93	(**)	[S11]
		2.31	2.28	[S16]
	4-Br	1.66	1.70	[S2]
	3-Cl	0.12	0.123	[S6]

Bromide	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	2700	(**)	[S16]	
		2790	2870	this work	
	4-CH <sub>3</sub> ,4'-NO <sub>2</sub>	1.561	(*)	[S3]	
	4-Cl,4'-Cl	0.84	0.88	[S11]	
	3,5-(CH <sub>3</sub> ) <sub>2</sub>	22.5	22.5	[S18]	
	H,H	191	(**)	[S4]	
		153	(**)	[S19]	
		200	(**)	[S8]	
		203	198	this work	
	4-CH <sub>3</sub>	4960	(**)	[S8]	
		4540	4160	this work	
	4-OC <sub>6</sub> H <sub>5</sub>	25910 <sup>g</sup>	(*)	[S8]	
	4-F	525	(**)	[S8]	
		371	369	this work	
	3,5-Dinitrobenzoate	4-Cl	67.3	(**)	[S8]
		68.1	73.4	this work	
4-NO <sub>2</sub>		0.333	0.298	[S4]	
3-Cl		4.42	4.66	[S8]	
3-CF <sub>3</sub>		0.156	(*)	[S7]	
4-CH <sub>3</sub> ,4'-NO <sub>2</sub>		32.13	(*)	[S3]	
4-OC <sub>6</sub> H <sub>5</sub> ,4'-NO <sub>2</sub>		518.6	519	[S3]	
4-Cl,4'-Cl		27.2	30.1	this work	
H,H		0.0000439 <sup>h</sup>	0.0000451	[S8]	
4-OCH <sub>3</sub>		1.13 <sup>i</sup>	1.01	this work	
4-OCH <sub>3</sub> ,4'-CH <sub>3</sub>		7.83 <sup>j</sup>	7.98	this work	
4-OCH <sub>3</sub> ,4'-OCH <sub>3</sub>		193	195	this work	
4-OCH <sub>3</sub> ,4'-OC <sub>6</sub> H <sub>5</sub>		25.2	26.6	this work	
Trifluoroacetate		H,H	2.04	1.98	[S8]
		4-F	3.24 <sup>k</sup>	3.44	this work
	4-CH <sub>3</sub>	28.5	29.6	this work	
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	377	327	this work	
	4-OCH <sub>3</sub>	4450	4810	this work	
Chloride		<b>100E</b>			
	H,H	4.85	(**)	[S20]	
		5.72	(**)	[S21]	
		5.75	(**)	[S22]	
		5.34	(**)	[S2]	
		5.3	(**)	[S23]	
		5.37	(**)	[S24]	
		5.39	(**)	[S25]	
		5.41	(**)	[S15]	
		5.42	(**)	[S6]	
		5.54 <sup>l</sup>	5.92	this work	
	4-CH <sub>3</sub>	124	(**)	[S23]	
		127	(**)	[S6]	
		154	144	this work	
	4-OCH <sub>3</sub>	50000	58800	[S1]	
	4-OC <sub>6</sub> H <sub>5</sub>	2220	2380	[S1]	
		2220	(**)	this work	
	4-Br	1.61	1.57	[S2]	
	4-Cl	2.06	2.1	[S2]	
	4-F	9.3	(**)	[S2]	
		10.7	11.4	this work	
	3-CH <sub>3</sub>	11.15	10.9	[S2]	

