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Supporting Information

How Fast Do R-X Bonds Ionize? A Semiquantitative Approach

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Table S1. Solvolysis rate constants k_s (25 °C) of X,Y-substituted benzhydryl chlorides and bromides in various solvents.

Electrofuge X, Y	E_f	Nucleofuge LG	solvent[a]	k_s [s^{-1}]	ref. short cut[b]
H	−6.05	Cl	90M10W	3.74 × 10^{-3}	[Win57]
4-Me	−4.68	Cl	90M10W	9.16 × 10^{-2}	[Liu98]
4-NO$_2$	−9.26	Cl	90M10W	2.51 × 10^{-6}	[Liu98]
3-Cl	−7.74	Cl	90M10W	9.16 × 10^{-5}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	90M10W	8.56 × 10^{-3}	[Liu02]
H	−6.05	Br	90M10W	7.15 × 10^{-2}	[Liu95]
4-F	−5.78	Br	90M10W	1.18 × 10^{-1}	[Liu95]
4-NO$_2$	−9.26	Br	90M10W	4.49 × 10^{-5}	[Liu95]
3-Cl	−7.74	Br	90M10W	1.59 × 10^{-3}	[Liu95]
4-OPh, 4'-NO$_2$	−5.64	Br	90M10W	1.69 × 10^{-1}	[Liu02]
4-Me	−4.68	Cl	80M20W	3.26 × 10^{-1}	[Liu98]
4-NO$_2$	−9.26	Cl	80M20W	7.91 × 10^{-6}	[Liu98]
3-Cl	−7.74	Cl	80M20W	3.14 × 10^{-4}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	80M20W	2.95 × 10^{-2}	[Liu02]
4-NO$_2$	−9.26	Br	80M20W	1.40 × 10^{-4}	[Liu95]
3-Cl	−7.74	Br	80M20W	4.98 × 10^{-3}	[Liu95]
4-OPh, 4'-NO$_2$	−5.64	Br	80M20W	5.41 × 10^{-1}	[Liu02]
H	−6.05	Cl	2-propanol	6.06 × 10^{-6}	[Nis67a]
4-Me	−4.68	Cl	2-propanol	1.23 × 10^{-4}	[Nis67a]
4-OMe	−2.06	Cl	2-propanol	2.70 × 10^{-2}	[Nis67a]
4-Br	−6.67	Cl	2-propanol	2.04 × 10^{-6}	[Nis67a]
4-Cl	−6.52	Cl	2-propanol	2.49 × 10^{-6}	[Nis67a]
4-F	−5.78	Cl	2-propanol	1.16 × 10^{-5}	[Nis67a]
3-Me	−5.78	Cl	2-propanol	1.14 × 10^{-5}	[Nis67a]
3-Cl	−7.74	Cl	2-propanol	1.45 × 10^{-7}	[Nis67a]
4-Me, 4'-Me	−3.47	Cl	2-propanol	1.56 × 10^{-3}	[Nis67b]
4-Cl, 4'-Cl	−6.96	Cl	2-propanol	1.06 × 10^{-6}	[Nis67b]
3,5-(Me)$_2$	−5.48	Cl	2-propanol	2.14 × 10^{-5}	[Nis67b]
H	−6.05	Cl	90E10W	4.93 × 10^{-4}	[War27]
4-Me	−4.68	Cl	90E10W	1.06 × 10^{-2}	[Liu98]
4-Cl	−6.52	Cl	90E10W	1.91 × 10^{-4}	[Har81]
4-NO$_2$	−9.26	Cl	90E10W	3.43 × 10^{-7}	[Liu98]
3-Me	−5.78	Cl	90E10W	8.81 × 10^{-4}	[Sch60]
4-OPh, 4'-NO$_2$	−5.64	Cl	90E10W	1.20 × 10^{-3}	[Liu02]
3,5-(Me)$_2$	−5.48	Cl	90E10W	1.63 × 10^{-3}	[Sch60]
H	−6.05	Br	90E10W	8.86 × 10^{-3}	[Liu97]

Table S1 (continued).

