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SUPPORTING INFORMATION

Title: Nucleophilicity Parameters for Carbanions in Methanol
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Equilibria

1. General

The equilibrium concentrations of carbanions and methoxide were calculated on the basis of the pK_{aH} or K_{CH} values of the CH acids in methanol.

$$CH + MeO^- \underset{}{\overset{K_{CH}}{\rightleftharpoons}} C^- + MeOH \quad \text{(S1)}$$

$$K_{CH} = K_{aH}/K_{MeOH} \quad \text{(S2)}$$

$$K_{CH} = ([C^-]/([CH][MeO^-]) \quad \text{(S3)}$$

When the initial concentrations of the CH acids and methoxide are $[CH]_o$ and $[MeO^-]_o$ respectively, their equilibrium concentrations are:

$$[CH] = [CH]_o - [C^-] \text{ and } [MeO^-] = [MeO^-]_o - [C^-] \quad \text{(S4)}$$

With the known initial concentrations of the CH acids and methoxide, based on equations (S2), (S3) and (S4), one can calculate $[C^-]$ and $[MeO^-]$, which will be used further for the determination of the rate constants of the carbanions with reference electrophiles.

In the cases of phenylnitromethane (**2d-**H), (*p*-tolyl)nitromethane (**2e-**H), and (*p*-cyanophenyl)nitromethane (**2h-**H), the pK_{aH} values were determined spectrophotometrically using the UV absorption of the nitronate anions. When the CH acids were added to solutions of methoxide in methanol, the absorbances of the generated carbanions increased steadily and reached constant values at certain $[CH]_o/[MeO^-]_o$ ratios. From the end absorbances A_{end} and the absorbances A at certain moments of the titration, one can calculate the K_{CH} values of the CH acids in methanol assuming the validity of Beer-Lambert´s law according to equation (S5).

$$[C^-] = (A[MeO]_o)/A_{end} \quad \text{(S5)}$$

The K_{CH} values for those compounds, which were presented in Table 1 of the paper, were obtained by least squares fitting method (software: What'sBest! by Lindo Systems Inc.) which optimizes the end absorbances and the individually calculated K_{CH} values. The pK_{aH} values (Table 1 of the paper) were then calculated based on K_{CH} according to equation (S2).

2. Acidities of CH acidic compounds in methanol

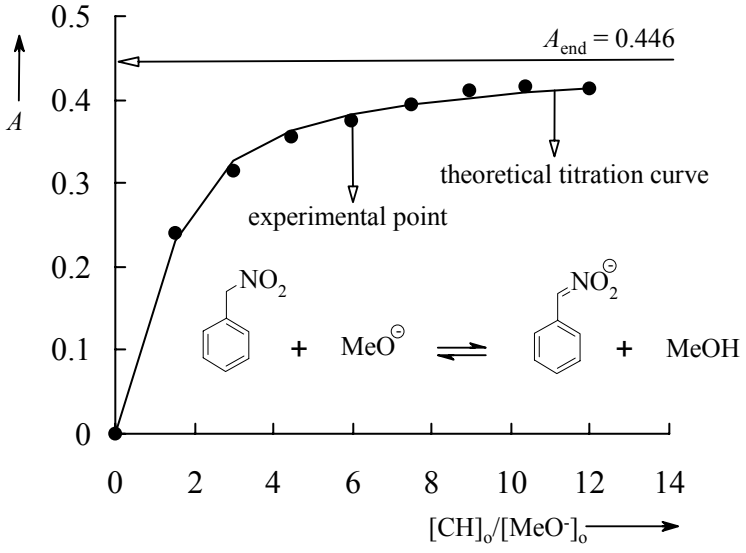
2.1. Phenylnitromethane (2d-H)

