–Supporting Information–

Solvent Nucleophilicity

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Water-Acetonitrile Mixtures

Water

$(dma)_2CH^+$ in water with phosphate buffer at pH 8.0 (conventional, λ = 605 nm)

No.	$[(dma)_2CH^+]_0$, mol L^{-1}	$[phosphate]_{total}$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
552-1	1.17×10^{-5}	5.14×10^{-3}	2.01×10^{-2}	98
552-2	1.23×10^{-5}	1.09×10^{-2}	2.13×10^{-2}	99
552-3	1.22×10^{-5}	1.61×10^{-2}	2.03×10^{-2}	98
				$k = 2.06 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in water (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F172-1	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	9.44×10^{4}

[a] OAc = acetate

91W9AN

$(thq)_2CH^+$ in 91W9AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
313-1	8.24×10^{-6}	2.59×10^{-3}	1.68×10^{-3}	98
313-2	8.41×10^{-6}	5.29×10^{-3}	1.67×10^{-3}	98
313-3	8.03×10^{-6}	7.57×10^{-3}	1.64×10^{-3}	96
313-4	7.96×10^{-6}	1.00×10^{-2}	1.67×10^{-3}	94
313-5	8.18×10^{-6}	1.29×10^{-2}	1.65×10^{-3}	96
				$k = 1.66 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

$(pyr)_2CH^+$ in 91W9AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 620 nm)

No.	$[(pyr)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
365-1	3.82×10^{-6}	2.17×10^{-3}	4.35×10^{-3}	93
365-2	3.41×10^{-6}	3.87×10^{-3}	4.25×10^{-3}	94
365-3	3.39×10^{-6}	5.77×10^{-3}	4.36×10^{-3}	92
365-4	3.32×10^{-6}	7.53×10^{-3}	4.19×10^{-3}	97
				$k = 4.29 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

Ar_2CH^+ in 91W9AN (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
333-1	$(mpa)_2CH^+$	1.05×10^{-5}	610	3.31×10^{-1}
309-1	$(mor)_2CH^+$	5.72×10^{-6}	610	6.73×10^{-1}
309-3	$(mfa)_2CH^+$	4.12×10^{-6}	585	4.39
309-4	$(pfa)_2CH^+$	7.22×10^{-6}	590	9.36×10^{1}

Ar_2CH^+ in91W9AN (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F152-1	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	9.55×10^{4}
F151-6	$(ani)(tol)CH^+$	(ani)(tol)CHOAc	1.52×10^{-4}	480	7.99×10^{5}

[a] OAc = acetate

80W20AN

$(thq)_2CH^+$ in 80W20AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
359-1	4.87×10^{-6}	1.19×10^{-3}	1.26×10^{-3}	96
359-2	4.74×10^{-6}	2.30×10^{-3}	1.21×10^{-3}	94
359-3	4.67×10^{-6}	3.41×10^{-3}	1.23×10^{-3}	97
				$k = 1.23 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

$(pyr)_2CH^+$ in 80W20AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 610 nm)

No.	$[(pyr)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
364-1	3.87×10^{-6}	2.47×10^{-3}	3.86×10^{-3}	90
364-2	3.84×10^{-6}	4.90×10^{-3}	3.76×10^{-3}	98
364-3	3.84×10^{-6}	7.35×10^{-3}	3.74×10^{-3}	97
364-4	3.86×10^{-6}	9.85×10^{-3}	3.72×10^{-3}	97
				$k = 3.77 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

Ar_2CH^+ in 80W20AN (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
333-2	$(mpa)_2CH^+$	1.05×10^{-5}	610	2.84×10^{-1}
309-5	$(mor)_2CH^+$	5.72×10^{-6}	610	4.93×10^{-1}
309-7	$(mfa)_2CH^+$	4.12×10^{-6}	585	3.98
309-8	$(pfa)_2CH^+$	7.22×10^{-6}	590	4.93×10^{1}

67W33AN

$(thq)_2CH^+$ in 67W33AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
361-1	4.60×10^{-6}	1.12×10^{-3}	1.17×10^{-3}	93
361-2	5.74×10^{-6}	2.80×10^{-3}	1.16×10^{-3}	96
361-3	5.30×10^{-6}	3.87×10^{-3}	1.17×10^{-3}	96
				$k = 1.17 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

$(pyr)_2CH^+$ in 67W33AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 610 nm)

No.	$[(pyr)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
366-1	4.61×10^{-6}	2.62×10^{-3}	4.23×10^{-3}	95
366-2	3.93×10^{-6}	4.45×10^{-3}	4.04×10^{-3}	95
366-3	4.15×10^{-6}	7.05×10^{-3}	4.00×10^{-3}	93
366-4	3.76×10^{-6}	8.52×10^{-3}	3.93×10^{-3}	93
				$k = 4.05 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

Ar_2CH^+ in 67W33AN (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
333-3	$(mpa)_2CH^+$	1.05×10^{-5}	610	2.83×10^{-1}
309-9	$(mor)_2CH^+$	5.72×10^{-6}	610	4.13×10^{-1}
309-11	$(mfa)_2CH^+$	4.12×10^{-6}	585	4.47
309-12	$(pfa)_2CH^+$	7.22×10^{-6}	590	4.96×10^{1}

50W50AN

$(thq)_2CH^+$ in 50W50AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
311-1	6.84×10^{-6}	9.44×10^{-4}	1.24×10^{-3}	93
311-2	8.57×10^{-6}	2.37×10^{-3}	1.22×10^{-3}	97
311-3	8.06×10^{-6}	3.33×10^{-3}	1.21×10^{-3}	74
311-4	7.84×10^{-6}	4.33×10^{-3}	1.22×10^{-3}	93
311-5	8.39×10^{-6}	5.79×10^{-3}	1.22×10^{-3}	97
				$k = 1.22 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

$(pyr)_2CH^+$ in 50W50AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 610 nm)

No.	$[(pyr)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
248-1	2.32×10^{-6}	1.18×10^{-3}	4.36×10^{-3}	94
	2.31×10^{-6}	2.95×10^{-3}	4.37×10^{-3}	95
	2.33×10^{-6}	3.57×10^{-3}	4.27×10^{-3}	94
	2.31×10^{-6}	4.72×10^{-3}	4.31×10^{-3}	94
	2.29×10^{-6}	5.85×10^{-3}	4.34×10^{-3}	96
				$k = 4.33 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

Ar_2CH^+ in 50W50AN (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
397-1	$(mpa)_2CH^+$	5.85×10^{-6}	610	2.52×10^{-1}
397-2	$(dpa)_2CH^+$	1.07×10^{-5}	660	4.44
397-3	$(pfa)_2CH^+$	7.06×10^{-6}	590	3.62×10^{1}

Ar_2CH^+ in 50W50AN (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F5-4	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	1.01×10^5
F47-4	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	8.55×10^5
F19-4	$(ani)PhCH^+$	(ani)PhCHOAr'	1.29×10^{-4}	455	1.84×10^6
F9-1	$(tol)_2CH^+$	$(tol)_2CHOAr'$	1.95×10^{-4}	460	3.28×10^7

[a] OAr' = 4-cyanophenoxide

33W67AN

$(thq)_2CH^+$ in 33W67AN with DABCO/DABCO-H^+ (1/1) buffer (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	[DABCO],[a] mol L^{-1}	k_{obs}, s^{-1}	conversion, %
475-1	1.12×10^{-5}	8.65×10^{-4}	1.24×10^{-3}	84
475-2	1.13×10^{-5}	2.52×10^{-3}	1.30×10^{-3}	89
475-3	1.09×10^{-5}	4.33×10^{-3}	1.30×10^{-3}	89
				$k = 1.28 \times 10^{-3}$ s^{-1}

[a] [DABCO] = [DABCO-H^+]

Ar_2CH^+ in 33W67AN (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
394-1	$(mpa)_2CH^+$	5.85×10^{-6}	610	2.24×10^{-1}
394-2	$(mor)_2CH^+$	7.82×10^{-6}	610	2.85×10^{-1}
394-3	$(dpa)_2CH^+$	1.07×10^{-5}	660	4.12
394-4	$(mfa)_2CH^+$	8.50×10^{-6}	585	3.58
394-5	$(pfa)_2CH^+$	7.06×10^{-6}	590	3.39×10^1

Ar_2CH^+ in 33W67AN (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F37-3	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	1.01×10^5
F47-3	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	8.95×10^5
F19-3	$(ani)PhCH^+$	(ani)PhCHOAr'	1.29×10^{-4}	455	1.91×10^6
F9-2	$(tol)_2CH^+$	$(tol)_2CHOAr'$	1.95×10^{-4}	460	3.47×10^7

[a] OAr' = 4-cyanophenoxide

20W80AN

Ar_2CH^+ in 20W80AN (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
395-1	$(mpa)_2CH^+$	5.85×10^{-6}	610	2.17×10^{-1}
395-2	$(mor)_2CH^+$	7.82×10^{-6}	610	2.51×10^{-1}
395-3	$(dpa)_2CH^+$	1.07×10^{-5}	660	3.97
395-4	$(mfa)_2CH^+$	8.50×10^{-6}	585	3.62
395-5	$(pfa)_2CH^+$	7.06×10^{-6}	590	3.32×10^1

Ar_2CH^+ in 20W80AN (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F37-2	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	9.82×10^4
F47-2	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	8.29×10^5
F19-2	$(ani)PhCH^+$	(ani)PhCHOAr'	1.29×10^{-4}	455	1.87×10^6
F9-3	$(tol)_2CH^+$	$(tol)_2CHOAr'$	1.95×10^{-4}	460	3.06×10^7

[a] OAr' = 4-cyanophenoxide

10W90AN

Ar_2CH^+ in 10W90AN (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
396-1	$(mpa)_2CH^+$	5.85×10^{-6}	610	8.08×10^{-2}
396-2	$(mor)_2CH^+$	7.82×10^{-6}	610	8.08×10^{-2}
396-3	$(dpa)_2CH^+$	1.07×10^{-5}	660	1.56
396-4	$(mfa)_2CH^+$	8.50×10^{-6}	585	1.57
396-5	$(pfa)_2CH^+$	7.06×10^{-6}	590	1.42×10^1
448-1	$(fur)_2CH^+$	3.11×10^{-5}	520	7.11×10^2

Ar_2CH^+ in 10W90AN (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F37-1	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.59×10^{-4}	500	9.87×10^4
F47-1	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	6.81×10^5
F28-1	$(ani)PhCH^+$	(ani)PhCHOAr'	2.03×10^{-4}	455	1.83×10^6
F9-4	$(tol)_2CH^+$	$(tol)_2CHOAr'$	1.95×10^{-4}	460	2.37×10^7

[a] OAr' = 4-cyanophenoxide

Ethanol-Water Mixtures

90E10W

$(lil)_2CH^+$ in 90E10W (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
484-1	8.75×10^{-6}	3.08×10^{-3}	95
484-2	7.89×10^{-6}	3.15×10^{-3}	94
484-3	7.17×10^{-6}	2.87×10^{-3}	98

$k = 3.03 \times 10^{-3}$ s^{-1}

$(ind)_2CH^+$ in 90E10W (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
483-1	8.01×10^{-6}	2.85×10^{-2}	98
483-2	8.87×10^{-6}	2.75×10^{-2}	99
483-3	7.45×10^{-6}	2.74×10^{-2}	97

$k = 2.78 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 90E10W (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
524-1	$(pyr)_2CH^+$	5.11×10^{-6}	610	3.02×10^{-1}
532-1	$(dma)_2CH^+$	1.84×10^{-5}	605	8.33×10^{-1}

Ar_2CH^+ in 90E10W (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F43-1	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.99×10^{-4}	500	2.53×10^{6}
F55-1	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	9.47×10^{6}
F147-5	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.36×10^{-4}*	*455*	*7.04×10^{6}*

[a] OAr' = 4-cyanophenoxide

80E20W

$(lil)_2CH^+$ in 80E20W (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
476-1	8.14×10^{-6}	1.60×10^{-3}	95
476-2	8.22×10^{-6}	1.69×10^{-3}	94
476-3	8.42×10^{-6}	1.65×10^{-3}	98

$k = 1.65 \times 10^{-3}$ s^{-1}

$(ind)_2CH^+$ in 80E20W (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
477-1	8.55×10^{-6}	1.50×10^{-2}	96
477-2	8.73×10^{-6}	1.43×10^{-2}	96
477-3	8.37×10^{-6}	1.41×10^{-2}	97

$k = 1.45 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 80E20W (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
524-2	$(pyr)_2CH^+$	5.11×10^{-6}	610	1.40×10^{-1}
532-2	$(dma)_2CH^+$	1.84×10^{-5}	605	4.05×10^{-1}

Ar_2CH^+ in 80E20W (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F43-2	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.99×10^{-4}	500	1.51×10^{6}
F55-2	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	7.88×10^{6}
F147-4	$(ani)PhCH^+$	(ani)PhCHOAr'	1.36×10^{-4}	455	1.22×10^{7}

[a] OAr' = 4-cyanophenoxide

60E40W

$(lil)_2CH^+$ in 60E40W (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
491-1	8.08×10^{-6}	7.13×10^{-4}	92
491-2	8.07×10^{-6}	7.26×10^{-4}	89
491-3	7.51×10^{-6}	7.18×10^{-4}	94
491-4	8.15×10^{-6}	7.07×10^{-4}	93

$k = 7.16 \times 10^{-4}$ s^{-1}

$(ind)_2CH^+$ in 60E40W (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
490-1	7.91×10^{-6}	5.67×10^{-4}	95
490-2	6.73×10^{-6}	6.04×10^{-4}	91
490-3	8.08×10^{-6}	5.83×10^{-4}	93

$k = 5.84 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 60E40W (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
524-3	$(pyr)_2CH^+$	5.11×10^{-6}	610	5.28×10^{-2}
532-3	$(dma)_2CH^+$	1.84×10^{-5}	605	1.70×10^{-1}

Ar_2CH^+ in 60E40W (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F43-3	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.99×10^{-4}	500	7.13×10^{5}
F55-3	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	6.55×10^{6}
F147-2	$(ani)PhCH^+$	(ani)PhCHOAr'	1.36×10^{-4}	455	1.06×10^{7}

[a] OAr' = 4-cyanophenoxide

50E50W

$(ind)_2CH^+$ in 50E50W (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
487-1	4.15×10^{-6}	3.54×10^{-3}	91
487-2	3.92×10^{-6}	3.97×10^{-3}	93
487-3	6.88×10^{-6}	4.05×10^{-3}	95
479-3	8.31×10^{-6}	3.80×10^{-3}	97

$k = 3.84 \times 10^{-3}$ s^{-1}

$(dma)_2CH^+$ in 50E50W (conventional, λ = 605 nm)

No.	$[(dma)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
526-1	6.27×10^{-6}	7.64×10^{-2}	92
526-2	5.91×10^{-6}	7.31×10^{-2}	90
526-3	6.08×10^{-6}	7.33×10^{-2}	88

$k = 7.43 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 50E50W (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F43-4	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.99×10^{-4}	500	4.96×10^{5}
F55-4	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	3.86×10^{6}
F147-1	$(ani)PhCH^+$	(ani)PhCHOAr'	1.36×10^{-4}	455	7.91×10^{6}

[a] OAr' = 4-cyanophenoxide

40E60W

$(ind)_2CH^+$ in 40E60W in presence of DABCO buffer (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	[DABCO], mol L^{-1}	$[DABCO\text{-}H^+]$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
535-1	7.28×10^{-6}	7.88×10^{-4}	4.59×10^{-4}	2.63×10^{-3}	93
535-2	7.25×10^{-6}	1.31×10^{-3}	4.57×10^{-4}	2.59×10^{-3}	95
535-3	7.06×10^{-6}	1.78×10^{-3}	4.46×10^{-4}	2.62×10^{-3}	93

$k = 2.61 \times 10^{-3}$ s^{-1}

$(dma)_2CH^+$ in 40E60W (conventional, λ = 605 nm)