	3-CH <sub>3</sub>	13.7	(**)	[S25]
	4-Cl	0.125	(**)	[S2]
		0.121	0.116	[S25]
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	2020	(**)	[S1]
		2170	2460	this work
	4-CH <sub>3</sub> ,4'-NO <sub>2</sub>	0.5	(*)	[S3]
	4-OCH <sub>3</sub> ,4'-CH <sub>3</sub>	514000 <sup>m</sup>	391000 [S1]	
	4-OCH <sub>3</sub> ,4'-OCH <sub>3</sub>	5716000 <sup>n</sup>	7370000	[S1]
	4-OCH <sub>3</sub> ,4'-OC <sub>6</sub> H <sub>5</sub>	1516000 <sup>o</sup>	1180000	[S1]
	4-Cl,4'-Cl	0.807	0.824	[S2]
	3,5-(CH <sub>3</sub> ) <sub>2</sub>	22.5	20.2	[S2]
Bromide	H,H	120	(**)	[S4]
		124	(**)	[S15]
		134	135	this work
	4-CH <sub>3</sub>	2950	2860	this work
	4-CH <sub>3</sub> ,4'-NO <sub>2</sub>	10.03	(*)	[S3]
	4-OC <sub>6</sub> H <sub>5</sub> ,4'-NO <sub>2</sub>	355.1	355	[S3]
	4-Cl,4'-Cl	21	20.4	this work
	4-F	238	252	this work
	4-Cl	50.4	49.9	this work
3,5-Dinitrobenzoate	4-OCH <sub>3</sub>	4.29 <sup>p</sup>	3.56	this work
	4-OCH <sub>3</sub> ,4'-CH <sub>3</sub>	18.1	24.4	this work
	4-OCH <sub>3</sub> ,4'-OCH <sub>3</sub>	548	482	this work
	4-OCH <sub>3</sub> ,4'-OC <sub>6</sub> H <sub>5</sub>	73.5	75.1	this work
Trifluoroacetate	H,H	0.937 <sup>q</sup>	0.961	this work
	4-F	1.84 <sup>r</sup>	1.7	this work
	4-CH <sub>3</sub>	14	15.4	this work
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	189	181	this work
	4-OCH <sub>3</sub>	2860	2860	this work
<b>80E20W</b>				
Chloride	H,H	172	(**)	[S22]
		208	(**)	[S26]
		193.6	(**)	[S18]
		204	191	this work
	4-CH <sub>3</sub>	4200	(**)	[S6]
		4640	4580	this work
	4-F	367	367	this work
	4-Cl	73.5	(**)	[S26]
		72.9	68	this work
	3-CH <sub>3</sub>	339.9	349	[S18]
	3-CF <sub>3</sub>	1.06	(*)	[S6]
	3-Cl	3.56	3.84	[S6]
	4-CH <sub>3</sub> ,4'-NO <sub>2</sub>	7.331	(*)	[S3]
	4-Cl,4'-Cl	28.9	(**)	[S26]
		28.6	26.9	this work
	3,5-(CH <sub>3</sub> ) <sub>2</sub>	584	649	[S18]
Bromide	H,H	3040	(**)	[S5]
		3440	3450	this work
	4-F	5880	(**)	[S5]
		6050	6810	this work
	4-Cl	1210	1170	this work
	4-NO <sub>2</sub>	2.63	2.91	[S5]
	3-CF <sub>3</sub>	17.6	(*)	[S5]
	3-Cl	64.8	58.1	[S5]

3,5-Dinitrobenzoate	4-CH <sub>3</sub> ,4'-NO <sub>2</sub>	124.7	(*)	[S3]
	4-OC <sub>6</sub> H <sub>5</sub> ,4'-NO <sub>2</sub>	4723	(*)	[S3]
	4-Cl,4'-Cl	481	444	this work
	4-OCH <sub>3</sub>	35	35	this work
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	1.78 <sup>s</sup>	1.7	this work
	4-OCH <sub>3</sub> ,4'-CH <sub>3</sub>	198	213	this work
	4-OCH <sub>3</sub> ,4'-OCH <sub>3</sub>	3930	3500	this work
	4-OCH <sub>3</sub> ,4'-OC <sub>6</sub> H <sub>5</sub>	559	612	this work
Trifluoroacetate	H,H	15.5	16.9	this work
	4-CH <sub>3</sub>	210	225	this work
	4-F	32.7	28.7	this work
	4-CH <sub>3</sub> ,4'-CH <sub>3</sub>	2300	2250	this work

(\*) Cancelled from the final optimization because of noticeable deviation between experimental and calculated rate constants (see text).

(\*\*) Cancelled from the final optimization because each *nucleofuge* (= leaving group/solvent combination) should be represented by only one rate constant.