Initial			Equilibrium at 20 °C		
$[CH]_o$ (M)	$[MeO^-]_o$ (M)	$[CH]_o/[MeO^-]_o$	A (300 nm)	$[C^-]$ (M)	[CH] (M)
0.00	5.86×10^{-5}	0.00	0	0	0
8.77×10^{-5}	5.86×10^{-5}	1.50	2.40×10^{-1}	3.16×10^{-5}	5.61×10^{-5}
1.75×10^{-4}	5.84×10^{-5}	3.00	3.15×10^{-1}	4.13×10^{-5}	1.34×10^{-4}
2.60×10^{-4}	5.83×10^{-5}	4.46	3.55×10^{-1}	4.65×10^{-5}	2.14×10^{-4}
3.48×10^{-4}	5.82×10^{-5}	5.98	3.75×10^{-1}	4.90×10^{-5}	2.99×10^{-4}
4.35×10^{-4}	5.81×10^{-5}	7.49	3.95×10^{-1}	5.15×10^{-5}	3.83×10^{-4}
5.20×10^{-4}	5.80×10^{-5}	8.97	4.10×10^{-1}	5.34×10^{-5}	4.67×10^{-4}
6.00×10^{-4}	5.78×10^{-5}	1.04×10^{1}	4.15×10^{-1}	5.38×10^{-5}	5.46×10^{-4}
6.90×10^{-4}	5.76×10^{-5}	1.20×10^{1}	4.14×10^{-1}	5.35×10^{-5}	6.36×10^{-4}

Least squares fitting optimization: $A_{end} = 0.446$

$K_{CH} = 2.00 \times 10^4\ M^{-1}$

$pK_{aH} = 12.62$



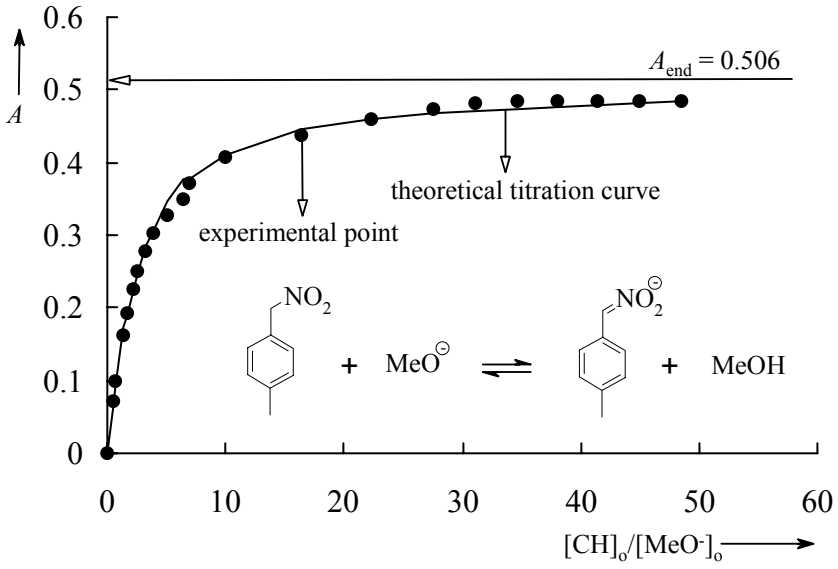
2.2. (*p*-Tolyl)nitromethane (2e-H)