No.	$[(dma)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
527-1	6.39×10^{-6}	6.42×10^{-2}	85
527-2	6.19×10^{-6}	5.05×10^{-2}	84
527-3	6.34×10^{-6}	6.00×10^{-2}	85
543-1	1.11×10^{-5}	5.58×10^{-2}	99
543-2	1.07×10^{-5}	5.67×10^{-2}	96
543-3	1.02×10^{-5}	5.56×10^{-2}	91

$k = 5.71 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 40E60W (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F43-5	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.99×10^{-4}	500	3.68×10^5
F55-5	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	3.38×10^6
F147-3	$(ani)PhCH^+$	(ani)PhCHOAr'	1.36×10^{-4}	455	6.62×10^6

[a] OAr' = 4-cyanophenoxide

20E80W

$(thq)_2CH^+$ in 20E80W in presence of DABCO buffer (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	[DABCO], mol L^{-1}	$[DABCO\text{-}H^+]$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
531-1	9.81×10^{-6}	6.66×10^{-4}	2.33×10^{-4}	2.76×10^{-3}	97
531-2	9.63×10^{-6}	1.31×10^{-3}	2.29×10^{-4}	2.96×10^{-3}	98
531-3	9.68×10^{-6}	1.97×10^{-3}	2.30×10^{-4}	3.00×10^{-3}	98

$k = 2.91 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 20E80W (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F43-6	$(ani)_2CH^+$	$(ani)_2CHOAr'$	3.99×10^{-5}	500	2.20×10^5
F55-6	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	5.52×10^{-5}	480	2.72×10^6

[a] OAr' = 4-cyanophenoxide

10E90W

$(thq)_2CH^+$ in 10E90W in presence of DABCO buffer (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	[DABCO], mol L^{-1}	$[DABCO\text{-}H^+]$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
533-1	9.95×10^{-6}	8.10×10^{-4}	4.72×10^{-4}	2.39×10^{-3}	92
533-2	9.99×10^{-6}	1.36×10^{-3}	4.74×10^{-4}	2.36×10^{-3}	95
533-3	9.54×10^{-6}	1.81×10^{-3}	4.53×10^{-4}	2.54×10^{-3}	94

$k = 2.43 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 10E90W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F152-2	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	1.38×10^5
F152-5	$(ani)(tol)CH^+$	(ani)(tol)CHOAc	1.52×10^{-4}	480	9.54×10^5

[a] OAc = acetate

Trifluoroethanol-Water Mixtures

90T10W

Ar_2CH^+ in 90T10W at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
525-1	$(dpa)_2CH^+$	1.22×10^{-5}	660	3.76×10^{-2}
525-2	$(mfa)_2CH^+$	1.12×10^{-5}	585	1.23×10^{-1}
525-3	$(pfa)_2CH^+$	2.10×10^{-5}	590	3.01×10^{-1}

Ar_2CH^+ in 90T10W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F142-1	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	6.50×10^{2}
F151-1	$(ani)(tol)CH^+$	(ani)(tol)CHOAc	1.52×10^{-4}	480	1.28×10^{4}
F24-1	$(ani)PhCH^+$	(ani)PhCHOAr'	2.03×10^{-4}	455	4.01×10^{4}
F11-1	$(tol)_2CH^+$	$(tol)_2CHOAr'$	9.44×10^{-5}	460	4.32×10^{5}
F62-1	$(tol)PhCH^+$	(tol)PhCHOAr'	9.44×10^{-5}	450	2.45×10^{6}

[a] OAr' = 4-cyanophenoxide, OAc = acetate

80T20W

Ar_2CH^+ in 80T20W at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
525-4	$(dpa)_2CH^+$	1.22×10^{-5}	660	6.59×10^{-2}
525-5	$(mfa)_2CH^+$	1.12×10^{-5}	585	1.53×10^{-1}
525-6	$(pfa)_2CH^+$	2.10×10^{-5}	590	5.55×10^{-1}

Ar_2CH^+ in 80T20W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F142-2	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	2.55×10^{3}
F151-2	$(ani)(tol)CH^+$	(ani)(tol)CHOAc	1.52×10^{-4}	480	2.35×10^{4}
F24-2	$(ani)PhCH^+$	(ani)PhCHOAr'	2.03×10^{-4}	455	3.45×10^{4}
F11-2	$(tol)_2CH^+$	$(tol)_2CHOAr'$	9.44×10^{-5}	460	9.11×10^{5}
F62-2	$(tol)PhCH^+$	(tol)PhCHOAr'	9.44×10^{-5}	450	4.19×10^{6}

[a] OAr' = 4-cyanophenoxide, OAc = acetate

60T40W

Ar_2CH^+ in 60T40W at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
525-7	$(dpa)_2CH^+$	1.22×10^{-5}	660	7.96×10^{-2}
525-8	$(mfa)_2CH^+$	1.12×10^{-5}	585	1.90×10^{-1}
525-9	$(pfa)_2CH^+$	2.10×10^{-5}	590	9.37×10^{-1}

Ar_2CH^+ in 60T40W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F142-3	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	6.04×10^{3}
F53-3	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	5.46×10^{4}
F151-3	$(ani)(tol)CH^+$	(ani)(tol)CHOAc	1.52×10^{-4}	480	5.23×10^{4}
F24-3	$(ani)PhCH^+$	(ani)PhCHOAr'	2.03×10^{-4}	455	1.27×10^{5}
F11-6	$(tol)_2CH^+$	$(tol)_2CHOAr'$	9.44×10^{-5}	460	1.24×10^{6}
F62-3	$(tol)PhCH^+$	(tol)PhCHOAr'	9.44×10^{-5}	450	6.95×10^{6}

[a] OAr' = 4-cyanophenoxide, OAc = acetate

50T50W

Ar_2CH^+ in 50T50W at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
525-10	$(dpa)_2CH^+$	1.22×10^{-5}	660	1.12×10^{-1}
525-11	$(mfa)_2CH^+$	1.12×10^{-5}	585	2.57×10^{-1}
525-12	$(pfa)_2CH^+$	2.10×10^{-5}	590	1.34

Ar_2CH^+ in 50T50W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F142-4	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	7.03×10^{3}
F53-4	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	7.15×10^{4}
F24-4	$(ani)PhCH^+$	(ani)PhCHOAr'	2.03×10^{-4}	455	1.66×10^{5}
F11-4	$(tol)_2CH^+$	$(tol)_2CHOAr'$	9.44×10^{-5}	460	1.39×10^{6}
F62-4	$(tol)PhCH^+$	(tol)PhCHOAr'	9.44×10^{-5}	450	8.20×10^{6}

[a] OAr' = 4-cyanophenoxide, OAc = acetate

40T60W

Ar_2CH^+ in 40T60W at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
525-13	$(mor)_2CH^+$	8.80×10^{-6}	610	4.79×10^{-2}
525-14	$(dpa)_2CH^+$	1.22×10^{-5}	660	1.20×10^{-1}
525-15	$(mfa)_2CH^+$	1.12×10^{-5}	595	3.27×10^{-1}
525-16	$(pfa)_2CH^+$	2.10×10^{-5}	590	1.79

Ar_2CH^+ in 40T60W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F142-5	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	9.95×10^{3}
F53-5	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	1.02×10^{5}
F24-5	$(ani)PhCH^+$	(ani)PhCHOAr'	2.03×10^{-4}	455	2.26×10^{5}
F11-7	$(tol)_2CH^+$	$(tol)_2CHOAr'$	9.44×10^{-5}	460	1.41×10^{6}
F146-1	$(tol)PhCH^+$	(tol)PhCHOAr'	9.48×10^{-5}	450	1.07×10^{7}

[a] OAr' = 4-cyanophenoxide, OAc = acetate

20T80W

Ar_2CH^+ in 20T80W at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
525-17	$(mor)_2CH^+$	8.80×10^{-6}	610	2.69×10^{-1}
525-18	$(dpa)_2CH^+$	1.22×10^{-5}	660	*a*
525-19	$(mfa)_2CH^+$	1.12×10^{-5}	590	1.48
525-20	$(pfa)_2CH^+$	2.10×10^{-5}	590	*a*

[a] non-single exponemtial curve.

Ar_2CH^+ in 20T80W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F142-6	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	4.05×10^{4}
F53-6	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	3.25×10^{5}
F24-6	$(ani)PhCH^+$	(ani)PhCHOAr'	7.68×10^{-5}	455	1.20×10^{6}
F146-5	$(tol)_2CH^+$	$(tol)_2CHOAr'$	7.60×10^{-5}	460	5.57×10^{6}
F146-2	$(tol)PhCH^+$	(tol)PhCHOAr'	9.48×10^{-5}	450	1.92×10^{7}

[a] OAr' = 4-cyanophenoxide, OAc = acetate

10T90W

Ar_2CH^+ in 10T90W at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
525-21	$(mor)_2CH^+$	8.80×10^{-6}	610	7.09×10^{-1}
525-22	$(dpa)_2CH^+$	1.22×10^{-5}	660	*a*
525-23	$(mfa)_2CH^+$	1.12×10^{-5}	595	3.80
525-24	$(pfa)_2CH^+$	2.10×10^{-5}	590	*a*

[a] non-single exponential curve.

Ar_2CH^+ in 10T90W at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F142-7	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	7.95×10^{4}
F151-4	$(ani)(tol)CH^+$	(ani)(tol)CHOAc	1.38×10^{-4}	480	5.78×10^{5}
F146-4	$(ani)PhCH^+$	(ani)PhCHOAr'	1.01×10^{-4}	455	2.59×10^{6}

[a] OAr' = 4-cyanophenoxide, OAc = acetate

Ethanol-Acetonitrile Mixtures

Ethanol

$(lil)_2CH^+$ in ethanol at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
280-1	4.15×10^{-6}	5.69×10^{-3}	98
280-2	4.07×10^{-6}	5.67×10^{-3}	98
280-3	4.13×10^{-6}	5.58×10^{-3}	99
280-4	4.00×10^{-6}	5.85×10^{-3}	97
			$k = 5.70 \times 10^{-3}$ s^{-1}

$(jul)_2CH^+$ in ethanol at 20 °C (conventional, λ = 635 nm)

No.	$[(jul)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
319-1	1.14×10^{-5}	1.51×10^{-2}	99
319-2	1.13×10^{-5}	1.51×10^{-2}	99
319-3	1.12×10^{-5}	1.53×10^{-2}	98
319-4	1.14×10^{-5}	1.53×10^{-2}	99
			$k = 1.52 \times 10^{-2}$ s^{-1}

$(ind)_2CH^+$ in ethanol at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
283-1	1.00×10^{-5}	5.79×10^{-2}	98
283-2	1.03×10^{-5}	5.68×10^{-2}	98
283-3	1.04×10^{-5}	5.91×10^{-2}	99
283-4	1.06×10^{-5}	5.64×10^{-2}	97
			$k = 5.75 \times 10^{-2}$ s^{-1}

$(thq)_2CH^+$ in ethanol at 20 °C (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
289-1	8.75×10^{-6}	1.62×10^{-1}	96
289-2	8.70×10^{-6}	1.64×10^{-1}	96
289-3	8.88×10^{-6}	1.64×10^{-1}	96
289-4	8.70×10^{-6}	1.64×10^{-1}	96
289-5	8.70×10^{-6}	1.64×10^{-1}	96
			$k = 1.63 \times 10^{-1}$ s^{-1}

Ar_2CH^+ in ethanol at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F51-1	*(ani)(tol)CH*$^+$	*(ani)(tol)CHOAr'*	*1.38×10^{-4}*	*480*	*8.68×10^{6}*
F22-8	*(ani)PhCH*$^+$	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*9.56×10^{6}*

[a] OAr' = 4-cyanophenoxide

91E9AN

$(lil)_2CH^+$ in 91E9AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
420-1	8.15×10^{-6}	3.52×10^{-3}	99
420-2	7.82×10^{-6}	3.52×10^{-3}	98
420-3	7.23×10^{-6}	3.53×10^{-3}	98

$k = 3.52 \times 10^{-3}$ s^{-1}

$(ind)_2CH^+$ in 91E9AN at 20 °C (conventional, λ = 615 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
415-1	7.38×10^{-6}	3.80×10^{-2}	97
415-2	6.48×10^{-6}	3.78×10^{-2}	95
415-3	7.09×10^{-6}	3.86×10^{-2}	96

$k = 3.82 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 91E9AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
325-1	$(pyr)_2CH^+$	2.60×10^{-6}	610	2.72×10^{-1}
325-2	$(dma)_2CH^+$	7.38×10^{-6}	605	9.24×10^{-1}
325-3	$(mpa)_2CH^+$	5.72×10^{-6}	610	1.45×10^{1}
325-4	$(mor)_2CH^+$	6.76×10^{-6}	610	1.38×10^{1}
325-5	$(dpa)_2CH^+$	3.00×10^{-6}	660	2.60×10^{2}
325-6	$(mfa)_2CH^+$	4.12×10^{-6}	585	2.55×10^{2}

Ar_2CH^+ in 91E9AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F15-7	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.35×10^{-4}	500	4.33×10^{6}
F51-2	*$(ani)(tol)CH^+$*	*(ani)(tol)CHOAr'*	*1.38×10^{-4}*	*480*	*1.05×10^{7}*
F22-7	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*9.04×10^{6}*

[a] OAr' = 4-cyanophenoxide

80E20A

$(lil)_2CH^+$ in 80E20AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
419-1	8.74×10^{-6}	2.12×10^{-3}	99
419-2	8.26×10^{-6}	2.13×10^{-3}	97
419-3	7.75×10^{-6}	2.09×10^{-3}	97

$k = 2.12 \times 10^{-3}$ s^{-1}

$(ind)_2CH^+$ in 80E20AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
422-1	8.04×10^{-6}	2.43×10^{-2}	93
422-2	8.46×10^{-6}	2.40×10^{-2}	96
422-3	8.54×10^{-6}	2.38×10^{-2}	96

$k = 2.40 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 80E20AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
328-1	$(pyr)_2CH^+$	2.60×10^{-6}	610	2.27×10^{-1}
328-2	$(dma)_2CH^+$	7.38×10^{-6}	605	6.78×10^{-1}
328-3	$(mpa)_2CH^+$	5.72×10^{-6}	610	1.14×10^{1}
328-4	$(mor)_2CH^+$	6.76×10^{-6}	610	1.07×10^{1}
328-5	$(dpa)_2CH^+$	3.00×10^{-6}	660	2.22×10^{2}
328-6	$(mfa)_2CH^+$	4.12×10^{-6}	585	2.07×10^{2}

Ar_2CH^+ in 80E20AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F15-6	$(ani)_2CH^+$	$(ani)_2CHOAr'$	2.95×10^{-4}	500	3.02×10^{6}
F51-3	*$(ani)(tol)CH^+$*	*(ani)(tol)CHOAr'*	*1.38×10^{-4}*	*480*	*1.08×10^{7}*
F22-6	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*8.98×10^{6}*

[a] OAr' = 4-cyanophenoxide

67E33AN

$(lil)_2CH^+$ in 67E33AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
417-1	9.16×10^{-6}	1.27×10^{-3}	98
417-2	8.31×10^{-6}	1.25×10^{-3}	99
417-3	8.34×10^{-6}	1.27×10^{-3}	98

$k = 1.26 \times 10^{-3}$ s^{-1}

$(ind)_2CH^+$ in 67E33AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
413-1	6.80×10^{-6}	1.43×10^{-2}	98
413-2	6.77×10^{-6}	1.47×10^{-2}	96
413-3	6.86×10^{-6}	1.48×10^{-2}	97

$k = 1.46 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 67E33AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
327-1	$(pyr)_2CH^+$	2.60×10^{-6}	610	1.39×10^{-1}
327-2	$(dma)_2CH^+$	7.38×10^{-6}	605	4.51×10^{-1}
327-3	$(mpa)_2CH^+$	5.72×10^{-6}	610	7.92
327-4	$(mor)_2CH^+$	6.76×10^{-6}	610	7.60
327-5	$(dpa)_2CH^+$	3.00×10^{-6}	660	1.65×10^{2}
327-6	$(mfa)_2CH^+$	4.12×10^{-6}	585	1.53×10^{2}