<sup>a-u</sup> Extrapolated from different temperatures:

<sup>a</sup>  $\Delta H^\ddagger = 81.4 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -67.8 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>b</sup>  $\Delta H^\ddagger = 75.7 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -71.2 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>c</sup>  $\Delta H^\ddagger = 98.6 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -19.4 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>d</sup>  $\Delta H^\ddagger = 88.7 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -36.3 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>e</sup>  $\Delta H^\ddagger = 87.0 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -35.5 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>f</sup>  $\Delta H^\ddagger = 82.5 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -48.0 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>g</sup>  $\Delta H^\ddagger = 52.3 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -80.7 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>h</sup>  $\Delta H^\ddagger = 116.4 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -33.8 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>i</sup>  $\Delta H^\ddagger = 108.1 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 22.8 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>j</sup>  $\Delta H^\ddagger = 98.6 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 7.1 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>k</sup>  $\Delta H^\ddagger = 90.7 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -26.5 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>l</sup>  $\Delta H^\ddagger = 88.4 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -29.8 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>m</sup>  $\Delta H^\ddagger = 68.5 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -1.55 \text{ J K}^{-1} \text{ mol}^{-1}$ , from ref. [S1b]

<sup>n</sup>  $\Delta H^\ddagger = 52.4 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -35.5 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>o</sup>  $\Delta H^\ddagger = 64.0 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -7.8 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>p</sup>  $\Delta H^\ddagger = 83.9 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -47.3 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>q</sup>  $\Delta H^\ddagger = 96.2 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -18.6 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>r</sup>  $\Delta H^\ddagger = 94.3 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -19.4 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>s</sup>  $\Delta H^\ddagger = 104.1 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 13.4 \text{ J K}^{-1} \text{ mol}^{-1}$

### 3. Solvent nucleophilicity of aqueous acetone (90A10W and 80A20W)<sup>[S27]</sup>

As the reactions of the colored benzhydrylium ions with the solvents gave rise to colorless products, the decay of the carbocation absorptions was followed by UV-Vis spectroscopy.

Hi-Tech SF-61DX2 stopped-flow spectrophotometer systems (controlled by Hi-Tech KinetAsyst2 software) were used for the investigation of the rapid reactions of benzhydrylium ions **18–22** with the solvents ( $\tau_{1/2} < 10$  s at 20 °C). For the stopped-flow measurements, the stock solutions of the benzhydrylium ions in acetone were mixed with aqueous acetone in a 1 : 10 ratio. First-order kinetics with an exponential decay of the benzhydrylium ion concentration were observed. First-order rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) were obtained by least-squares fitting of the absorbance data (averaged from at least 4 kinetic runs for each solvent) to the single-exponential  $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ .

The rates of the slow reactions ( $\tau_{1/2} > 10$  s) of the benzhydrylium ions **23** and **24** with aqueous acetone were determined by using a J&M TIDAS diode array spectrophotometer which was controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. The temperature of the solutions during all kinetic studies was kept constant ( $20 \pm 0.2$  °C) by using a circulating bath thermostat and was monitored with a thermo-couple probe that was inserted into the reaction mixture. To accelerate the proton transfer rates, N-methylmorpholine and sodium acetate (NaOAc) were added to the reaction mixtures of **23** and **24**, respectively. Whereas the decay of **23** in aqueous acetone was independent of the N-methylmorpholine concentration, the rate constants of the decay of **24** linearly increased with increasing NaOAc concentration. Therefore, the first-order rate constants of **24** in aqueous acetone were extrapolated to  $[\text{NaOAc}] = 0$  from  $k_{\text{obs}}$  vs.  $[\text{NaOAc}]$  plots.



**80A20W**<sup>[S27]</sup>

 Benzhydrylium ions **18–22** in 80A20W (Stopped-flow)

No.	Electrophile	[Ar <sub>2</sub> CH <sup>+</sup> ] <sub>0</sub> / M	Detection / nm	<i>k</i> <sub>2</sub> / s <sup>-1</sup>
575-5	<b>18</b>	4.09 × 10 <sup>-5</sup>	590	1.90 × 10 <sup>2</sup>
575-4	<b>19</b>	1.71 × 10 <sup>-5</sup>	585	1.90 × 10 <sup>1</sup>
575-3	<b>20</b>	7.73 × 10 <sup>-6</sup>	660	3.07 × 10 <sup>1</sup>
575-2	<b>21</b>	8.36 × 10 <sup>-6</sup>	610	9.34 × 10 <sup>-1</sup>
575-1	<b>22</b>	9.26 × 10 <sup>-6</sup>	610	1.20

 Benzhydrylium ion **23** in 80A20W in the presence of *N*-methylmorpholine (J&M, 615 nm)