Initial			Equilibrium at 20 °C		
$[CH]_o$ (M)	$[MeO^-]_o$ (M)	$[CH]_o/[MeO^-]_o$	A (315nm)	$[C^-]$ (M)	[CH] (M)
0.00	5.95×10^{-5}	0.00	0	0	0
2.88×10^{-5}	5.93×10^{-5}	4.85×10^{-1}	7.20×10^{-2}	8.45×10^{-6}	2.03×10^{-5}
4.17×10^{-5}	5.92×10^{-5}	7.05×10^{-1}	1.00×10^{-1}	1.17×10^{-5}	3.00×10^{-5}
8.01×10^{-5}	5.90×10^{-5}	1.36	1.63×10^{-1}	1.90×10^{-5}	6.11×10^{-5}
9.87×10^{-5}	5.89×10^{-5}	1.68	1.93×10^{-1}	2.25×10^{-5}	7.62×10^{-5}
1.26×10^{-4}	5.88×10^{-5}	2.14	2.26×10^{-1}	2.63×10^{-5}	9.97×10^{-5}
1.49×10^{-4}	5.87×10^{-5}	2.54	2.50×10^{-1}	2.90×10^{-5}	1.20×10^{-4}
1.88×10^{-4}	5.86×10^{-5}	3.22	2.78×10^{-1}	3.22×10^{-5}	1.56×10^{-4}
2.26×10^{-4}	5.85×10^{-5}	3.86	3.04×10^{-1}	3.52×10^{-5}	1.90×10^{-4}
2.97×10^{-4}	5.84×10^{-5}	5.08	3.27×10^{-1}	3.78×10^{-5}	2.59×10^{-4}
3.78×10^{-4}	5.83×10^{-5}	6.49	3.50×10^{-1}	4.04×10^{-5}	3.38×10^{-4}
4.04×10^{-4}	5.82×10^{-5}	6.94	3.71×10^{-1}	4.27×10^{-5}	3.61×10^{-4}
5.85×10^{-4}	5.82×10^{-5}	1.00×10^{1}	4.08×10^{-1}	4.70×10^{-5}	5.38×10^{-4}
9.50×10^{-4}	5.81×10^{-5}	1.64×10^{1}	4.38×10^{-1}	5.03×10^{-5}	9.00×10^{-4}
1.30×10^{-3}	5.81×10^{-5}	2.24×10^{1}	4.61×10^{-1}	5.30×10^{-5}	1.25×10^{-3}
1.60×10^{-3}	5.80×10^{-5}	2.76×10^{1}	4.74×10^{-1}	5.43×10^{-5}	1.55×10^{-3}
1.80×10^{-3}	5.80×10^{-5}	3.10×10^{1}	4.80×10^{-1}	5.51×10^{-5}	1.74×10^{-3}
2.01×10^{-3}	5.80×10^{-5}	3.47×10^{1}	4.83×10^{-1}	5.55×10^{-5}	1.95×10^{-3}
2.20×10^{-3}	5.79×10^{-5}	3.80×10^{1}	4.85×10^{-1}	5.55×10^{-5}	2.14×10^{-3}
2.40×10^{-3}	5.79×10^{-5}	4.15×10^{1}	4.86×10^{-1}	5.56×10^{-5}	2.34×10^{-3}
2.60×10^{-3}	5.78×10^{-5}	4.50×10^{1}	4.86×10^{-1}	5.55×10^{-5}	2.54×10^{-3}
2.80×10^{-3}	5.78×10^{-5}	4.84×10^{1}	4.86×10^{-1}	5.55×10^{-5}	2.74×10^{-3}

Least squares fitting optimization: $A_{end} = 0.506$

$K_{CH} = 8.01 \times 10^{3}\ M^{-1}$

$pK_{aH} = 13.02$



2.3. (*p*-Cyanophenyl)nitromethane (2h-H)