Ar_2CH^+ in 67E33AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F15-5	$(ani)_2CH^+$	$(ani)_2CHOAr'$	2.95×10^{-4}	500	2.30×10^{6}
F51-4	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	1.23×10^{7}
F22-5	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*1.07×10^{7}*

[a] OAr' = 4-cyanophenoxide

50E50AN

$(lil)_2CH^+$ in 50E50AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
281-1	3.97×10^{-6}	6.72×10^{-4}	98
281-2	3.95×10^{-6}	6.62×10^{-4}	95
281-3	3.95×10^{-6}	6.64×10^{-4}	99
281-4	3.98×10^{-6}	6.60×10^{-4}	99
			$k = 6.65 \times 10^{-4}$ s^{-1}

$(ind)_2CH^+$ in 50E50AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
282-1	5.06×10^{-6}	7.99×10^{-3}	91
282-2	1.01×10^{-5}	7.93×10^{-3}	93
282-3	1.01×10^{-5}	7.98×10^{-3}	93
282-4	1.02×10^{-5}	7.91×10^{-3}	93
			$k = 7.95 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 50E50AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
280-1	$(thq)_2CH^+$	5.42×10^{-6}	615	2.32×10^{-2}
280-2	$(pyr)_2CH^+$	3.89×10^{-6}	610	7.04×10^{-2}
280-3	$(dma)_2CH^+$	4.06×10^{-6}	605	2.46×10^{-1}
280-4	$(mpa)_2CH^+$	1.24×10^{-5}	610	2.49
280-5	$(dpa)_2CH^+$	8.50×10^{-6}	660	5.39×10^{1}
280-6	$(mfa)_2CH^+$	1.75×10^{-5}	585	5.23×10^{1}
280-7	$(pfa)_2CH^+$	2.45×10^{-6}	590	4.05×10^{2}

Ar_2CH^+ in 50E50AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F15-4	$(ani)_2CH^+$	$(ani)_2CHOAr'$	2.95×10^{-4}	500	1.41×10^{6}
F51-5	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	1.21×10^{7}
F94-4	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*1.10×10^{7}*

[a] OAr' = 4-cyanophenoxide

33E67AN

$(ind)_2CH^+$ in 33E67AN at 20 °C (conventional, λ = 630 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
412-1	6.75×10^{-6}	3.97×10^{-3}	95
412-2	7.00×10^{-6}	3.99×10^{-3}	96
412-3	6.74×10^{-6}	3.93×10^{-3}	99

$k = 3.97 \times 10^{-3}$ s^{-1}

$(pyr)_2CH^+$ in 33E67AN at 20 °C (conventional, λ = 615 nm)

No.	$[(pyr)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
421-1	4.06×10^{-6}	3.70×10^{-2}	92
421-2	4.44×10^{-6}	3.63×10^{-2}	96
421-3	4.81×10^{-6}	3.68×10^{-2}	95

$k = 3.67 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 33E67AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
411-1	$(dma)_2CH^+$	6.83×10^{-6}	605	1.40×10^{-1}
411-2	$(mpa)_2CH^+$	1.47×10^{-5}	610	1.63
411-3	$(mor)_2CH^+$	1.97×10^{-5}	610	1.68
411-4	$(dpa)_2CH^+$	9.67×10^{-6}	660	4.03×10^{1}
411-5	$(mfa)_2CH^+$	2.42×10^{-6}	585	4.05×10^{1}
411-6	$(pfa)_2CH^+$	1.77×10^{-5}	590	3.11×10^{2}

Ar_2CH^+ in 33E67AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F15-3	$(ani)_2CH^+$	$(ani)_2CHOAr'$	2.95×10^{-4}	500	8.77×10^{5}
F51-6	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	8.48×10^{6}
F94-3	$(ani)PhCH^+$	(ani)PhCHOAr'	1.92×10^{-4}	455	1.18×10^{7}

[a] OAr' = 4-cyanophenoxide

20E80AN

$(ind)_2CH^+$ in 20E80AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
414-1	6.82×10^{-6}	2.37×10^{-3}	58
414-2	6.48×10^{-6}	2.26×10^{-3}	67
414-3	6.50×10^{-6}	2.33×10^{-3}	60

$k = 2.32 \times 10^{-3}$ s^{-1}

$(pyr)_2CH^+$ in 20E80AN at 20 °C (conventional, λ = 610 nm)

No.	$[(pyr)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
418-1	5.03×10^{-6}	1.80×10^{-2}	78
418-2	4.73×10^{-6}	1.78×10^{-2}	84
418-3	4.47×10^{-6}	1.77×10^{-2}	81

$k = 1.78 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 20E80AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
411-7	$(mpa)_2CH^+$	1.47×10^{-5}	610	9.54×10^{-1}
411-8	$(mor)_2CH^+$	1.97×10^{-5}	610	9.05×10^{-1}
411-9	$(dpa)_2CH^+$	9.67×10^{-6}	660	2.18×10^{1}
411-10	$(mfa)_2CH^+$	2.42×10^{-6}	585	2.24×10^{1}
411-11	$(pfa)_2CH^+$	1.77×10^{-5}	590	1.72×10^{2}

Ar_2CH^+ in 20E80AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F15-2	$(ani)_2CH^+$	$(ani)_2CHOAr'$	2.95×10^{-4}	500	5.33×10^{5}
F51-7	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	5.99×10^{6}
F101-2	$(ani)PhCH^+$	(ani)PhCHOAr'	1.92×10^{-4}	455	9.41×10^{6}

[a] OAr' = 4-cyanophenoxide

10E90AN

Ar_2CH^+ in 10E90AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
442-1	$(mpa)_2CH^+$	3.66×10^{-6}	610	2.87×10^{-1}
442-2	$(mor)_2CH^+$	3.06×10^{-6}	610	2.96×10^{-1}
442-3	$(dpa)_2CH^+$	1.61×10^{-5}	660	7.28
442-4	$(mfa)_2CH^+$	8.78×10^{-6}	585	7.07
442-5	$(pfa)_2CH^+$	1.06×10^{-5}	590	5.86×10^{1}

Ar_2CH^+ in 10E90AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F15-1	$(ani)_2CH^+$	$(ani)_2CHOAr'$	2.95×10^{-4}	500	3.06×10^{5}
F51-8	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	2.44×10^{6}
F94-2	$(ani)PhCH^+$	(ani)PhCHOAr'	1.92×10^{-4}	455	4.80×10^{6}

[a] OAr' = 4-cyanophenoxide

Methanol-Acetonitrile Mixtures

MeOH

$(lil)_2CH^+$ in methanol at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
257-1	7.06×10^{-6}	6.39×10^{-3}	99
257-2	8.65×10^{-6}	6.10×10^{-3}	98
257-3	7.83×10^{-6}	6.30×10^{-3}	99
257-4	9.40×10^{-6}	6.10×10^{-3}	96

$k = 6.23 \times 10^{-3}$ s^{-1}

$(ind)_2CH^+$ in methanol at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
259-1	6.54×10^{-6}	6.09×10^{-2}	99
259-2	5.65×10^{-6}	5.79×10^{-2}	96
259-3	5.81×10^{-6}	6.15×10^{-2}	97
259-4	5.99×10^{-6}	5.99×10^{-2}	97

$k = 6.00 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in methanol at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F49-1	*(ani)(tol)CH⁺*	*(ani)(tol)CHOAr'*	*1.38×10^{-4}*	*480*	*1.33×10^{7}*
F121-1	*(ani)PhCH⁺*	*(ani)PhCHOAr'*	*2.13×10^{-4}*	*455*	*1.15×10^{7}*

[a] OAr' = 4-cyanophenoxide

91M9AN

$(lil)_2CH^+$ in 91M9AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
299-1	4.37×10^{-6}	6.41×10^{-3}	96
299-2	4.43×10^{-6}	6.20×10^{-3}	94
299-3	4.34×10^{-6}	6.10×10^{-3}	98
299-4	4.41×10^{-6}	6.11×10^{-3}	97
299-5	4.24×10^{-6}	5.88×10^{-3}	97

$k = 6.14 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 91M9AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
308-1	$(thq)_2CH^+$	5.92×10^{-6}	620	2.17×10^{-1}
305-2	$(pyr)_2CH^+$	4.24×10^{-6}	610	9.32×10^{-1}
305-3	$(dma)_2CH^+$	7.38×10^{-6}	605	2.31
305-1	$(mpa)_2CH^+$	6.76×10^{-6}	610	2.79×10^{1}
305-4	$(mor)_2CH^+$	5.72×10^{-6}	610	2.65×10^{1}
308-2	$(dpa)_2CH^+$	3.00×10^{-6}	660	3.60×10^{2}
308-3	$(mfa)_2CH^+$	4.12×10^{-6}	585	4.02×10^{2}

Ar_2CH^+ in 91M9AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F13-8	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	4.95×10^{6}
F49-2	*$(ani)(tol)CH^+$*	*(ani)(tol)CHOAr'*	*1.38×10^{-4}*	*480*	*1.38×10^{7}*
F121-2	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*2.13×10^{-4}*	*455*	*9.88×10^{6}*

[a] OAr' = 4-cyanophenoxide

80M20AN

$(lil)_2CH^+$ in 80M20AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
341-1	4.35×10^{-6}	3.52×10^{-3}	89
341-2	4.65×10^{-6}	3.41×10^{-3}	96
341-3	4.57×10^{-6}	3.63×10^{-3}	91
341-4	4.57×10^{-6}	3.39×10^{-3}	93

$k = 3.49 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 80M20AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
306-1	$(pyr)_2CH^+$	4.24×10^{-6}	615	4.64×10^{-1}
306-2	$(dma)_2CH^+$	7.38×10^{-6}	610	1.30
306-3	$(mpa)_2CH^+$	6.76×10^{-6}	615	1.85×10^{1}
306-4	$(mor)_2CH^+$	5.72×10^{-6}	615	1.82×10^{1}
308-4	$(dpa)_2CH^+$	3.00×10^{-6}	660	2.89×10^{2}
308-5	$(mfa)_2CH^+$	4.12×10^{-6}	585	3.11×10^{2}

Ar_2CH^+ in 80M20AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F13-7	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	4.12×10^{6}
F49-3	*$(ani)(tol)CH^+$*	*(ani)(tol)CHOAr'*	*1.38×10^{-4}*	*480*	*1.20×10^{7}*
F121-3	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*2.13×10^{-4}*	*455*	*8.55×10^{6}*

[a] OAr' = 4-cyanophenoxide

67M33AN

$(lil)_2CH^+$ in 67M33AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
261-1	1.03×10^{-5}	2.00×10^{-3}	96
261-2	9.93×10^{-6}	1.96×10^{-3}	98
261-3	1.03×10^{-5}	2.03×10^{-3}	98
261-4	9.77×10^{-6}	2.00×10^{-3}	97

$k = 1.99 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 67M33AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
307-1	$(pyr)_2CH^+$	4.24×10^{-6}	615	3.27×10^{-1}
307-2	$(dma)_2CH^+$	7.38×10^{-6}	610	8.82×10^{-1}
307-3	$(mpa)_2CH^+$	6.76×10^{-6}	615	1.32×10^{1}
307-4	$(mor)_2CH^+$	5.72×10^{-6}	615	1.28×10^{1}
308-6	$(dpa)_2CH^+$	3.00×10^{-6}	660	2.23×10^{2}
308-7	$(mfa)_2CH^+$	4.12×10^{-6}	585	2.42×10^{2}

Ar_2CH^+ in 67M33AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F13-6	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	3.48×10^{6}
F49-4	*$(ani)(tol)CH^+$*	*(ani)(tol)CHOAr'*	*1.38×10^{-4}*	*480*	*1.24×10^{7}*
F121-4	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*2.13×10^{-4}*	*455*	*8.87×10^{6}*

[a] OAr' = 4-cyanophenoxide

50M50AN

$(lil)_2CH^+$ in 50M50AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
262-1	6.13×10^{-6}	1.17×10^{-3}	98
262-2	5.77×10^{-6}	1.17×10^{-3}	97
262-3	5.88×10^{-6}	1.18×10^{-3}	98
262-4	5.55×10^{-6}	1.16×10^{-3}	98

$k = 1.17 \times 10^{-3}$ s^{-1}

$(ind)_2CH^+$ in 50M50AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
264-1	7.84×10^{-6}	1.34×10^{-2}	99
264-2	7.36×10^{-6}	1.35×10^{-2}	99
264-3	7.14×10^{-6}	1.33×10^{-2}	99
264-4	6.83×10^{-6}	1.33×10^{-2}	99

$k = 1.34 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 50M50AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
266-1	$(dma)_2CH^+$	3.16×10^{-6}	605	4.36×10^{-1}
266-2	$(mpa)_2CH^+$	6.25×10^{-6}	610	4.81
266-3	$(dpa)_2CH^+$	6.37×10^{-6}	660	9.52×10^{1}
266-4	$(mfa)_2CH^+$	3.59×10^{-6}	585	1.23×10^{2}

Ar_2CH^+ in 50M50AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F13-5	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	2.33×10^{6}
F49-5	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	1.47×10^{7}
F121-5	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*2.13×10^{-4}*	*455*	*9.16×10^{6}*

[a] OAr' = 4-cyanophenoxide

33M67AN

$(lil)_2CH^+$ in 33M67AN at 20 °C (conventional, λ = 630 nm)

No.	$[(lil)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
369-1	4.46×10^{-6}	5.75×10^{-4}	98
369-2	4.81×10^{-6}	6.22×10^{-4}	97
369-3	4.41×10^{-6}	5.90×10^{-4}	96
			$k = 5.96 \times 10^{-4}$ s^{-1}

$(ind)_2CH^+$ in 33M67AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
378-1	6.78×10^{-6}	5.77×10^{-3}	99
378-2	6.80×10^{-6}	5.85×10^{-3}	96
378-3	6.83×10^{-6}	5.77×10^{-3}	96
			$k = 5.80 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 33M67AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
391-1	$(dma)_2CH^+$	1.22×10^{-5}	610	2.62×10^{-1}
391-2	$(mpa)_2CH^+$	4.79×10^{-6}	610	3.85
391-3	$(mor)_2CH^+$	7.04×10^{-6}	610	3.51
391-4	$(dpa)_2CH^+$	9.67×10^{-6}	665	8.87×10^{1}
391-5	$(mfa)_2CH^+$	1.06×10^{-5}	585	8.46×10^{1}
391-6	$(pfa)_2CH^+$	6.36×10^{-6}	590	4.85×10^{2}

Ar_2CH^+ in 33M67AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F13-4	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	1.54×10^{6}
F49-6	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	1.33×10^{7}
F21-3	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*1.00×10^{7}*

[a] OAr' = 4-cyanophenoxide

20M80AN

$(ind)_2CH^+$ in 20M80AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
371-1	6.44×10^{-6}	3.08×10^{-3}	93
371-2	6.56×10^{-6}	3.08×10^{-3}	97
371-3	6.54×10^{-6}	3.12×10^{-3}	98

$k = 3.09 \times 10^{-3}$ s^{-1}

$(thq)_2CH^+$ in 20M80AN at 20 °C (conventional, λ = 620 nm)

No.	$[(thq)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
377-1	5.08×10^{-6}	6.54×10^{-3}	95
377-2	4.87×10^{-6}	6.71×10^{-3}	95
377-3	5.01×10^{-6}	6.41×10^{-3}	91

$k = 6.55 \times 10^{-3}$ s^{-1}

Ar_2CH^+ in 20M80AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
392-1	$(dma)_2CH^+$	1.22×10^{-5}	610	1.22×10^{-1}
392-2	$(mpa)_2CH^+$	4.79×10^{-6}	610	2.15
392-3	$(mor)_2CH^+$	7.04×10^{-6}	610	1.96
392-4	$(dpa)_2CH^+$	9.67×10^{-6}	665	5.43×10^{1}
392-5	$(mfa)_2CH^+$	1.06×10^{-5}	585	4.81×10^{1}
392-6	$(pfa)_2CH^+$	6.36×10^{-6}	595	3.58×10^{2}

Ar_2CH^+ in 20M80AN at 20 °C (Laser flash photolysis)