Electrofuge	E_f	Nucleofuge		k_s [s^{-1}]	ref. short cut[b]
X, Y		LG	solvent[a]		
4-NO$_2$	−9.26	Br	90E10W	7.80×10^{-6}	[Liu97]
4-OPh, 4'-NO$_2$	−5.64	Br	90E10W	1.52×10^{-2}	[Liu02]
H	−6.05	Cl	70E30W	6.03×10^{-3}	[Liu98]
4-NO$_2$	−9.26	Cl	70E30W	4.59×10^{-6}	[Liu98]
3-Cl	−7.74	Cl	70E30W	9.02×10^{-5}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	70E30W	1.04×10^{-2}	[Liu02]
4-Cl, 4'-Cl	−6.96	Cl	70E30W	8.30×10^{-4}	[Har81]
H	−6.05	Br	70E30W	9.27×10^{-2}	[Liu95]
4-F	−5.78	Br	70E30W	1.39×10^{-1}	[Liu95]
4-NO$_2$	−9.26	Br	70E30W	6.39×10^{-5}	[Liu95]
3-Cl	−7.74	Br	70E30W	1.58×10^{-3}	[Liu95]
4-OPh, 4'-NO$_2$	−5.64	Br	70E30W	1.46×10^{-1}	[Liu02]
H	−6.05	Cl	60E40W	1.59×10^{-2}	[Liu98]
3-Cl	−7.74	Cl	60E40W	3.02×10^{-4}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	60E40W	2.89×10^{-2}	[Liu02]
H	−6.05	Cl	70A30W	5.10×10^{-4}	[Liu98]
4-Me	−4.68	Cl	70A30W	1.21×10^{-2}	[Liu98]
4-NO$_2$	−9.26	Cl	70A30W	3.39×10^{-7}	[Liu98]
3-Cl	−7.74	Cl	70A30W	8.94×10^{-6}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	70A30W	1.29×10^{-3}	[Liu02]
H	−6.05	Br	70A30W	1.20×10^{-2}	[Swa53]
4-F	−5.78	Br	70A30W	2.09×10^{-2}	[Liu95]
4-NO$_2$	−9.26	Br	70A30W	1.15×10^{-5}	[Liu95]
3-Cl	−7.74	Br	70A30W	2.30×10^{-4}	[Liu95]
4-OPh, 4'-NO$_2$	−5.64	Br	70A30W	2.72×10^{-2}	[Liu02]
H	−6.05	Cl	60A40W	2.76×10^{-3}	[Liu98]
4-Me	−4.68	Cl	60A40W	6.16×10^{-2}	[Liu98]
4-NO$_2$	−9.26	Cl	60A40W	1.95×10^{-6}	[Liu98]
3-Cl	−7.74	Cl	60A40W	4.80×10^{-5}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	60A40W	5.77×10^{-3}	[Liu02]
H	−6.05	Br	60A40W	5.45×10^{-2}	[Liu98]
4-F	−5.78	Br	60A40W	1.05×10^{-1}	[Liu98]
4-NO$_2$	−9.26	Br	60A40W	4.42×10^{-5}	[Liu98]
3-Cl	−7.74	Br	60A40W	9.21×10^{-4}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Br	60A40W	1.12×10^{-1}	[Liu02]