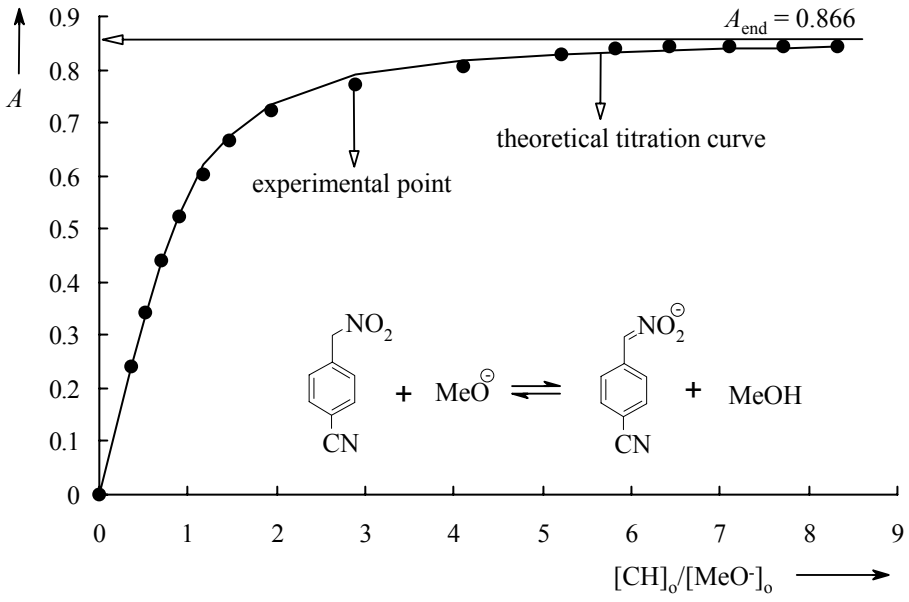
In MeOH

Initial			Equilibrium at 20 °C		
$[CH]_o$ (M)	$[MeO^-]_o$ (M)	$[CH]_o/[MeO^-]_o$	A (340 nm)	$[C^-]$ (M)	[CH] (M)
0.00	5.90×10^{-5}	0.00	0	0	0
3.07×10^{-5}	5.90×10^{-5}	5.20×10^{-1}	2.42×10^{-1}	1.65×10^{-5}	4.49×10^{-6}
6.14×10^{-5}	5.89×10^{-5}	1.04	3.45×10^{-1}	2.34×10^{-5}	7.53×10^{-6}
9.20×10^{-5}	5.88×10^{-5}	1.56	4.39×10^{-1}	2.98×10^{-5}	1.18×10^{-5}
1.23×10^{-4}	5.87×10^{-5}	2.10	5.24×10^{-1}	3.55×10^{-5}	1.79×10^{-5}
1.53×10^{-4}	5.87×10^{-5}	2.61	6.02×10^{-1}	4.08×10^{-5}	2.86×10^{-5}
1.80×10^{-4}	5.87×10^{-5}	3.07	6.68×10^{-1}	4.53×10^{-5}	4.02×10^{-5}
2.14×10^{-4}	5.87×10^{-5}	3.65	7.25×10^{-1}	4.91×10^{-5}	6.42×10^{-5}
2.44×10^{-4}	5.86×10^{-5}	4.16	7.72×10^{-1}	5.22×10^{-5}	1.18×10^{-4}
2.70×10^{-4}	5.85×10^{-5}	4.62	8.07×10^{-1}	5.45×10^{-5}	1.86×10^{-4}
3.05×10^{-4}	5.85×10^{-5}	5.21	8.28×10^{-1}	5.60×10^{-5}	2.49×10^{-4}
3.40×10^{-4}	5.84×10^{-5}	5.82	8.38×10^{-1}	5.65×10^{-5}	2.83×10^{-4}
3.75×10^{-4}	5.84×10^{-5}	6.42	8.43×10^{-1}	5.69×10^{-5}	3.18×10^{-4}
4.15×10^{-4}	5.84×10^{-5}	7.11	8.45×10^{-1}	5.70×10^{-5}	3.58×10^{-4}
4.50×10^{-4}	5.83×10^{-5}	7.72	8.45×10^{-1}	5.69×10^{-5}	3.93×10^{-4}
4.85×10^{-4}	5.83×10^{-5}	8.32	8.45×10^{-1}	5.69×10^{-5}	4.28×10^{-4}