No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F13-2	$(ani)_2CH^+$	$(ani)_2CHOAr'$	1.18×10^{-4}	500	8.58×10^{5}
F49-7	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	9.91×10^{6}
F21-2	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*1.07×10^{7}*

[a] OAr' = 4-cyanophenoxide

10M90AN

$(ind)_2CH^+$ in 10M90AN at 20 °C (conventional, λ = 615 nm)

No.	$[(ind)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
374-1	6.61×10^{-6}	8.47×10^{-4}	94
374-2	5.56×10^{-6}	7.46×10^{-4}	91
374-3	6.06×10^{-6}	7.24×10^{-4}	94

$k = 7.72 \times 10^{-4}$ s^{-1}

$(pyr)_2CH^+$ in 10M90AN at 20 °C (conventional, λ = 610 nm)

No.	$[(pyr)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
376-1	3.60×10^{-6}	7.15×10^{-3}	88
376-2	3.55×10^{-6}	6.93×10^{-3}	93
376-3	3.46×10^{-6}	7.14×10^{-3}	82

$k = 7.07 \times 10^{-3}$ s^{-1}

$(dma)_2CH^+$ in 10M90AN at 20 °C (conventional, λ = 605 nm)

No.	$[(dma)_2CH^+]_0$, mol L^{-1}	k_{obs}, s^{-1}	conversion, %
385-1	1.15×10^{-5}	4.25×10^{-2}	89
385-2	1.14×10^{-5}	3.60×10^{-2}	86
416-1	2.60×10^{-5}	3.24×10^{-2}	98
416-2	2.18×10^{-5}	3.80×10^{-2}	93
416-3	1.90×10^{-5}	4.37×10^{-2}	86
416-4	2.38×10^{-5}	4.10×10^{-2}	84
416-5	2.17×10^{-5}	4.13×10^{-2}	84

$k = 3.93 \times 10^{-2}$ s^{-1}

Ar_2CH^+ in 10M90AN at 20 °C (Stopped-flow)

No.	Cation	$[Ar_2CH^+]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
393-1	$(mpa)_2CH^+$	4.79×10^{-6}	610	7.21×10^{-1}
393-2	$(mor)_2CH^+$	7.04×10^{-6}	610	6.83×10^{-1}
393-3	$(dpa)_2CH^+$	9.67×10^{-6}	665	1.78×10^{1}
393-4	$(mfa)_2CH^+$	1.06×10^{-5}	585	1.64×10^{1}
393-5	$(pfa)_2CH^+$	6.36×10^{-6}	595	1.60×10^{2}

Ar_2CH^+ in 10M90AN at 20 °C (Laser flash photolysis)

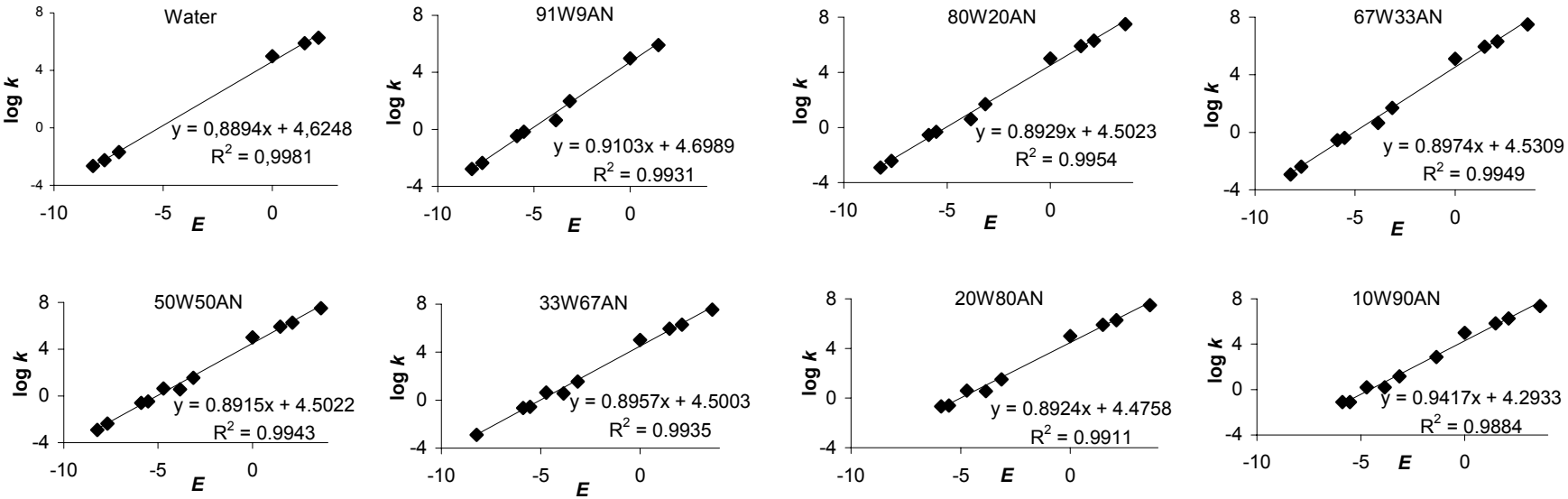
No.	Cation	Precursor [a]	$[Precursor]_0$, mol L^{-1}	Detection, nm	k_{obs}, s^{-1}
F148-1	$(ani)_2CH^+$	$(ani)_2CHOAc$	1.59×10^{-4}	500	4.20×10^{5}
F49-8	$(ani)(tol)CH^+$	(ani)(tol)CHOAr'	1.38×10^{-4}	480	6.22×10^{6}
F21-1	*$(ani)PhCH^+$*	*(ani)PhCHOAr'*	*1.92×10^{-4}*	*455*	*7.47×10^{6}*

[a] OAc = acetate, OAr' = 4-cyanophenoxide

TableS1. First-order rate constants (s^{-1}) of the reactions of water-acetonitrile mixtures with benzhydrylium ions at 20 ºC.[a]

Cation	*E*	Water	91W9AN	80W20AN	67W33AN	50W50AN	33W67AN	20W80AN	10W90AN
Ph_2CH^+						*1.33E+9* [e]			
$(tol)_2CH^+$	3.63			3.2E+7 [d]	3.2E+7 [d]	3.28E+7	3.47E+7	3.06E+7	2.37E+7
$(ani)PhCH^+$	2.11	1.9E+6 [b]		2.0E+6 [d]	2.1E+6 [d]	1.84E+6	1.91E+6	1.87E+6	1.83E+6
$(ani)(tol)CH^+$	1.48	7.8E+5 [b]	7.99E+5	8.2E+5 [d]	9.1E+5 [d]	8.55E+5	8.95E+5	8.29E+5	6.81E+5
$(ani)_2CH^+$	0.00	9.44E+4	9.55E+4	1.0E+5 [d]	1.3E+5 [d]	1.04E+5	1.01E+5	9.82E+4	9.87E+4
$(fur)_2CH^+$	-1.36								7.11E+2
$(pfa)_2CH^+$	-3.14		9.36E+1	4.93E+1	4.96E+1	3.62E+1	3.39E+1	3.32E+1	1.42E+1
$(mfa)_2CH^+$	-3.85		4.39	3.98	4.47	3.78 [c]	3.58	3.62	1.57
$(dpa)_2CH^+$	-4.72					4.44	4.12	3.97	1.56
$(mor)_2CH^+$	-5.53		6.73E-1	4.93E-1	4.13E-1	3.31E-1 [c]	2.85E-1	2.51E-1	8.03E-2
$(mpa)_2CH^+$	-5.89		3.31E-1	2.84E-1	2.83E-1	2.52E-1	2.24E-1	2.17E-1	8.08E-2
$(dma)_2CH^+$	-7.02	2.06E-2							
$(pyr)_2CH^+$	-7.69	5.57E-3 [c]	4.29E-3	3.77E-3	4.05E-3	4.33E-3			
$(thq)_2CH^+$	-8.22	2.20E-3 [c]	1.66E-3	1.23E-3	1.17E-3	1.22E-3	1.28E-3		

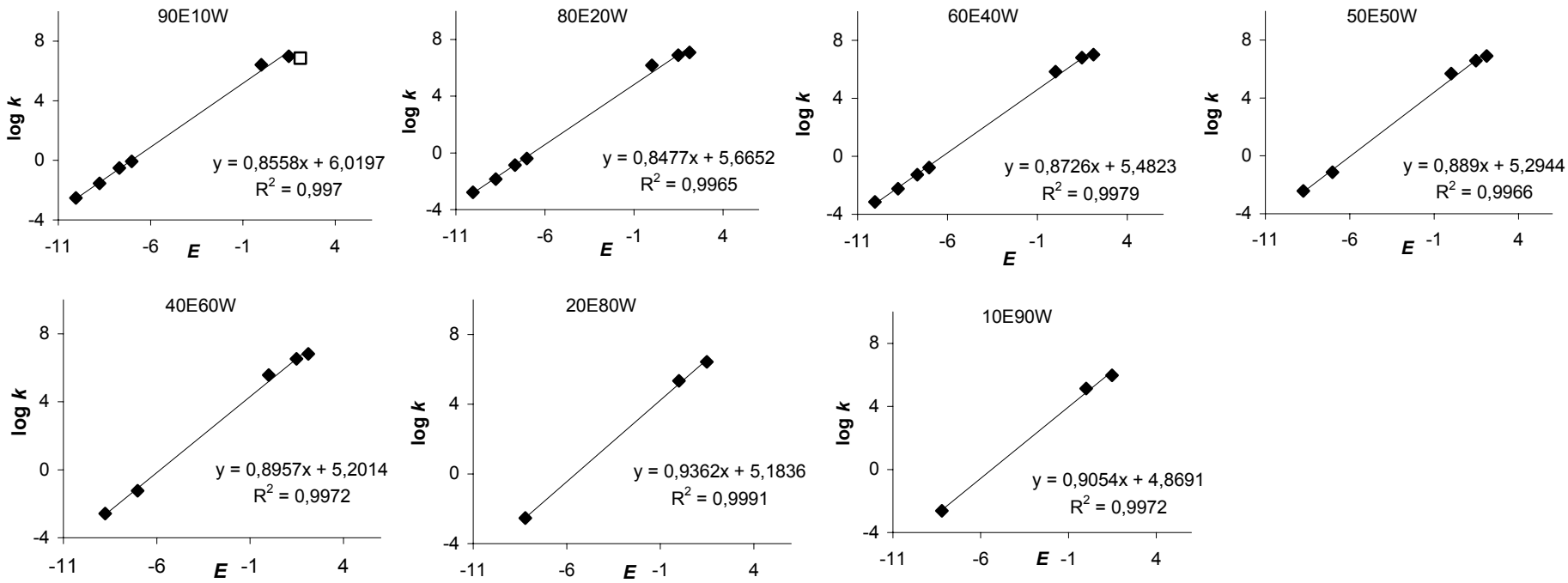
[a] The ratio of solvent mixtures is by volume. [b] Ref. 17. [c] Ref. 20. [d] Ref. 13c. [e] Ref. 13d, not included in the correlation.



TableS2. First-order rate constants (s^{-1}) of the reactions of water-ethanol mixtures with benzhydrylium ions at 20 ºC.[a]

Cation	*E*	90E10W	80E20W	60E40W	50E50W	40E60W	20E80W	10E90W
(ani)PhCH$^+$	2.11	*7.04E+6* [b]	1.22E+7	1.06E+7	7.91E+6	6.62E+6		
(ani)(tol)CH$^+$	1.48	9.47E+6	7.88E+6	6.55E+6	3.86E+6	3.38E+6	2.72E+6	9.54E+5
(ani)$_2$CH$^+$	0.00	2.53E+6	1.51E+6	7.13E+5	4.96E+5	3.68E+5	2.20E+5	1.38E+5
(dma)$_2$CH$^+$	-7.02	8.33E-1	4.05E-1	1.70E-1	7.43E-2	5.71E-2		
(pyr)$_2$CH$^+$	-7.69	3.02E-1	1.40E-1	5.28E-2				
(thq)$_2$CH$^+$	-8.22						2.91E-3	2.43E-3
(ind)$_2$CH$^+$	-8.76	2.78E-2	1.45E-2	5.84E-3	3.84E-3	2.61E-3		
(lil)$_2$CH$^+$	-10.04	3.03E-3	1.65E-3	7.16E-4				

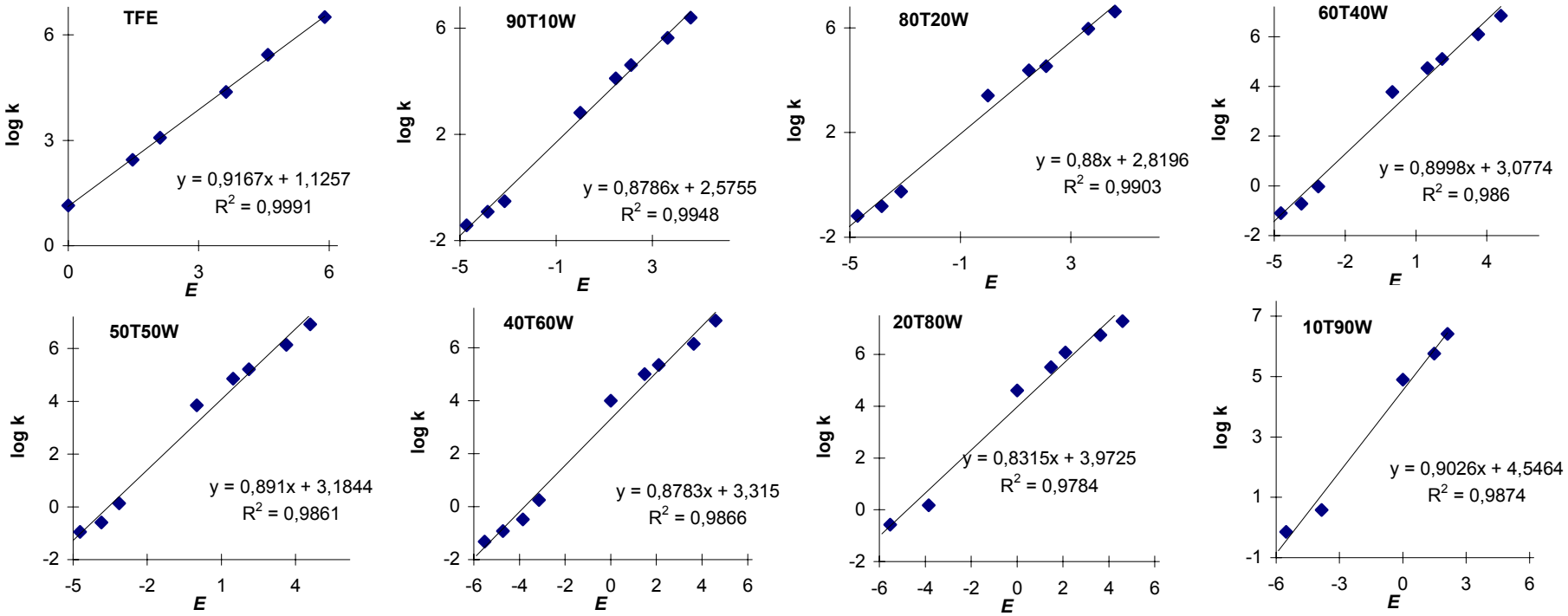
[a] The ratio of solvent mixtures is by volume. [b] Not included in the correlation.