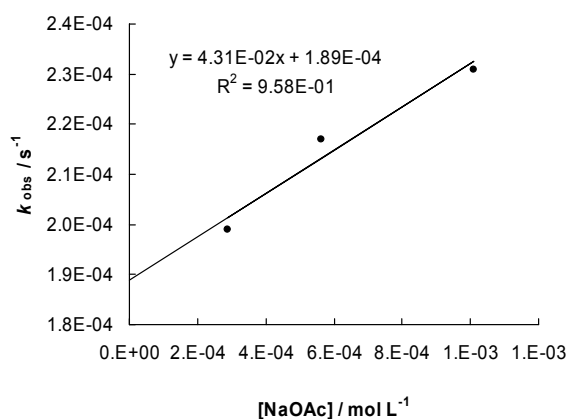
No.	[ <b>23</b> ] <sub>0</sub> / M	[ <i>N</i> -methylmorpholine] / M	<i>k</i> <sub>obs</sub> / s <sup>-1</sup>
713-1	1.39 × 10 <sup>-5</sup>	2.33 × 10 <sup>-4</sup>	2.06 × 10 <sup>-3</sup>
713-2	1.40 × 10 <sup>-5</sup>	4.70 × 10 <sup>-4</sup>	2.10 × 10 <sup>-3</sup>
713-3	1.41 × 10 <sup>-5</sup>	7.10 × 10 <sup>-4</sup>	2.08 × 10 <sup>-3</sup>

*k*<sub>2</sub> = 2.08 × 10<sup>-3</sup> s<sup>-1</sup>

 Benzhydrylium ion **24** in 80A20W in the presence of sodium acetate (J&M, 630 nm)

No.	[ <b>24</b> ] <sub>0</sub> / M	[NaOAc] / M	<i>k</i> <sub>obs</sub> / s <sup>-1</sup>
715-2	1.18 × 10 <sup>-5</sup>	2.88 × 10 <sup>-4</sup>	1.99 × 10 <sup>-4</sup>
715-1	1.15 × 10 <sup>-5</sup>	5.64 × 10 <sup>-4</sup>	2.17 × 10 <sup>-4</sup>
709-1	7.06 × 10 <sup>-6</sup>	1.01 × 10 <sup>-3</sup>	2.31 × 10 <sup>-4</sup>

*k*<sub>2</sub> = 1.89 × 10<sup>-4</sup> s<sup>-1</sup>


**Table S2.** Comparison of experimental and calculated (Eq. (2)) rate constants for the reactions of 80A20W<sup>[S27]</sup> with benzhydrylium ions **18–24** (20 °C).

Solvent	<i>N</i>	<i>s</i>	Electrophile <i>E</i> <sup>[a]</sup>	<i>k</i> <sub>2</sub> / s <sup>-1</sup>	<i>k</i> <sub>2</sub> <sup>calc</sup> / s <sup>-1</sup>	log <i>k</i> <sub>2</sub>	log <i>k</i> <sub>2</sub> <sup>calc</sup>	Δ <sup>2</sup> log <i>k</i>
20W80A	5.77	0.87	<b>18</b>	1.90E+2	1.97E+2	2.28	2.29	2.37E-4
	5.77	0.87	<b>19</b>	1.90E+1	4.75E+1	1.28	1.68	1.58E-1
	5.77	0.87	<b>20</b>	3.07E+1	8.30	1.49	0.92	3.23E-1
	5.77	0.87	<b>21</b>	9.34E-1	1.64	-0.03	0.21	5.91E-2
	5.77	0.87	<b>22</b>	1.20E+0	7.94E-1	0.08	-0.10	3.21E-2
	5.77	0.87	<b>23</b>	2.08E-3	2.51E-3	-2.68	-2.60	6.80E-3
	5.77	0.87	<b>24</b>	1.89E-4	1.93E-4	-3.72	-3.71	8.65E-5

<sup>[a]</sup> From ref. [6].