Least squares fitting optimization: $A_{end} = 0.866$

$K_{CH} = 8.61 \times 10^4\ M^{-1}$

$pK_{aH} = 11.99$



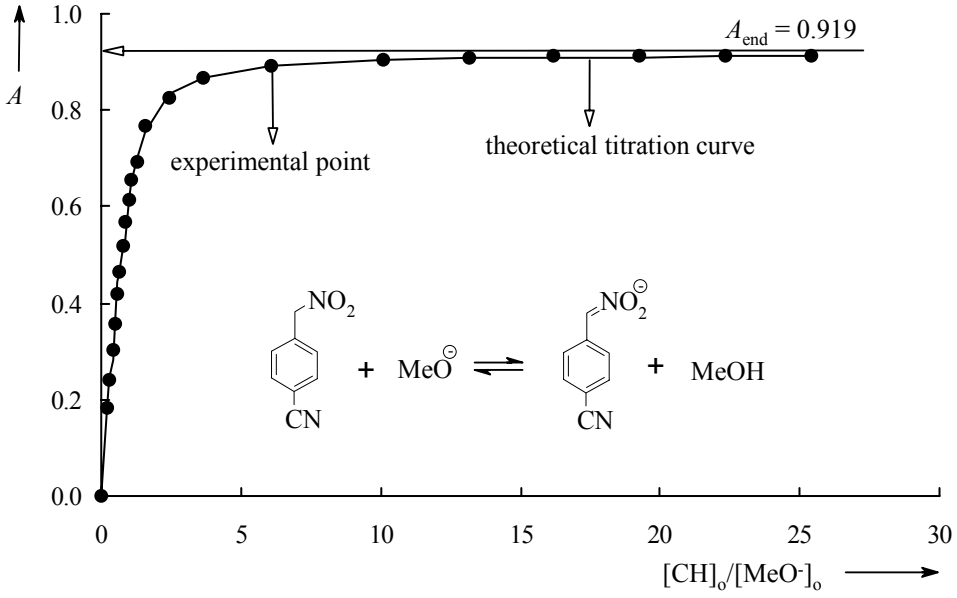
In 91 % MeOH/9 % MeCN

Initial			Equilibrium at 20 °C		
$[CH]_o$ (M)	$[MeO^-]_o$ (M)	$[CH]_o/[MeO^-]_o$	A (340 nm)	$[C^-]$ (M)	[CH] (M)
0.00	6.33×10^{-5}	0.00	0	0	0
1.51×10^{-5}	6.33×10^{-5}	2.39×10^{-1}	1.83×10^{-1}	1.26×10^{-5}	2.54×10^{-6}
2.03×10^{-5}	6.33×10^{-5}	3.21×10^{-1}	2.42×10^{-1}	1.67×10^{-5}	3.63×10^{-6}
2.55×10^{-5}	6.33×10^{-5}	4.03×10^{-1}	3.01×10^{-1}	2.07×10^{-5}	4.79×10^{-6}
3.12×10^{-5}	6.33×10^{-5}	4.93×10^{-1}	3.57×10^{-1}	2.46×10^{-5}	6.59×10^{-6}
3.79×10^{-5}	6.33×10^{-5}	5.98×10^{-1}	4.20×10^{-1}	2.89×10^{-5}	8.92×10^{-6}
4.25×10^{-5}	6.33×10^{-5}	6.71×10^{-1}	4.66×10^{-1}	3.21×10^{-5}	1.04×10^{-5}
4.88×10^{-5}	6.33×10^{-5}	7.71×10^{-1}	5.19×10^{-1}	3.57×10^{-5}	1.31×10^{-5}
5.40×10^{-5}	6.33×10^{-5}	8.53×10^{-1}	5.68×10^{-1}	3.91×10^{-5}	1.49×10^{-5}
6.29×10^{-5}	6.32×10^{-5}	9.95×10^{-1}	6.13×10^{-1}	4.22×10^{-5}	2.08×10^{-5}
6.97×10^{-5}	6.32×10^{-5}	1.10	6.55×10^{-1}	4.51×10^{-5}	2.46×10^{-5}
7.99×10^{-5}	6.32×10^{-5}	1.26	6.95×10^{-1}	4.78×10^{-5}	3.21×10^{-5}
1.00×10^{-4}	6.32×10^{-5}	1.59	7.67×10^{-1}	5.28×10^{-5}	4.75×10^{-5}
1.54×10^{-4}	6.32×10^{-5}	2.43	8.25×10^{-1}	5.67×10^{-5}	9.69×10^{-5}
2.30×10^{-4}	6.32×10^{-5}	3.63	8.67×10^{-1}	5.96×10^{-5}	1.70×10^{-4}
3.85×10^{-4}	6.32×10^{-5}	6.09	8.91×10^{-1}	6.13×10^{-5}	3.24×10^{-4}
6.38×10^{-4}	6.32×10^{-5}	10.1	9.03×10^{-1}	6.21×10^{-5}	5.76×10^{-4}
8.31×10^{-4}	6.32×10^{-5}	13.1	9.09×10^{-1}	6.25×10^{-5}	7.68×10^{-4}
1.02×10^{-3}	6.32×10^{-5}	16.2	9.12×10^{-1}	6.27×10^{-5}	9.61×10^{-4}
1.22×10^{-3}	6.32×10^{-5}	19.3	9.13×10^{-1}	6.27×10^{-5}	1.15×10^{-3}
1.41×10^{-3}	6.31×10^{-5}	22.3	9.13×10^{-1}	6.27×10^{-5}	1.35×10^{-3}
1.60×10^{-3}	6.31×10^{-5}	25.4	9.13×10^{-1}	6.27×10^{-5}	1.54×10^{-3}