TableS3. First-order rate constants (s^{-1}) of the reactions of water-trifluoroethanol mixtures with benzhydrylium ions at 20 ºC.[a]

Cation	E	TFE	90T10W	80T20W	60T40W	50T50W	40T60W	20T80W	10T90W
Ph_2CH^+	5.90	3.2E+6 [b]				*2.8E+8* [c]			
$(tol)PhCH^+$	4.59	2.7E+5 [b]	2.45E+6	4.19E+6	6.95E+6	8.20E+6	1.07E+7	1.92E+7	
$(tol)_2CH^+$	3.63	2.4E+4 [b]	4.32E+5	9.11E+5	1.24E+6	1.39E+6	1.41E+6	5.57E+6	
$(ani)PhCH^+$	2.11	1.2E+3 [b]	4.01E+4	3.45E+4	1.27E+5	1.66E+5	2.26E+5	1.20E+6	2.59E+6
$(ani)(tol)CH^+$	1.48	2.8E+2 [b]	1.28E+4	2.35E+4	5.46E+4	7.15E+4	1.02E+5	3.25E+5	5.78E+5
$(ani)_2CH^+$	0.00	1.4E+1 [b]	6.50E+2	2.55E+3	6.04E+3	7.03E+3	9.95E+3	4.05E+4	7.95E+4
$(pfa)_2CH^+$	-3.14		3.01E-1	5.55E-1	9.37E-1	1.34E+0	1.79E+0		
$(mfa)_2CH^+$	-3.85		1.23E-1	1.53E-1	1.90E-1	2.57E-1	3.27E-1	1.48E+0	3.80E+0
$(dpa)_2CH^+$	-4.72		3.76E-2	6.59E-2	7.96E-2	1.12E-1	1.20E-1		
$(mor)_2CH^+$	-5.53						4.79E-2	2.69E-1	7.09E-1

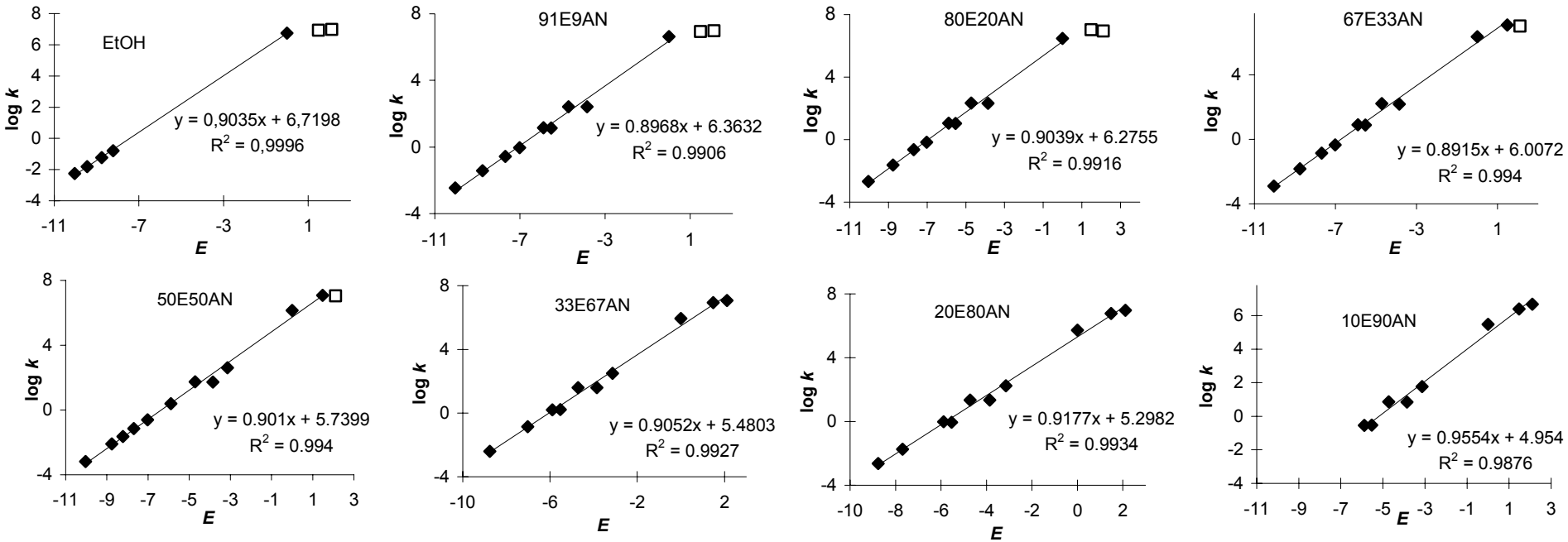
[a] The ratio of solvent mixtures is by volume. [b] Ref. 13b. [c] Ref. 14g, not included in the correlation.



TableS4. First-order rate constants (s^{-1}) of the reactions of ethanol-acetonitrile mixtures with benzhydrylium ions at 20 ºC.[a]

Cation	*E*	EtOH	91E9AN	80E20AN	67E33AN	50E50AN	33E67AN	20E80AN	10E90AN
(ani)PhCH$^+$	2.11	*9.56E+6* [b]	*9.04E+6* [b]	*8.98E+6*	*1.07E+7* [b]	*1.10E+7* [b]	1.18E+7	9.41E+6	4.80E+6
(ani)(tol)CH$^+$	1.48	*8.68E+6* [b]	*1.05E+7* [b]	*1.08E+7* [b]	1.23E+7	1.21E+7	8.48E+6	5.99E+6	2.44E+6
(ani)$_2$CH$^+$	0.00	5.5E+6 [c]	4.33E+6	3.02E+6	2.30E+6	1.41E+6	8.77E+5	5.33E+5	3.06E+5
(pfa)$_2$CH$^+$	-3.14					4.05E+2	3.11E+2	1.72E+2	5.86E+1
(mfa)$_2$CH$^+$	-3.85		2.55E+2	2.07E+2	1.53E+2	5.23E+1	4.05E+1	2.24E+1	7.07E+0
(dpa)$_2$CH$^+$	-4.72		2.60E+2	2.22E+2	1.65E+2	5.39E+1	4.03E+1	2.18E+1	7.28E+0
(mor)$_2$CH$^+$	-5.53		1.38E+1	1.07E+1	7.60E+0		1.68E+0	9.05E-1	2.96E-1
(mpa)$_2$CH$^+$	-5.89		1.45E+1	1.14E+1	7.92E+0	2.49E+0	1.63E+0	9.54E-1	2.87E-1
(dma)$_2$CH$^+$	-7.02		9.24E-1	6.78E-1	4.51E-1	2.46E-1	1.40E-1		
(pyr)$_2$CH$^+$	-7.69		2.72E-1	2.27E-1	1.39E-1	7.04E-2	3.67E-2	1.78E-2	
(thq)$_2$CH$^+$	-8.22	1.63E-1				2.32E-2			
(ind)$_2$CH$^+$	-8.76	5.75E-2	3.82E-2	2.40E-2	1.46E-2	7.95E-3	3.97E-3	2.32E-3	
(jul)$_2$CH$^+$	-9.45	1.52E-2							
(lil)$_2$CH$^+$	-10.04	5.70E-3	3.52E-3	2.12E-3	1.26E-3	6.65E-4			

[a] The ratio of solvent mixtures is by volume. [b] Not included in the correlation. [c] Ref. 13h.



TableS5. First-order rate constants (s^{-1}) of the reactions of methanol acetonitrile mixtures with benzhydrylium ions at 20 ºC.[a]

Cation	*E*	MeOH	91M9AN	80M20AN	67M33AN	50M50AN	33M67AN	20M80AN	10M90AN
(ani)PhCH$^+$	2.11	*1.15E+7* [b]	*9.88E+6* [b]	*8.55E+6* [b]	*8.87E+6* [b]	*9.16E+6* [b]	*1.00E+7* [b]	*1.07E+7* [b]	*7.47E+6* [b]
(ani)(tol)CH$^+$	1.48	*1.33E+7* [b]	*1.39E+7* [b]	*1.20E+7* [b]	*1.24E+7* [b]	1.47E+7	1.33E+7	9.91E+6	6.22E+6
(ani)$_2$CH$^+$	0.00	8.6E+6 [c]	4.95E+6	4.12E+6	3.48E+6	2.33E+6	1.54E+6	8.58E+5	4.20E+5
(pfa)$_2$CH$^+$	-3.14						4.85E+2	3.58E+2	1.60E+2
(mfa)$_2$CH$^+$	-3.85		4.02E+2	3.11E+2	2.42E+2	1.22E+2	8.46E+1	4.81E+1	1.64E+1
(dpa)$_2$CH$^+$	-4.72		3.60E+2	2.89E+2	2.23E+2	9.52E+1	8.87E+1	5.43E+1	1.78E+1
(mor)$_2$CH$^+$	-5.53		2.65E+1	1.82E+1	1.28E+1		3.51E+0	1.96E+0	6.83E-1
(mpa)$_2$CH$^+$	-5.89		2.79E+1	1.85E+1	1.32E+1	4.81E+0	3.85E+0	2.15E+0	7.21E-1
(dma)$_2$CH$^+$	-7.02		2.31E+0	1.30E+0	8.82E-1	4.36E-1	2.62E-1	1.22E-1	3.93E-2
(pyr)$_2$CH$^+$	-7.69		9.32E-1	4.64E-1	3.27E-1				7.07E-3
(thq)$_2$CH$^+$	-8.22		2.17E-1					6.55E-3	
(ind)$_2$CH$^+$	-8.76	6.00E-2				1.34E-2	5.80E-3	3.09E-3	7.72E-4
(jul)$_2$CH$^+$	-9.45								
(lil)$_2$CH$^+$	-10.04	6.23E-3	6.14E-3	3.49E-3	1.99E-3	1.17E-3	5.96E-4		

[a] The ratio of solvent mixtures is by volume. [b] Not included in the correlation. [c] Ref. 13b.

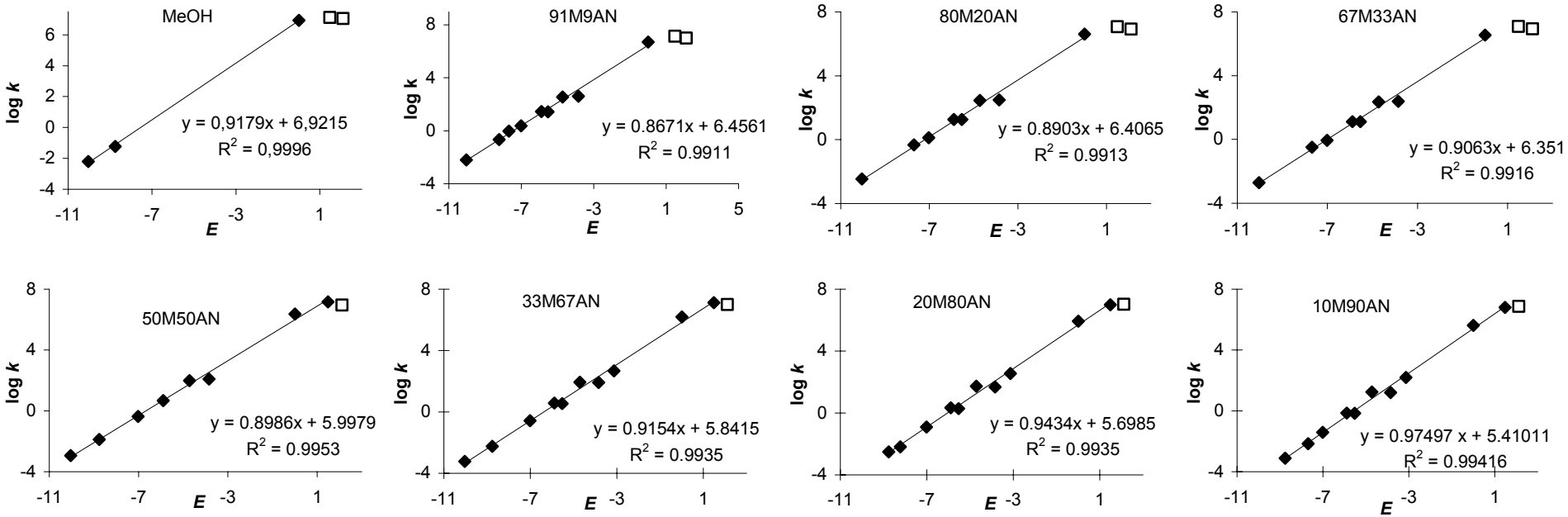


Table S6. Comparison of experimental and calculated (log $k = s\ (N_1 + E)$, eq. 5) first-order rate constants (20 °C, s^{-1}) for the reactions of solvents with benzhydrylium ions.

Solvent	Electrophile	s	N_1	E	k_{exp}	k_{calc}	log k_{exp}	log k_{calc}	Δ^2 log k
Water	$(thq)_2CH^+$	0.89	5.20	-8.22	2.20E-3	2.06E-3	-2.66	-2.69	8.10E-4
	$(pyr)_2CH^+$	0.89	5.20	-7.69	5.57E-3	6.10E-3	-2.25	-2.21	1.56E-3
	$(dma)_2CH^+$	0.89	5.20	-7.02	2.06E-2	2.41E-2	-1.69	-1.62	4.54E-3
	$(ani)_2CH^+$	0.89	5.20	0.00	9.44E+4	4.22E+4	4.97	4.62	1.23E-1
	$(ani)(tol)CH^+$	0.89	5.20	1.48	7.8E+5	8.73E+5	5.89	5.94	2.41E-3
	$(ani)PhCH^+$	0.89	5.20	2.11	1.9E+6	3.17E+6	6.28	6.50	4.96E-2
91W9AN	$(thq)_2CH^+$	0.91	5.16	-8.22	1.66E-3	1.65E-3	-2.78	-2.78	1.55E-5
	$(pyr)_2CH^+$	0.91	5.16	-7.69	4.29E-3	5.00E-3	-2.37	-2.30	4.38E-3
	$(mpa)_2CH^+$	0.91	5.16	-5.89	3.31E-1	2.17E-1	-0.48	-0.66	3.34E-2
	$(mor)_2CH^+$	0.91	5.16	-5.53	6.73E-1	4.62E-1	-0.17	-0.34	2.66E-2
	$(mfa)_2CH^+$	0.91	5.16	-3.85	4.39E+0	1.56E+1	0.64	1.19	3.04E-1
	$(pfa)_2CH^+$	0.91	5.16	-3.14	9.36E+1	6.93E+1	1.97	1.84	1.71E-2
	$(ani)_2CH^+$	0.91	5.16	0.00	9.55E+4	5.00E+4	4.98	4.70	7.90E-2
	$(ani)(tol)CH^+$	0.91	5.16	1.48	7.99E+5	1.11E+6	5.90	6.05	2.06E-2
80W20AN	$(thq)_2CH^+$	0.89	5.04	-8.22	1.23E-3	1.45E-3	-2.91	-2.84	5.27E-3
	$(pyr)_2CH^+$	0.89	5.04	-7.69	3.77E-3	4.32E-3	-2.42	-2.36	3.53E-3
	$(mpa)_2CH^+$	0.89	5.04	-5.89	2.84E-1	1.75E-1	-0.55	-0.76	4.42E-2
	$(mor)_2CH^+$	0.89	5.04	-5.53	4.93E-1	3.67E-1	-0.31	-0.44	1.65E-2
	$(mfa)_2CH^+$	0.89	5.04	-3.85	3.98E+0	1.16E+1	0.60	1.06	2.16E-1
	$(pfa)_2CH^+$	0.89	5.04	-3.14	4.93E+1	5.00E+1	1.69	1.70	3.26E-5
	$(ani)_2CH^+$	0.89	5.04	0.00	1.0E+5	3.18E+4	5.00	4.50	2.48E-1
	$(ani)(tol)CH^+$	0.89	5.04	1.48	8.2E+5	6.67E+5	5.91	5.82	8.09E-3
	$(ani)PhCH^+$	0.89	5.04	2.11	2.0E+6	2.43E+6	6.30	6.39	7.29E-3
	$(tol)_2CH^+$	0.89	5.04	3.63	3.2E+7	5.54E+7	7.51	7.74	5.69E-2
67W33AN	$(thq)_2CH^+$	0.90	5.05	-8.22	1.17E-3	1.43E-3	-2.93	-2.85	7.42E-3
	$(pyr)_2CH^+$	0.90	5.05	-7.69	4.05E-3	4.27E-3	-2.39	-2.37	5.07E-4
	$(mpa)_2CH^+$	0.90	5.05	-5.89	2.83E-1	1.76E-1	-0.55	-0.75	4.27E-2
	$(mor)_2CH^+$	0.90	5.05	-5.53	4.13E-1	3.70E-1	-0.38	-0.43	2.27E-3
	$(mfa)_2CH^+$	0.90	5.05	-3.85	4.47E+0	1.19E+1	0.65	1.08	1.81E-1
	$(pfa)_2CH^+$	0.90	5.05	-3.14	4.96E+1	5.17E+1	1.70	1.71	3.10E-4
	$(ani)_2CH^+$	0.90	5.05	0.00	1.3E+5	3.40E+4	5.11	4.53	3.40E-1
	$(ani)(tol)CH^+$	0.90	5.05	1.48	9.1E+5	7.23E+5	5.96	5.86	1.00E-2
	$(ani)PhCH^+$	0.90	5.05	2.11	2.1E+6	2.66E+6	6.32	6.42	1.04E-2
	$(tol)_2CH^+$	0.90	5.05	3.63	3.2E+7	6.14E+7	7.51	7.79	8.02E-2
50W50AN	$(thq)_2CH^+$	0.89	5.05	-8.22	1.22E-3	1.49E-3	-2.91	-2.83	7.74E-3
	$(pyr)_2CH^+$	0.89	5.05	-7.69	4.33E-3	4.43E-3	-2.36	-2.35	1.06E-4
	$(mpa)_2CH^+$	0.89	5.05	-5.89	2.52E-1	1.78E-1	-0.60	-0.75	2.25E-2
	$(mor)_2CH^+$	0.89	5.05	-5.53	3.31E-1	3.74E-1	-0.48	-0.43	2.76E-3
	$(dpa)_2CH^+$	0.89	5.05	-4.72	4.44E+0	1.97E+0	0.65	0.29	1.25E-1
	$(mfa)_2CH^+$	0.89	5.05	-3.85	3.78E+0	1.17E+1	0.58	1.07	2.43E-1
	$(pfa)_2CH^+$	0.89	5.05	-3.14	3.62E+1	5.05E+1	1.56	1.70	2.08E-2
	$(ani)_2CH^+$	0.89	5.05	0.00	1.04E+5	3.18E+4	5.02	4.50	2.65E-1
	$(ani)(tol)CH^+$	0.89	5.05	1.48	8.55E+5	6.63E+5	5.93	5.82	1.22E-2
	$(ani)PhCH^+$	0.89	5.05	2.11	1.84E+6	2.42E+6	6.26	6.38	1.40E-2
	$(tol)_2CH^+$	0.89	5.05	3.63	3.28E+7	5.47E+7	7.52	7.74	4.94E-2
33W67AN	$(thq)_2CH^+$	0.90	5.02	-8.22	1.28E-3	1.37E-3	-2.89	-2.86	9.13E-4
	$(mpa)_2CH^+$	0.90	5.02	-5.89	2.24E-1	1.68E-1	-0.65	-0.78	1.58E-2
	$(mor)_2CH^+$	0.90	5.02	-5.53	2.85E-1	3.52E-1	-0.55	-0.45	8.48E-3