Table S1 (continued)**.**

Electrofuge	E_f	Nucleofuge		$k_s\ [s^{-1}]$	ref. short cut[b]
X, Y		LG	solvent[a]		
H	−6.05	Cl	50A50W	1.38×10^{-2}	[Liu98]
4-Me	−4.68	Cl	50A50W	6.65×10^{-1}	[Liu98]
4-NO$_2$	−9.26	Cl	50A50W	9.71×10^{-6}	[Liu98]
3-Cl	−7.74	Cl	50A50W	2.83×10^{-4}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	50A50W	2.49×10^{-2}	[Liu02]
4-NO$_2$	−9.26	Br	50A50W	1.62×10^{-4}	[Liu95]
3-Cl	−7.74	Br	50A50W	4.13×10^{-3}	[Liu95]
4-Cl, 4'-Cl	−6.96	Br	50A50W	2.12×10^{-2}	this work
H	−6.05	Cl	80T20E	1.19×10^{-1}	[Liu98]
4-NO$_2$	−9.26	Cl	80T20E	1.17×10^{-5}	[Liu98]
4-Cl, 4'-Cl	−6.96	Cl	80T20E	1.29×10^{-2}	[Rap83]
3-Cl	−7.74	Cl	80T20E	1.77×10^{-3}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	80T20E	1.25×10^{-1}	[Liu02]
H	−6.05	Br	80T20E	9.75×10^{-1}	[Liu95]
4-NO$_2$	−9.26	Br	80T20E	9.92×10^{-5}	[Liu95]
3-Cl	−7.74	Br	80T20E	1.33×10^{-2}	[Liu95]
4-OPh, 4'-NO$_2$	−5.64	Br	80T20E	1.07	[Liu02]
H	−6.05	Cl	60T40E	1.47×10^{-2}	[Liu98]
4-Me	−4.68	Cl	60T40E	7.57×10^{-1}	[Liu98]
4-NO$_2$	−9.26	Cl	60T40E	2.52×10^{-6}	[Liu98]
3-Cl	−7.74	Cl	60T40E	2.47×10^{-4}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	60T40E	2.49×10^{-2}	[Liu02]
4-Cl, 4'-Cl	−6.96	Cl	60T40E	1.76×10^{-3}	[Rap83]
H	−6.05	Br	60T40E	1.43×10^{-1}	[Liu95]
4-F	−5.78	Br	60T40E	2.44×10^{-1}	[Liu95]
4-NO$_2$	−9.26	Br	60T40E	3.23×10^{-5}	[Liu95]
3-Cl	−7.74	Br	60T40E	2.47×10^{-3}	[Liu95]
4-OPh, 4'-NO$_2$	−5.64	Br	60T40E	2.15×10^{-1}	[Liu02]
H	−6.05	Cl	40T60E	2.10×10^{-3}	[Liu98]
4-Me	−4.68	Cl	40T60E	7.03×10^{-2}	[Liu98]
4-OPh, 4'-NO$_2$	−5.64	Cl	40T60E	4.37×10^{-3}	[Liu02]
4-Cl, 4'-Cl	−6.96	Cl	40T60E	2.90×10^{-4}	[Rap83]
H	−6.05	Br	40T60E	2.64×10^{-2}	[Liu97]
4-OPh, 4'-NO$_2$	−5.64	Br	40T60E	4.48×10^{-2}	[Liu02]

Table S1 (continued)**.**

Electrofuge	E_f	Nucleofuge		k_s [s^{-1}]	ref. short cut[b]
X, Y		LG	solvent[a]		
H	−6.05	Cl	60M40W	1.59×10^{-1}	[Bun84]
H	−6.05	Cl	40E60W	2.26×10^{-1}	[Bun84]
H	−6.05	Cl	60AN40W[c]	5.00×10^{-3}	[Bun84]
H	−6.05	Cl	50AN50W[c]	1.77×10^{-2}	[Bun84]
H	−6.05	Cl	40AN60W[c]	6.57×10^{-2}	[Bun84]
H	−6.05	Cl	30AN70W[c]	1.94×10^{-1}	[Bun84]
H	−6.05	Cl	90D10W	1.68×10^{-6}	[Win57]
H	−6.05	Cl	80D20W	2.67×10^{-5}	[Win57]
H	−6.05	Cl	70D30W	2.04×10^{-4}	[Win57]
H	−6.05	Cl	60D40W	1.28×10^{-3}	[Win57]
H	−6.05	Br	90D10W	4.35×10^{-5}	[Win57]
H	−6.05	Br	80D20W	5.60×10^{-4}	[Win57]
H	−6.05	Br	70D30W	3.77×10^{-3}	[Win57]
H	−6.05	Br	60D40E	4.60×10^{-5}	[Win57]
H	−6.05	Br	40D60E	1.86×10^{-4}	[Win57]
H	−6.05	Br	20D80E	5.25×10^{-4}	[Win57]