Least squares fitting optimization: $A_{end} = 0.919$

$K_{CH} = 9.89 \times 10^4\ M^{-1}$

$pK_{aH} = 11.92$



Kinetics

3. General

The general method for the kinetic investigations is presented in the experimental part of the paper.

The pseudo-first-order rate constants k_{obs} (s^{-1}) were obtained by least-squares fitting of the absorbance A of the electrophiles to the single-exponential $A_t = A_o\exp(-k_{obs}t) + C$.

$$d[Ar_2CH^+]/dt = -k_{obs}\,[Ar_2CH^+] \quad \text{(S6)}$$

$$k_{obs} = k_{2,C}\text{-}[C^-] + k_{2,MeO}\text{-}[MeO^-] + k_{1,MeOH} \quad \text{(S7)}$$

The terms k_{MeO}-[MeO^-] were subtracted from the observed pseudo-first-order rate constants k_{obs}, then the obtained values $k_{1\Psi}$ (s^{-1}) were plotted against the concentrations of the carbanions giving rise to linear correlations with the slopes corresponding to the second-order rate constants of the reactions of carbanions with the reference electrophiles $k_{2,C}$- (M^{-1} s^{-1}).

$$k_{1\Psi} = k_{obs} - k_{2,MeO}\text{-}[MeO^-] = k_{2,C}\text{-}[C^-] + k_{1,MeOH} \quad \text{(S8)}$$

The rate constants of the reactions of methoxide anion with the reference electrophiles have already been reported. Those which are used for the evaluation of the data in this work are presented in Table S1.

Table S1. Second-order rate constants k_2 (M^{-1} s^{-1}) for the reactions of methoxide anion and first-order rate constants for the reactions of methanol with reference electrophiles at 20 °C, in MeOH/MeCN mixtures[a].

	Electrophile	k_2 (M^{-1} s^{-1})	$k_{1,MeOH}$ (s^{-1})
1a	$(pyr)_2CH^+$	4.80×10^4	9.32×10^{-1}
1b	$(thq)_2CH^+$	1.56×10^4	2.17×10^{-1}
1c	$(ind)_2CH^+$	7.41×10^3	
1d	$(jul)_2CH^+$	2.48×10^3	
1e	$(lil)_2CH^+$	1.17×10^3	6.14×10^{-3}
1f	tolQM	6.12×10^{-1}	
1g	aniQM	4.96×10^{-1}	

[a] Data from T. B. Phan, H. Mayr, *Can. J. Chem*. **2005**, *83*, 1554–1560; Reactions with electrophiles **1a-e** were studied in 91 % MeOH/9 % MeCN (v/v) whereas those of **1f-g** were studied in MeOH.

The experiments performed with a stopped-flow instrument, 1 volume part of the solutions of the reference electrophiles was mixed with 10 volume parts of the solutions of the carbanions in methanol. Because of the 10 : 1 mixing ratio, the effective concentrations of carbanions $[C^-]_{eff}$ and methoxide $[MeO^-]_{eff}$ must be the concentrations before mixing the solution of the nucleophiles with the solution of the reference electrophiles divided by 1.1.