Solvent	Electrophile	s	N_1	E	k_{exp}	k_{calc}	log k_{exp}	log k_{calc}	Δ^2 log k
33W67AN	$(dpa)_2CH^+$	0.90	5.02	-4.72	4.12E+0	1.87E+0	0.61	0.27	1.17E-1
(continued)	$(mfa)_2CH^+$	0.90	5.02	-3.85	3.58E+0	1.13E+1	0.55	1.05	2.48E-1
	$(pfa)_2CH^+$	0.90	5.02	-3.14	3.39E+1	4.87E+1	1.53	1.69	2.48E-2
	$(ani)_2CH^+$	0.90	5.02	0.00	1.01E+5	3.16E+4	5.00	4.50	2.54E-1
	$(ani)(tol)CH^+$	0.90	5.02	1.48	8.95E+5	6.70E+5	5.95	5.83	1.59E-2
	$(ani)PhCH^+$	0.90	5.02	2.11	1.91E+6	2.46E+6	6.28	6.39	1.19E-2
	$(tol)_2CH^+$	0.90	5.02	3.63	3.47E+7	5.65E+7	7.54	7.75	4.47E-2
20W80AN	$(mpa)_2CH^+$	0.89	5.02	-5.89	2.17E-1	1.66E-1	-0.66	-0.78	1.37E-2
	$(mor)_2CH^+$	0.89	5.02	-5.53	2.51E-1	3.47E-1	-0.60	-0.46	1.98E-2
	$(dpa)_2CH^+$	0.89	5.02	-4.72	3.97E+0	1.83E+0	0.60	0.26	1.12E-1
	$(mfa)_2CH^+$	0.89	5.02	-3.85	3.62E+0	1.10E+1	0.56	1.04	2.31E-1
	$(pfa)_2CH^+$	0.89	5.02	-3.14	3.32E+1	4.71E+1	1.52	1.67	2.32E-2
	$(ani)_2CH^+$	0.89	5.02	0.00	9.82E+4	2.99E+4	4.99	4.48	2.67E-1
	$(ani)(tol)CH^+$	0.89	5.02	1.48	8.29E+5	6.26E+5	5.92	5.80	1.49E-2
	$(ani)PhCH^+$	0.89	5.02	2.11	1.87E+6	2.28E+6	6.27	6.36	7.56E-3
	$(tol)_2CH^+$	0.89	5.02	3.63	3.06E+7	5.19E+7	7.49	7.72	5.27E-2
10W90AN	$(mpa)_2CH^+$	0.94	4.56	-5.89	8.08E-2	5.58E-2	-1.09	-1.25	2.58E-2
	$(mor)_2CH^+$	0.94	4.56	-5.53	8.03E-2	1.22E-1	-1.10	-0.91	3.28E-2
	$(dpa)_2CH^+$	0.94	4.56	-4.72	1.56E+0	7.06E-1	0.19	-0.15	1.19E-1
	$(mfa)_2CH^+$	0.94	4.56	-3.85	1.57E+0	4.65E+0	0.20	0.67	2.23E-1
	$(pfa)_2CH^+$	0.94	4.56	-3.14	1.42E+1	2.17E+1	1.15	1.34	3.39E-2
	$(fur)_2CH^+$	0.94	4.56	-1.36	7.11E+2	1.03E+3	2.85	3.01	2.58E-2
	$(ani)_2CH^+$	0.94	4.56	0.00	9.87E+4	1.96E+4	4.99	4.29	4.91E-1
	$(ani)(tol)CH^+$	0.94	4.56	1.48	6.81E+5	4.86E+5	5.83	5.69	2.14E-2
	$(ani)PhCH^+$	0.94	4.56	2.11	1.83E+6	1.91E+6	6.26	6.28	3.14E-4
	$(tol)_2CH^+$	0.94	4.56	3.63	2.37E+7	5.15E+7	7.37	7.71	1.13E-1
TFE	$(ani)_2CH^+$	0.92	1.23	0.00	1.4E+1	1.34E+1	1.15	1.13	4.19E-4
	$(ani)(tol)CH^+$	0.92	1.23	1.48	2.8E+2	3.04E+2	2.45	2.48	1.24E-3
	$(ani)PhCH^+$	0.92	1.23	2.11	1.2E+3	1.15E+3	3.08	3.06	3.70E-4
	$(tol)_2CH^+$	0.92	1.23	3.63	2.4E+4	2.84E+4	4.38	4.45	5.35E-3
	$(tol)PhCH^+$	0.92	1.23	4.59	2.7E+5	2.15E+5	5.43	5.33	9.59E-3
	Ph_2CH^+	0.92	1.23	5.9	3.2E+6	3.42E+6	6.51	6.53	8.52E-4
90T10W	$(dpa)_2CH^+$	0.88	2.93	-4.72	3.76E-2	2.68E-2	-1.42	-1.57	2.15E-2
	$(mfa)_2CH^+$	0.88	2.93	-3.85	1.23E-1	1.56E-1	-0.91	-0.81	1.06E-2
	$(pfa)_2CH^+$	0.88	2.93	-3.14	3.01E-1	6.56E-1	-0.52	-0.18	1.14E-1
	$(ani)_2CH^+$	0.88	2.93	0.00	6.50E+2	3.76E+2	2.81	2.58	5.64E-2
	$(ani)(tol)CH^+$	0.88	2.93	1.48	1.28E+4	7.51E+3	4.11	3.88	5.36E-2
	$(ani)PhCH^+$	0.88	2.93	2.11	4.01E+4	2.69E+4	4.60	4.43	3.02E-2
	$(tol)_2CH^+$	0.88	2.93	3.63	4.32E+5	5.82E+5	5.64	5.76	1.67E-2
	$(tol)PhCH^+$	0.88	2.93	4.59	2.45E+6	4.06E+6	6.39	6.61	4.80E-2
80T20W	$(dpa)_2CH^+$	0.88	3.20	-4.72	6.59E-2	4.63E-2	-1.18	-1.33	2.34E-2
	$(mfa)_2CH^+$	0.88	3.20	-3.85	1.53E-1	2.70E-1	-0.82	-0.57	6.09E-2
	$(pfa)_2CH^+$	0.88	3.20	-3.14	5.55E-1	1.14E+0	-0.26	0.06	9.74E-2
	$(ani)_2CH^+$	0.88	3.20	0.00	2.55E+3	6.60E+2	3.41	2.82	3.44E-1
	$(ani)(tol)CH^+$	0.88	3.20	1.48	2.35E+4	1.32E+4	4.37	4.12	6.20E-2
	$(ani)PhCH^+$	0.88	3.20	2.11	3.45E+4	4.75E+4	4.54	4.68	1.92E-2
	$(tol)_2CH^+$	0.88	3.20	3.63	9.11E+5	1.03E+6	5.96	6.01	2.98E-3
	$(tol)PhCH^+$	0.88	3.20	4.59	4.19E+6	7.23E+6	6.62	6.86	5.60E-2
60T40W	$(dpa)_2CH^+$	0.90	3.42	-4.72	7.96E-2	6.76E-2	-1.10	-1.17	5.01E-3
	$(mfa)_2CH^+$	0.90	3.42	-3.85	1.90E-1	4.10E-1	-0.72	-0.39	1.12E-1

Solvent	Electrophile	s	N_1	E	k_{exp}	k_{calc}	log k_{exp}	log k_{calc}	Δ^2 log k
60T40W	$(pfa)_2CH^+$	0.90	3.42	-3.14	9.37E-1	1.79E+0	-0.03	0.25	7.85E-2
(continued)	$(ani)_2CH^+$	0.90	3.42	0.00	6.04E+3	1.19E+3	3.78	3.08	4.95E-1
	$(ani)(tol)CH^+$	0.90	3.42	1.48	5.46E+4	2.57E+4	4.74	4.41	1.08E-1
	$(ani)PhCH^+$	0.90	3.42	2.11	1.27E+5	9.46E+4	5.10	4.98	1.63E-2
	$(tol)_2CH^+$	0.90	3.42	3.63	1.24E+6	2.21E+6	6.09	6.34	6.27E-2
	$(tol)PhCH^+$	0.90	3.42	4.59	6.95E+6	1.61E+7	6.84	7.21	1.34E-1
50T50W	$(dpa)_2CH^+$	0.89	3.57	-4.72	1.12E-1	9.52E-2	-0.95	-1.02	4.96E-3
	$(mfa)_2CH^+$	0.89	3.57	-3.85	2.57E-1	5.68E-1	-0.59	-0.25	1.18E-1
	$(pfa)_2CH^+$	0.89	3.57	-3.14	1.34E+0	2.44E+0	0.13	0.39	6.73E-2
	$(ani)_2CH^+$	0.89	3.57	0.00	7.03E+3	1.53E+3	3.85	3.18	4.39E-1
	$(ani)(tol)CH^+$	0.89	3.57	1.48	7.15E+4	3.19E+4	4.85	4.50	1.23E-1
	$(ani)PhCH^+$	0.89	3.57	2.11	1.66E+5	1.16E+5	5.22	5.06	2.42E-2
	$(tol)_2CH^+$	0.89	3.57	3.63	1.39E+6	2.62E+6	6.14	6.42	7.61E-2
	$(tol)PhCH^+$	0.89	3.57	4.59	8.20E+6	1.88E+7	6.91	7.27	1.30E-1
40T60W	$(mor)_2CH^+$	0.88	3.77	-5.53	4.79E-2	2.87E-2	-1.32	-1.54	4.94E-2
	$(dpa)_2CH^+$	0.88	3.77	-4.72	1.20E-1	1.48E-1	-0.92	-0.83	8.15E-3
	$(mfa)_2CH^+$	0.88	3.77	-3.85	3.27E-1	8.58E-1	-0.49	-0.07	1.76E-1
	$(pfa)_2CH^+$	0.88	3.77	-3.14	1.79E+0	3.61E+0	0.25	0.56	9.26E-2
	$(ani)_2CH^+$	0.88	3.77	0.00	9.95E+3	2.07E+3	4.00	3.32	4.66E-1
	$(ani)(tol)CH^+$	0.88	3.77	1.48	1.02E+5	4.12E+4	5.01	4.61	1.55E-1
	$(ani)PhCH^+$	0.88	3.77	2.11	2.26E+5	1.47E+5	5.35	5.17	3.45E-2
	$(tol)_2CH^+$	0.88	3.77	3.63	1.41E+6	3.19E+6	6.15	6.50	1.25E-1
	$(tol)PhCH^+$	0.88	3.77	4.59	1.07E+7	2.22E+7	7.03	7.35	1.01E-1
20T80W	$(mor)_2CH^+$	0.83	4.78	-5.53	2.69E-1	2.37E-1	-0.57	-0.63	3.05E-3
	$(mfa)_2CH^+$	0.83	4.78	-3.85	1.48E+0	5.91E+0	0.17	0.77	3.61E-1
	$(ani)_2CH^+$	0.83	4.78	0.00	4.05E+4	9.39E+3	4.61	3.97	4.03E-1
	$(ani)(tol)CH^+$	0.83	4.78	1.48	3.25E+5	1.60E+5	5.51	5.20	9.54E-2
	$(ani)PhCH^+$	0.83	4.78	2.11	1.20E+6	5.33E+5	6.08	5.73	1.24E-1
	$(tol)_2CH^+$	0.83	4.78	3.63	5.57E+6	9.79E+6	6.75	6.99	5.99E-2
	$(tol)PhCH^+$	0.83	4.78	4.59	1.92E+7	6.15E+7	7.28	7.79	2.56E-1
10T90W	$(mor)_2CH^+$	0.90	5.04	-5.53	7.09E-1	3.59E-1	-0.15	-0.45	8.74E-2
	$(mfa)_2CH^+$	0.90	5.04	-3.85	3.80E+0	1.18E+1	0.58	1.07	2.42E-1
	$(ani)_2CH^+$	0.90	5.04	0.00	7.95E+4	3.52E+4	4.90	4.55	1.25E-1
	$(ani)(tol)CH^+$	0.90	5.04	1.48	5.78E+5	7.63E+5	5.76	5.88	1.45E-2
	$(ani)PhCH^+$	0.90	5.04	2.11	2.59E+6	2.82E+6	6.41	6.45	1.42E-3
90E10W	$(lil)_2CH^+$	0.86	7.03	-10.04	3.03E-3	2.67E-3	-2.52	-2.57	2.96E-3
	$(ind)_2CH^+$	0.86	7.03	-8.76	2.78E-2	3.33E-2	-1.56	-1.48	6.16E-3
	$(pyr)_2CH^+$	0.86	7.03	-7.69	3.02E-1	2.74E-1	-0.52	-0.56	1.74E-3
	$(dma)_2CH^+$	0.86	7.03	-7.02	8.33E-1	1.03E+0	-0.08	0.01	8.29E-3
	$(ani)_2CH^+$	0.86	7.03	0.00	2.53E+6	1.05E+6	6.40	6.02	1.47E-1
	$(ani)(tol)CH^+$	0.86	7.03	1.48	9.47E+6	1.93E+7	6.98	7.29	9.61E-2
80E20W	$(lil)_2CH^+$	0.85	6.68	-10.04	1.65E-3	1.43E-3	-2.78	-2.85	3.96E-3
	$(ind)_2CH^+$	0.85	6.68	-8.76	1.45E-2	1.74E-2	-1.84	-1.76	6.12E-3
	$(pyr)_2CH^+$	0.85	6.68	-7.69	1.40E-1	1.40E-1	-0.85	-0.85	2.48E-7
	$(dma)_2CH^+$	0.85	6.68	-7.02	4.05E-1	5.18E-1	-0.39	-0.29	1.15E-2
	$(ani)_2CH^+$	0.85	6.68	0.00	1.51E+6	4.63E+5	6.18	5.67	2.64E-1
	$(ani)(tol)CH^+$	0.85	6.68	1.48	7.88E+6	8.31E+6	6.90	6.92	5.42E-4
	$(ani)PhCH^+$	0.85	6.68	2.11	1.22E+7	2.84E+7	7.09	7.45	1.35E-1
60E40W	$(lil)_2CH^+$	0.87	6.28	-10.04	7.16E-4	5.27E-4	-3.15	-3.28	1.77E-2
	$(ind)_2CH^+$	0.87	6.28	-8.76	5.84E-3	6.90E-3	-2.23	-2.16	5.22E-3