**90A10W**<sup>[S27]</sup>

 Benzhydrylium ions **18–22** in 90A10W (Stopped-flow)

No.	Electrophile	[Ar <sub>2</sub> CH <sup>+</sup> ] <sub>0</sub> / M	Detection, nm	$k_2 / \text{s}^{-1}$
575-10	<b>18</b>	$4.09 \times 10^{-5}$	590	$1.37 \times 10^2$
575-9	<b>19</b>	$1.71 \times 10^{-5}$	585	$1.78 \times 10^1$
575-8	<b>20</b>	$7.73 \times 10^{-6}$	660	$2.47 \times 10^1$
575-7	<b>21</b>	$8.36 \times 10^{-6}$	610	$7.75 \times 10^{-1}$
575-6	<b>22</b>	$9.26 \times 10^{-6}$	610	$9.40 \times 10^{-1}$

 Benzhydrylium ion **23** in 90A10W in the presence of *N*-methylmorpholine (J&M, 615 nm)

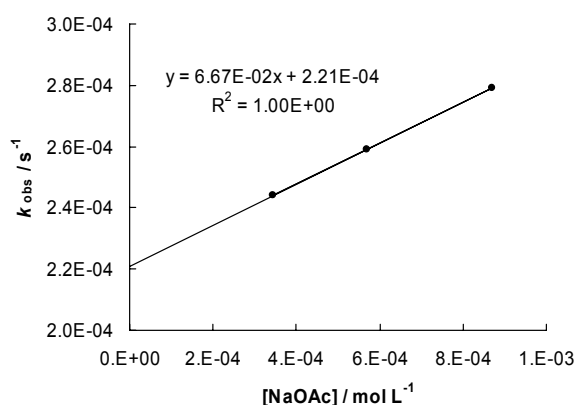
No.	[ <b>23</b> ] <sub>0</sub> / M	[ <i>N</i> -methylmorpholine] / M	$k_{\text{obs}} / \text{s}^{-1}$
712-1	$1.34 \times 10^{-5}$	$2.82 \times 10^{-3}$	$1.84 \times 10^{-3}$
712-2	$1.38 \times 10^{-5}$	$5.80 \times 10^{-3}$	$1.80 \times 10^{-3}$
712-3	$1.39 \times 10^{-5}$	$8.75 \times 10^{-3}$	$1.87 \times 10^{-3}$

$k_2 = 1.84 \times 10^{-3} \text{ s}^{-1}$

 Benzhydrylium ion **24** in 90A10W in the presence of sodium acetate (J&M, 630 nm)

No.	[ <b>24</b> ] <sub>0</sub> / M	[NaOAc] / M	$k_{\text{obs}} / \text{s}^{-1}$
711-1	$7.21 \times 10^{-6}$	$3.45 \times 10^{-4}$	$2.44 \times 10^{-4}$
714-1	$1.16 \times 10^{-5}$	$5.69 \times 10^{-4}$	$2.59 \times 10^{-4}$
714-2	$1.19 \times 10^{-5}$	$8.70 \times 10^{-4}$	$2.79 \times 10^{-4}$

$k_2 = 2.21 \times 10^{-4} \text{ s}^{-1}$


**Table S3.** Comparison of experimental and calculated (Eq. (2)) rate constants for the reactions of 90A10W<sup>[S27]</sup> with benzhydrylium ions **18–24** (20 °C).

Solvent	<i>N</i>	<i>s</i>	Electrophile	$E^{\text{[a]}}$	$k_2 / \text{s}^{-1}$	$k_2^{\text{calc}} / \text{s}^{-1}$	$\log k_2$	$\log k_2^{\text{calc}}$	$\Delta^2 \log k$
10W90A	5.70	0.85	<b>18</b>	-3.14	$1.37\text{E}+2$	$1.50\text{E}+2$	2.14	2.18	$1.62\text{E}-3$
	5.70	0.85	<b>19</b>	-3.85	$1.78\text{E}+1$	$3.73\text{E}+1$	1.25	1.57	$1.02\text{E}-1$
	5.70	0.85	<b>20</b>	-4.72	$2.47\text{E}+1$	6.77	1.39	0.83	$3.15\text{E}-1$
	5.70	0.85	<b>21</b>	-5.53	$7.75\text{E}-1$	1.39	-0.11	0.14	$6.35\text{E}-2$
	5.70	0.85	<b>22</b>	-5.89	$9.40\text{E}-1$	$6.84\text{E}-1$	-0.03	-0.16	$1.90\text{E}-2$
	5.70	0.85	<b>23</b>	-8.76	$1.84\text{E}-3$	$2.47\text{E}-3$	-2.74	-2.61	$1.64\text{E}-2$
	5.70	0.85	<b>24</b>	-10.04	$2.21\text{E}-4$	$2.01\text{E}-4$	-3.66	-3.70	$1.67\text{E}-3$

[a] From ref. [6].

## 4. References

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