4. Reactivities of carbanions

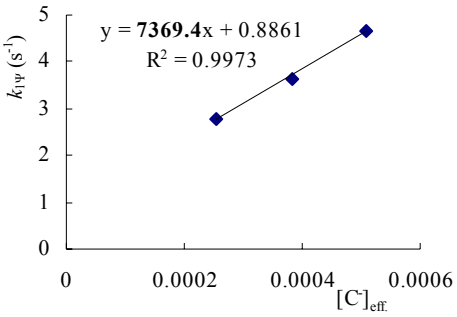
4.1. Nitromethyl anion (2a)

4.1.1. Rate constants

Reaction with $(pyr)_2CH^+BF_4^-$ (1a): $k_{2,C^-} = 7.37 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 610 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
3.70×10^{-1}	3.15×10^{-4}	2.80×10^{-4}	3.44×10^{-5}	2.55×10^{-4}	3.13×10^{-5}	4.29	2.79
3.70×10^{-1}	4.72×10^{-4}	4.20×10^{-4}	5.17×10^{-5}	3.82×10^{-4}	4.70×10^{-5}	5.90	3.65
3.70×10^{-1}	6.29×10^{-4}	5.60×10^{-4}	6.89×10^{-5}	5.10×10^{-4}	6.26×10^{-5}	7.68	4.67

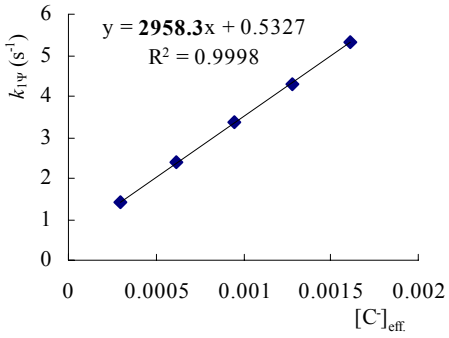


[a] Concentration of $(pyr)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 22.0\ M^{-1}$.

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 2.96 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
3.70×10^{-1}	3.63×10^{-4}	3.23×10^{-4}	3.97×10^{-5}	2.94×10^{-4}	3.61×10^{-5}	1.95	1.39
7.40×10^{-1}	7.26×10^{-4}	6.84×10^{-4}	4.20×10^{-5}	6.22×10^{-4}	3.82×10^{-5}	2.99	2.39
1.11	1.09×10^{-3}	1.05×10^{-3}	4.28×10^{-5}	9.51×10^{-4}	3.89×10^{-5}	3.95	3.35
1.48	1.45×10^{-3}	1.41×10^{-3}	4.33×10^{-5}	1.28×10^{-3}	3.93×10^{-5}	4.90	4.29
1.85	1.81×10^{-3}	1.77×10^{-3}	4.35×10^{-5}	1.61×10^{-3}	3.96×10^{-5}	5.93	5.31

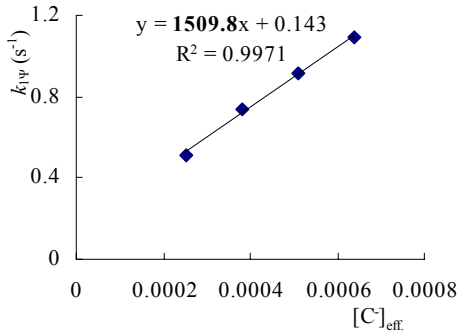


[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.02×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 22.0\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 1.51 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

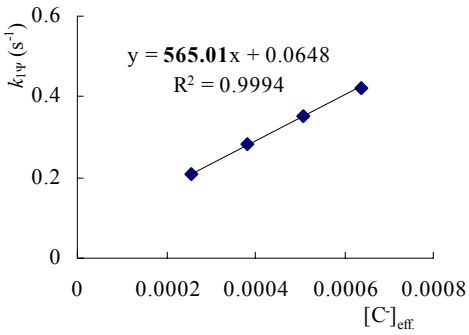
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
3.70×10^{-1}	3.15×10^{-4}	2.80×10^{-4}	3.44×10^{-5}	2.55×10^{-4}	3.13×10^{-5}	7.47×10^{-1}	5.15×10^{-1}
3.70×10^{-1}	4.72×10^{-4}	4.20×10^{-4}	5.17×10^{-5}	3.82×10^{-4}	4.70×10^{-5}	1.09	7.37×10^{-1}
3.70×10^{-1}	6.29×10^{-4}	5.60×10^{-4}	6.89×10^{-5}	5.10×10^{-4}	6.26×10^{-5}	1.38	9.16×10^{-1}
3.70×10^{-1}	7.87×10^{-4}	7.01×10^{-4}	8.62×10^{-5}	6.37×10^{-4}	7.83×10^{-5}	1.68	1.10