Solvent	Electrophile	s	N_1	E	k_{exp}	k_{calc}	log k_{exp}	log k_{calc}	Δ^2 log k
60E40W	$(pyr)_2CH^+$	0.87	6.28	-7.69	5.28E-2	5.92E-2	-1.28	-1.23	2.47E-3
(continued)	$(dma)_2CH^+$	0.87	6.28	-7.02	1.70E-1	2.27E-1	-0.77	-0.64	1.60E-2
	$(ani)_2CH^+$	0.87	6.28	0.00	7.13E+5	3.04E+5	5.85	5.48	1.37E-1
	$(ani)(tol)CH^+$	0.87	6.28	1.48	6.55E+6	5.94E+6	6.82	6.77	1.81E-3
	$(ani)PhCH^+$	0.87	6.28	2.11	1.06E+7	2.11E+7	7.03	7.32	8.89E-2
50E50W	$(ind)_2CH^+$	0.89	5.96	-8.76	3.84E-3	3.21E-3	-2.42	-2.49	5.96E-3
	$(dma)_2CH^+$	0.89	5.96	-7.02	7.43E-2	1.13E-1	-1.13	-0.95	3.35E-2
	$(ani)_2CH^+$	0.89	5.96	0.00	4.96E+5	1.97E+5	5.70	5.29	1.61E-1
	$(ani)(tol)CH^+$	0.89	5.96	1.48	3.86E+6	4.07E+6	6.59	6.61	5.49E-4
	$(ani)PhCH^+$	0.89	5.96	2.11	7.91E+6	1.48E+7	6.90	7.17	7.39E-2
40E60W	$(ind)_2CH^+$	0.90	5.81	-8.76	2.61E-3	2.27E-3	-2.58	-2.64	3.75E-3
	$(dma)_2CH^+$	0.90	5.81	-7.02	5.71E-2	8.20E-2	-1.24	-1.09	2.47E-2
	$(ani)_2CH^+$	0.90	5.81	0.00	3.68E+5	1.59E+5	5.57	5.20	1.33E-1
	$(ani)(tol)CH^+$	0.90	5.81	1.48	3.38E+6	3.36E+6	6.53	6.53	3.81E-6
	$(ani)PhCH^+$	0.90	5.81	2.11	6.62E+6	1.23E+7	6.82	7.09	7.31E-2
20E80W	$(thq)_2CH^+$	0.94	5.54	-8.22	2.91E-3	3.08E-3	-2.54	-2.51	5.88E-4
	$(ani)_2CH^+$	0.94	5.54	0.00	2.20E+5	1.53E+5	5.34	5.18	2.52E-2
	$(ani)(tol)CH^+$	0.94	5.54	1.48	2.72E+6	3.71E+6	6.43	6.57	1.81E-2
10E90W	$(thq)_2CH^+$	0.91	5.38	-8.22	2.43E-3	2.67E-3	-2.61	-2.57	1.71E-3
	$(ani)_2CH^+$	0.91	5.38	0.00	1.38E+5	7.40E+4	5.14	4.87	7.33E-2
	$(ani)(tol)CH^+$	0.91	5.38	1.48	9.54E+5	1.62E+6	5.98	6.21	5.27E-2
EtOH	$(lil)_2CH^+$	0.90	7.44	-10.04	5.70E-3	4.46E-3	-2.24	-2.35	1.14E-2
	$(jul)_2CH^+$	0.90	7.44	-9.45	1.52E-2	1.52E-2	-1.82	-1.82	8.82E-8
	$(ind)_2CH^+$	0.90	7.44	-8.76	5.75E-2	6.39E-2	-1.24	-1.19	2.10E-3
	$(thq)_2CH^+$	0.90	7.44	-8.22	1.63E-1	1.97E-1	-0.79	-0.71	6.59E-3
	$(ani)_2CH^+$	0.90	7.44	0.00	5.5E+6	5.25E+6	6.74	6.72	4.24E-4
91E9AN	$(lil)_2CH^+$	0.90	7.10	-10.04	3.52E-3	2.29E-3	-2.45	-2.64	3.52E-2
	$(ind)_2CH^+$	0.90	7.10	-8.76	3.82E-2	3.21E-2	-1.42	-1.49	5.64E-3
	$(pyr)_2CH^+$	0.90	7.10	-7.69	2.72E-1	2.93E-1	-0.57	-0.53	1.02E-3
	$(dma)_2CH^+$	0.90	7.10	-7.02	9.24E-1	1.17E+0	-0.03	0.07	1.04E-2
	$(mpa)_2CH^+$	0.90	7.10	-5.89	1.45E+1	1.20E+1	1.16	1.08	6.49E-3
	$(mor)_2CH^+$	0.90	7.10	-5.53	1.38E+1	2.53E+1	1.14	1.40	6.96E-2
	$(dpa)_2CH^+$	0.90	7.10	-4.72	2.60E+2	1.35E+2	2.41	2.13	8.11E-2
	$(mfa)_2CH^+$	0.90	7.10	-3.85	2.55E+2	8.13E+2	2.41	2.91	2.54E-1
	$(ani)_2CH^+$	0.90	7.10	0.00	4.33E+6	2.31E+6	6.64	6.36	7.48E-2
80E20AN	$(lil)_2CH^+$	0.90	6.94	-10.04	2.12E-3	1.59E-3	-2.67	-2.80	1.58E-2
	$(ind)_2CH^+$	0.90	6.94	-8.76	2.40E-2	2.28E-2	-1.62	-1.64	5.13E-4
	$(pyr)_2CH^+$	0.90	6.94	-7.69	2.27E-1	2.11E-1	-0.64	-0.68	9.80E-4
	$(dma)_2CH^+$	0.90	6.94	-7.02	6.78E-1	8.52E-1	-0.17	-0.07	9.82E-3
	$(mpa)_2CH^+$	0.90	6.94	-5.89	1.14E+1	8.95E+0	1.06	0.95	1.11E-2
80E20AN	$(mor)_2CH^+$	0.90	6.94	-5.53	1.07E+1	1.89E+1	1.03	1.28	6.14E-2
	$(dpa)_2CH^+$	0.90	6.94	-4.72	2.22E+2	1.02E+2	2.35	2.01	1.14E-1
	$(mfa)_2CH^+$	0.90	6.94	-3.85	2.07E+2	6.25E+2	2.32	2.80	2.30E-1
	$(ani)_2CH^+$	0.90	6.94	0.00	3.02E+6	1.89E+6	6.48	6.28	4.18E-2
67E33AN	$(lil)_2CH^+$	0.89	6.74	-10.04	1.26E-3	1.14E-3	-2.90	-2.94	1.94E-3
	$(ind)_2CH^+$	0.89	6.74	-8.76	1.46E-2	1.58E-2	-1.84	-1.80	1.10E-3
	$(pyr)_2CH^+$	0.89	6.74	-7.69	1.39E-1	1.42E-1	-0.86	-0.85	7.06E-5
	$(dma)_2CH^+$	0.89	6.74	-7.02	4.51E-1	5.61E-1	-0.35	-0.25	8.94E-3
	$(mpa)_2CH^+$	0.89	6.74	-5.89	7.92E+0	5.70E+0	0.90	0.76	2.03E-2
	$(mor)_2CH^+$	0.89	6.74	-5.53	7.60E+0	1.19E+1	0.88	1.08	3.85E-2

Solvent	Electrophile	s	N_1	E	k_{exp}	k_{calc}	log k_{exp}	log k_{calc}	Δ^2 log k
67E33AN	$(dpa)_2CH^+$	0.89	6.74	-4.72	1.65E+2	6.30E+1	2.22	1.80	1.75E-1
(continued)	$(mfa)_2CH^+$	0.89	6.74	-3.85	1.53E+2	3.76E+2	2.18	2.57	1.52E-1
	$(ani)_2CH^+$	0.89	6.74	0.00	2.30E+6	1.02E+6	6.36	6.01	1.26E-1
	$(ani)(tol)CH^+$	0.89	6.74	1.48	1.23E+7	2.12E+7	7.09	7.33	5.61E-2
50E50AN	$(lil)_2CH^+$	0.90	6.37	-10.04	6.65E-4	4.94E-4	-3.18	-3.31	1.68E-2
	$(ind)_2CH^+$	0.90	6.37	-8.76	7.95E-3	7.03E-3	-2.10	-2.15	2.88E-3
	$(pyr)_2CH^+$	0.90	6.37	-8.22	2.32E-2	2.15E-2	-1.63	-1.67	1.04E-3
	$(dma)_2CH^+$	0.90	6.37	-7.69	7.04E-2	6.47E-2	-1.15	-1.19	1.35E-3
	$(mpa)_2CH^+$	0.90	6.37	-7.02	2.46E-1	2.60E-1	-0.61	-0.59	5.56E-4
	$(mor)_2CH^+$	0.90	6.37	-5.89	2.49E+0	2.71E+0	0.40	0.43	1.33E-3
	$(dpa)_2CH^+$	0.90	6.37	-4.72	5.39E+1	3.07E+1	1.73	1.49	5.99E-2
	$(mfa)_2CH^+$	0.90	6.37	-3.85	5.23E+1	1.87E+2	1.72	2.27	3.05E-1
	$(pfa)_2CH^+$	0.90	6.37	-3.14	4.05E+2	8.14E+2	2.61	2.91	9.19E-2
	$(ani)_2CH^+$	0.90	6.37	0.00	1.41E+6	5.49E+5	6.15	5.74	1.68E-1
	$(ani)(tol)CH^+$	0.90	6.37	1.48	1.21E+7	1.18E+7	7.08	7.07	8.77E-5
33E67AN	$(ind)_2CH^+$	0.90	6.06	-8.76	3.97E-3	3.64E-3	-2.40	-2.44	1.43E-3
	$(pyr)_2CH^+$	0.90	6.06	-7.69	3.67E-2	3.37E-2	-1.44	-1.47	1.33E-3
	$(dma)_2CH^+$	0.90	6.06	-7.02	1.40E-1	1.36E-1	-0.85	-0.87	1.52E-4
	$(mpa)_2CH^+$	0.90	6.06	-5.89	1.63E+0	1.43E+0	0.21	0.16	3.24E-3
	$(mor)_2CH^+$	0.90	6.06	-5.53	1.68E+0	3.02E+0	0.23	0.48	6.52E-2
	$(dpa)_2CH^+$	0.90	6.06	-4.72	4.03E+1	1.63E+1	1.61	1.21	1.54E-1
	$(mfa)_2CH^+$	0.90	6.06	-3.85	4.05E+1	9.98E+1	1.61	2.00	1.54E-1
	$(pfa)_2CH^+$	0.90	6.06	-3.14	3.11E+2	4.38E+2	2.49	2.64	2.20E-2
	$(ani)_2CH^+$	0.90	6.06	0.00	8.77E+5	3.02E+5	5.94	5.48	2.15E-1
	$(ani)(tol)CH^+$	0.90	6.06	1.48	8.48E+6	6.57E+6	6.93	6.82	1.23E-2
	$(ani)PhCH^+$	0.90	6.06	2.11	1.18E+7	2.44E+7	7.07	7.39	9.92E-2
20E80AN	$(ind)_2CH^+$	0.92	5.77	-8.76	2.32E-3	1.82E-3	-2.63	-2.74	1.13E-2
	$(pyr)_2CH^+$	0.92	5.77	-7.69	1.78E-2	1.74E-2	-1.75	-1.76	8.75E-5
	$(mpa)_2CH^+$	0.92	5.77	-5.89	9.54E-1	7.82E-1	-0.02	-0.11	7.50E-3
	$(mor)_2CH^+$	0.92	5.77	-5.53	9.05E-1	1.67E+0	-0.04	0.22	7.11E-2
	$(dpa)_2CH^+$	0.92	5.77	-4.72	2.18E+1	9.26E+0	1.34	0.97	1.38E-1
	$(mfa)_2CH^+$	0.92	5.77	-3.85	2.24E+1	5.82E+1	1.35	1.77	1.72E-1
	$(pfa)_2CH^+$	0.92	5.77	-3.14	1.72E+2	2.61E+2	2.24	2.42	3.28E-2
	$(ani)_2CH^+$	0.92	5.77	0.00	5.33E+5	1.99E+5	5.73	5.30	1.84E-1
	$(ani)(tol)CH^+$	0.92	5.77	1.48	5.99E+6	4.53E+6	6.78	6.66	1.46E-2
	$(ani)PhCH^+$	0.92	5.77	2.11	9.41E+6	1.72E+7	6.97	7.23	6.81E-2
10E90AN	$(mpa)_2CH^+$	0.96	5.19	-5.89	2.87E-1	2.12E-1	-0.54	-0.67	1.73E-2
	$(mor)_2CH^+$	0.96	5.19	-5.53	2.96E-1	4.68E-1	-0.53	-0.33	3.97E-2
	$(dpa)_2CH^+$	0.96	5.19	-4.72	7.28E+0	2.78E+0	0.86	0.44	1.75E-1
	$(mfa)_2CH^+$	0.96	5.19	-3.85	7.07E+0	1.89E+1	0.85	1.28	1.82E-1
	$(pfa)_2CH^+$	0.96	5.19	-3.14	5.86E+1	8.99E+1	1.77	1.95	3.46E-2
	$(ani)_2CH^+$	0.96	5.19	0.00	3.06E+5	9.00E+4	5.49	4.95	2.83E-1
	$(ani)(tol)CH^+$	0.96	5.19	1.48	2.44E+6	2.33E+6	6.39	6.37	3.73E-4
	$(ani)PhCH^+$	0.96	5.19	2.11	4.80E+6	9.33E+6	6.68	6.97	8.34E-2
MeOH	$(lil)_2CH^+$	0.92	7.54	-10.04	6.23E-3	5.07E-3	-2.21	-2.29	7.95E-3
	$(ind)_2CH^+$	0.92	7.54	-8.76	6.00E-2	7.59E-2	-1.22	-1.12	1.04E-2
	$(ani)_2CH^+$	0.92	7.54	0.00	8.60E+6	8.35E+6	6.93	6.92	1.70E-4
91M9AN	$(lil)_2CH^+$	0.87	7.45	-10.04	6.14E-3	5.62E-3	-2.21	-2.25	1.45E-3
	$(thq)_2CH^+$	0.87	7.45	-8.22	2.17E-1	2.13E-1	-0.66	-0.67	6.68E-5
	$(pyr)_2CH^+$	0.87	7.45	-7.69	9.32E-1	6.14E-1	-0.03	-0.21	3.30E-2