[a] Mixtures of solvents are given as (v/v), solvents: W = water, A = acetone, AN = acetonitrile, D = 1,4-dioxane, E = ethanol, M = methanol, T = trifluoroethanol. [b] See Table S2 for references. [c] Mixtures of solvents are given as (w/w).

Table S2. References used in Table S1.

ref. short cut	reference
[Bun84]	C. A. Bunton, M. M. Mhala, J. R. Moffatt, *J. Org. Chem.* **1984**, *49*, 3639–3641.
[Har81]	S. G. Shafer, J. M. Harris, *J. Org. Chem.* **1981**, *46*, 2164–2169.
[Liu95]	K.-T. Liu, C.-P. Chin, Y.-S. Lin, M.-L. Tsao, *Tetrahedron Lett.* **1995**, *36*, 6919–6922.
[Liu97]	K.-T. Liu, C.-P. Chin, Y.-S. Lin, M.-L. Tsao, *J. Chem. Res. (S)* **1997**, 18–19.
[Liu98]	K.-T. Liu, Y.-S. Lin, M.-L. Tsao, *J. Phys. Org. Chem.* **1998**, *11*, 223–229.
[Liu02]	K.-T. Liu, C.-S. Chuang, B.-Y. Jin, *J. Phys. Org. Chem.* **2002**, *15*, 21–28.
[Nis67a]	S. Nishida, *J. Org. Chem.* **1967**, *32*, 2692–2695.
[Nis67b]	S. Nishida, *J. Org. Chem.* **1967**, *32*, 2695–2697.
[Rap83]	Z. Rappoport, H. Ben-Yacov, J. Kaspi, *J. Org. Chem.* **1978**, 43, 3678–3684.
[Sch60]	W. M. Schubert, R. G. Minton, *J. Am. Chem. Soc.* **1960**, *82*, 6188–6193.
[Swa53]	C. G. Swain, C. B. Scott, K. H. Lohmann, *J. Am. Chem. Soc.* **1953**, *75*, 136–140.
[War27]	A. M. Ward, *J. Chem. Soc.* **1927**, 2285–2295.
[Win57]	S. Winstein, A. H. Fainberg, E. Grunwald, *J. Am. Chem. Soc.* **1957**, *79*, 4146–4155.

90M10W

● Bromide
▲ Chloride

$y = 0.9844x + 4.7878$
$R^2 = 0.9997$

$y = 0.9854x + 3.5424$
$R^2 = 0.9995$

log k

E_f

80M20W

● Bromide
▲ Chloride

$y = 0.9895x + 5.3265$
$R^2 = 0.9998$

$y = 0.9958x + 4.1463$
$R^2 = 0.9993$

log k

E_f

2-PrOH

▲ Chloride

$y = 0.9167x + 0.3575$
$R^2 = 0.9991$

log k

E_f

90E10W

● Bromide
▲ Chloride

$y = 0.9254x + 3.4697$
$R^2 = 0.9984$

$y = 0.9771x + 2.5985$
$R^2 = 0.9997$

log k

E_f

70E30W

● Bromide
▲ Chloride

$y = 0.9575x + 4.6566$
$R^2 = 0.9976$

$y = 0.9561x + 3.4832$
$R^2 = 0.995$

log k

E_f

60E40W

▲ Chloride

$y = 0.9653x + 3.9661$
$R^2 = 0.9959$

log k

E_f

S6