Solvent	Electrophile	s	N_1	E	k_{exp}	k_{calc}	log k_{exp}	log k_{calc}	Δ^2 log k
91M9AN	$(dma)_2CH^+$	0.87	7.45	-7.02	2.31E+0	2.34E+0	0.36	0.37	2.73E-5
(continued)	$(mpa)_2CH^+$	0.87	7.45	-5.89	2.79E+1	2.23E+1	1.45	1.35	9.39E-3
	$(mor)_2CH^+$	0.87	7.45	-5.53	2.65E+1	4.58E+1	1.42	1.66	5.65E-2
	$(dpa)_2CH^+$	0.87	7.45	-4.72	3.60E+2	2.31E+2	2.56	2.36	3.73E-2
	$(mfa)_2CH^+$	0.87	7.45	-3.85	4.02E+2	1.31E+3	2.60	3.12	2.64E-1
	$(ani)_2CH^+$	0.87	7.45	0.00	4.95E+6	2.86E+6	6.69	6.46	5.69E-2
80M20AN	$(lil)_2CH^+$	0.89	7.20	-10.04	3.49E-3	2.94E-3	-2.46	-2.53	5.65E-3
	$(pyr)_2CH^+$	0.89	7.20	-7.69	4.64E-1	3.63E-1	-0.33	-0.44	1.14E-2
	$(dma)_2CH^+$	0.89	7.20	-7.02	1.30E+0	1.43E+0	0.11	0.16	1.81E-3
	$(mpa)_2CH^+$	0.89	7.20	-5.89	1.85E+1	1.45E+1	1.27	1.16	1.10E-2
	$(mor)_2CH^+$	0.89	7.20	-5.53	1.82E+1	3.04E+1	1.26	1.48	4.97E-2
	$(dpa)_2CH^+$	0.89	7.20	-4.72	2.89E+2	1.60E+2	2.46	2.20	6.59E-2
	$(mfa)_2CH^+$	0.89	7.20	-3.85	3.11E+2	9.52E+2	2.49	2.98	2.36E-1
	$(ani)_2CH^+$	0.89	7.20	0.00	4.12E+6	2.55E+6	6.61	6.41	4.34E-2
67M33AN	$(lil)_2CH^+$	0.91	7.01	-10.04	1.99E-3	1.79E-3	-2.70	-2.75	2.22E-3
	$(pyr)_2CH^+$	0.91	7.01	-7.69	3.27E-1	2.41E-1	-0.49	-0.62	1.77E-2
	$(dma)_2CH^+$	0.91	7.01	-7.02	8.82E-1	9.75E-1	-0.05	-0.01	1.88E-3
	$(mpa)_2CH^+$	0.91	7.01	-5.89	1.32E+1	1.03E+1	1.12	1.01	1.16E-2
	$(mor)_2CH^+$	0.91	7.01	-5.53	1.28E+1	2.18E+1	1.11	1.34	5.38E-2
	$(dpa)_2CH^+$	0.91	7.01	-4.72	2.23E+2	1.18E+2	2.35	2.07	7.56E-2
	$(mfa)_2CH^+$	0.91	7.01	-3.85	2.42E+2	7.27E+2	2.38	2.86	2.28E-1
	$(ani)_2CH^+$	0.91	7.01	0.00	3.48E+6	2.24E+6	6.54	6.35	3.63E-2
50M50AN	$(lil)_2CH^+$	0.90	6.67	-10.04	1.17E-3	9.46E-4	-2.93	-3.02	8.50E-3
	$(ind)_2CH^+$	0.90	6.67	-8.76	1.34E-2	1.34E-2	-1.87	-1.87	7.29E-7
	$(dma)_2CH^+$	0.90	6.67	-7.02	4.36E-1	4.90E-1	-0.36	-0.31	2.54E-3
	$(mpa)_2CH^+$	0.90	6.67	-5.89	4.81E+0	5.07E+0	0.68	0.71	5.41E-4
	$(dpa)_2CH^+$	0.90	6.67	-4.72	9.52E+1	5.71E+1	1.98	1.76	4.92E-2
	$(mfa)_2CH^+$	0.90	6.67	-3.85	1.23E+2	3.46E+2	2.09	2.54	2.01E-1
	$(ani)_2CH^+$	0.90	6.67	0.00	2.33E+6	9.97E+5	6.37	6.00	1.36E-1
	$(ani)(tol)CH^+$	0.90	6.67	1.48	1.47E+7	2.13E+7	7.17	7.33	2.60E-2
33M67AN	$(lil)_2CH^+$	0.92	6.38	-10.04	5.96E-4	4.47E-4	-3.22	-3.35	1.55E-2
	$(ind)_2CH^+$	0.92	6.38	-8.76	5.80E-3	6.64E-3	-2.24	-2.18	3.48E-3
	$(dma)_2CH^+$	0.92	6.38	-7.02	2.62E-1	2.60E-1	-0.58	-0.58	9.18E-6
	$(mpa)_2CH^+$	0.92	6.38	-5.89	3.85E+0	2.82E+0	0.59	0.45	1.84E-2
	$(mor)_2CH^+$	0.92	6.38	-5.53	3.51E+0	6.02E+0	0.55	0.78	5.47E-2
	$(dpa)_2CH^+$	0.92	6.38	-4.72	8.87E+1	3.32E+1	1.95	1.52	1.82E-1
	$(mfa)_2CH^+$	0.92	6.38	-3.85	8.46E+1	2.08E+2	1.93	2.32	1.52E-1
	$(pfa)_2CH^+$	0.92	6.38	-3.14	4.85E+2	9.27E+2	2.69	2.97	7.92E-2
	$(ani)_2CH^+$	0.92	6.38	0.00	1.54E+6	6.94E+5	6.19	5.84	1.20E-1
	$(ani)(tol)CH^+$	0.92	6.38	1.48	1.33E+7	1.57E+7	7.12	7.20	5.25E-3
20M80AN	$(ind)_2CH^+$	0.94	6.04	-8.76	3.09E-3	2.72E-3	-2.51	-2.57	3.12E-3
	$(thq)_2CH^+$	0.94	6.04	-8.22	6.55E-3	8.78E-3	-2.18	-2.06	1.62E-2
	$(dma)_2CH^+$	0.94	6.04	-7.02	1.22E-1	1.19E-1	-0.91	-0.92	1.15E-4
	$(mpa)_2CH^+$	0.94	6.04	-5.89	2.15E+0	1.39E+0	0.33	0.14	3.64E-2
	$(mor)_2CH^+$	0.94	6.04	-5.53	1.96E+0	3.03E+0	0.29	0.48	3.58E-2
	$(dpa)_2CH^+$	0.94	6.04	-4.72	5.43E+1	1.76E+1	1.73	1.25	2.39E-1
	$(mfa)_2CH^+$	0.94	6.04	-3.85	4.81E+1	1.16E+2	1.68	2.07	1.48E-1
	$(pfa)_2CH^+$	0.94	6.04	-3.14	3.58E+2	5.45E+2	2.55	2.74	3.32E-2
	$(ani)_2CH^+$	0.94	6.04	0.00	8.58E+5	4.99E+5	5.93	5.70	5.52E-2
	$(ani)(tol)CH^+$	0.94	6.04	1.48	9.91E+6	1.24E+7	7.00	7.09	9.74E-3

Solvent	Electrophile	s	N_1	E	k_{exp}	k_{calc}	log k_{exp}	log k_{calc}	Δ^2 log k
10M90AN	$(ind)_2CH^+$	0.97	5.55	-8.76	7.72E-4	7.40E-4	-3.11	-3.13	3.35E-4
	$(pyr)_2CH^+$	0.97	5.55	-7.69	7.07E-3	8.18E-3	-2.15	-2.09	3.99E-3
	$(dma)_2CH^+$	0.97	5.55	-7.02	3.93E-2	3.68E-2	-1.41	-1.43	8.19E-4
	$(mpa)_2CH^+$	0.97	5.55	-5.89	7.21E-1	4.65E-1	-0.14	-0.33	3.63E-2
	$(mor)_2CH^+$	0.97	5.55	-5.53	6.83E-1	1.04E+0	-0.17	0.02	3.39E-2
	$(dpa)_2CH^+$	0.97	5.55	-4.72	1.78E+1	6.43E+0	1.25	0.81	1.96E-1
	$(mfa)_2CH^+$	0.97	5.55	-3.85	1.64E+1	4.53E+1	1.21	1.66	1.95E-1
	$(pfa)_2CH^+$	0.97	5.55	-3.14	1.60E+2	2.23E+2	2.20	2.35	2.09E-2
	$(ani)_2CH^+$	0.97	5.55	0.00	4.20E+5	2.57E+5	5.62	5.41	4.54E-2
	$(ani)(tol)CH^+$	0.97	5.55	1.48	6.22E+6	7.13E+6	6.79	6.85	3.51E-3
								$\Sigma\ \Delta^2$ log k =	2.09E+1
								standard deviation in k= 10^(20.9/308)$^{1/2}$ =	1.82

Table S7. The relationship of N_T, N'_T, N'_{OTs}, and N_{OTs} with nucleophilicity parameters N_1 of solvents derived from the reactions with benzhydrylium ions.

Solvents [a]	N_1	N_T [b]	N'_T [c]	N'_{OTs} [d]	N_{OTs} [e]
M	7.54	0.17	0.33	0.19	-0.04
E	7.44	0.37	0.54	0.43	0.06
90E10W	7.03	0.16		0.19	0.07
80E20W	6.68	0.00	0.00	0.00	0.00
60E40W	6.28	-0.39	-0.35	-0.31	-0.08
50E50W	5.96	-0.58		-0.41	-0.09
40E60W	5.81	-0.74	-0.65	-0.72	-0.23
20E80W	5.54	-1.16	-1.01	-1.17	-0.34
10E90W	5.38	-1.31		-1.36	-0.41
W	5.20	-1.38	-1.26	-1.47	-0.44
80A20W	5.77 [f]	-0.37	-0.25	-0.27	-0.42
90A10W	5.70 [f]	-0.35	-0.25	-0.05	-0.39
42T58W (50T50W w/w)	3.73 [g]	-1.73	-1.49	-1.47	-0.93
52T48W (60T40W w/w)	3.54 [g]	-1.85		-1.54	
63T37W (70T30W w/w)	3.39 [g]	-1.98	-1.77	-1.70	-1.20
80T20W (85T15W w/w)	3.20				-2.01
87T13W (90T10W w/w)	3.01 [g]	-2.25	-2.28	-2.87	
T	1.23	-3.93	-3.80	-3.51	-3.07

[a] Mixtures of solvents are given as (v/v), solvents: W = water, E = ethanol, M = methanol, T = trifluoroethanol. [b] Based on reactions with *S*-methyldibenzothiophenium ion, from ref. 2. [c] Based on reactions with *S*-methylbenzothiophenium ion, from ref. 2. [d] Based on methyltosylate, from ref. 2. [e] Based on methyltosylate, from ref. 1. [f] From ref. 33. [g] Interpolated value.

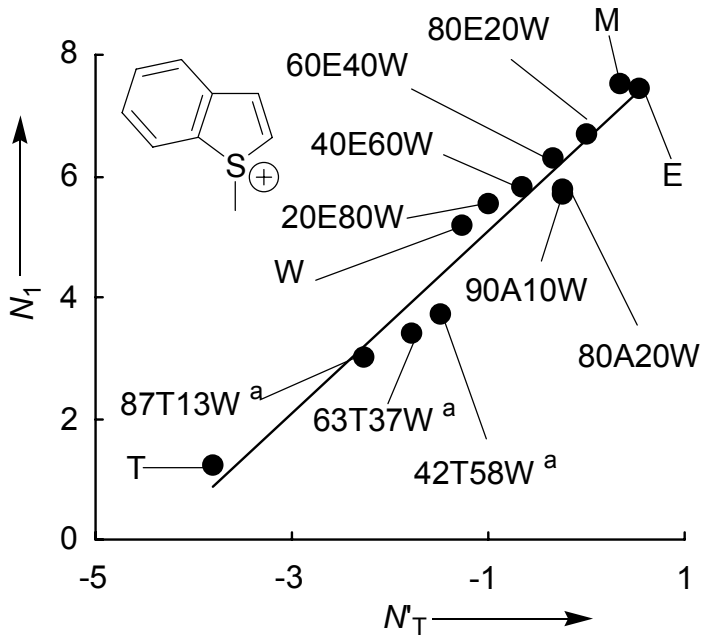


Figure S1. The relationship of nucleophilicity parameters N_1 derived from reactions with benzhydryl cations and N'_T derived from reactions with *S*-methyl-benzothiophenium ion ($N_1 = 1.51N'_T + 6.60$, $n = 13$, $R^2 = 0.950$). [a] N_1 by interpolation of values for comparable trifluoroethanol/water solvent mixtures.

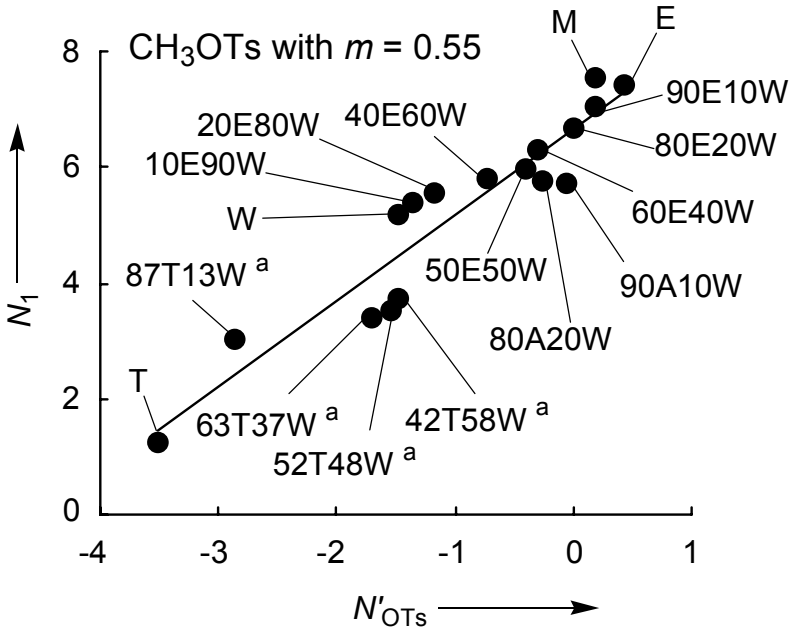


Figure S2. The relationship of nucleophilic parameters N_1 derived from reactions with benzhydryl cations and N'_{OTs} derived from reactions with methyl tosylate ($N_1 = 1.48N'_{OTs} + 6.65$, $n = 17$, $R^2 = 0.892$). [a] N_1 by interpolation of values for comparable trifluoroethanol/water solvent mixtures.

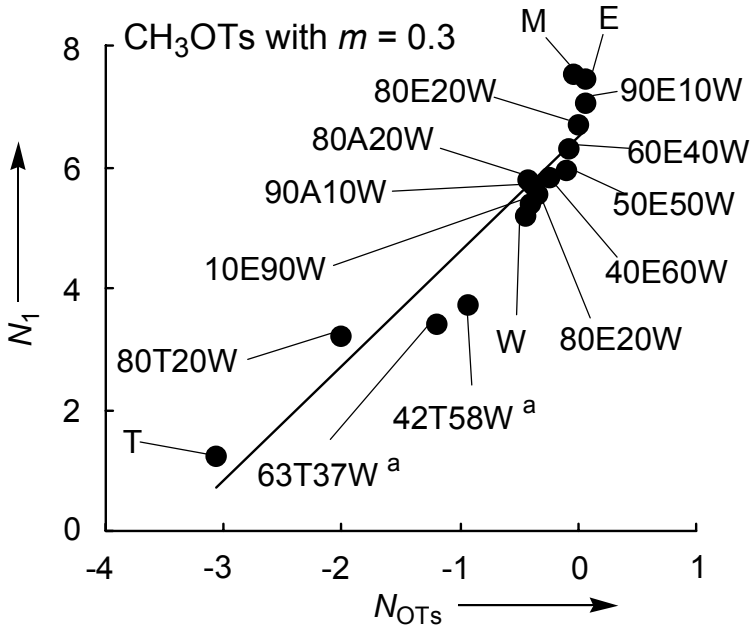


Figure S3. The relationship of nucleophilic parameters N_1 derived from reactions with benzhydryl cations and N_{OTs} derived from reactions with methyl tosylate ($N_1 = 1.87N_{OTs} + 6.48$ $n = 16$, $R^2 = 0.885$). [a] N_1 by interpolation of values for comparable trifluoroethanol/water solvent mixtures.