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 22.0\ M^{-1}$.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): $k_{2,C^-} = 5.65 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

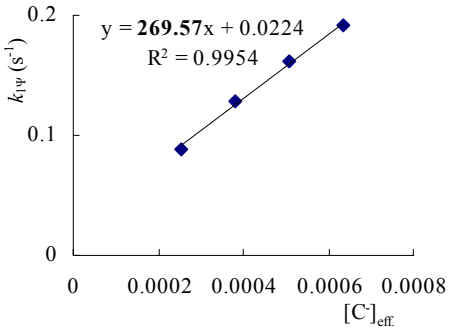
Concentrations[a] (M)						Rates	
In syringes				In reaction cell			
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$	k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
3.70×10^{-1}	3.15×10^{-4}	2.80×10^{-4}	3.44×10^{-5}	2.55×10^{-4}	3.13×10^{-5}	2.84×10^{-1}	2.07×10^{-1}
3.70×10^{-1}	4.72×10^{-4}	4.20×10^{-4}	5.17×10^{-5}	3.82×10^{-4}	4.70×10^{-5}	4.00×10^{-1}	2.83×10^{-1}
3.70×10^{-1}	6.29×10^{-4}	5.60×10^{-4}	6.89×10^{-5}	5.10×10^{-4}	6.26×10^{-5}	5.10×10^{-1}	3.54×10^{-1}
3.70×10^{-1}	7.87×10^{-4}	7.01×10^{-4}	8.62×10^{-5}	6.37×10^{-4}	7.83×10^{-5}	6.17×10^{-1}	4.23×10^{-1}



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 22.0\ M^{-1}$.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): $k_{2,C^-} = 2.70 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

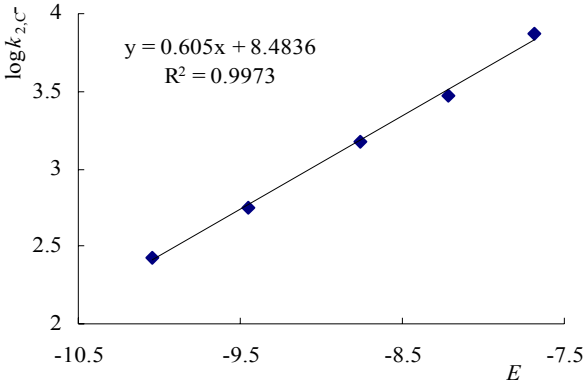
Concentrations[a] (M)						Rates	
In syringes				In reaction cell			
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$	k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
3.70×10^{-1}	3.15×10^{-4}	2.80×10^{-4}	3.44×10^{-5}	2.55×10^{-4}	3.13×10^{-5}	1.25×10^{-1}	8.83×10^{-2}
3.70×10^{-1}	4.72×10^{-4}	4.20×10^{-4}	5.17×10^{-5}	3.82×10^{-4}	4.70×10^{-5}	1.84×10^{-1}	1.29×10^{-1}
3.70×10^{-1}	6.29×10^{-4}	5.60×10^{-4}	6.89×10^{-5}	5.10×10^{-4}	6.26×10^{-5}	2.35×10^{-1}	1.61×10^{-1}
3.70×10^{-1}	7.87×10^{-4}	7.01×10^{-4}	8.62×10^{-5}	6.37×10^{-4}	7.83×10^{-5}	2.84×10^{-1}	1.92×10^{-1}



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.00×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 22.0\ M^{-1}$.

4.1.2. Reactivity parameters: $N = 14.02$; $s = 0.60_5$

Reference electrophile			Rate constants	
	Name	E	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1a	$(pyr)_2CH^+$	-7.69	7.37×10^3	3.87
1b	$(thq)_2CH^+$	-8.22	2.96×10^3	3.47
1c	$(ind)_2CH^+$	-8.76	1.51×10^3	3.18
1d	$(jul)_2CH^+$	-9.45	5.65×10^2	2.75
1e	$(lil)_2CH^+$	-10.04	2.70×10^2	2.43



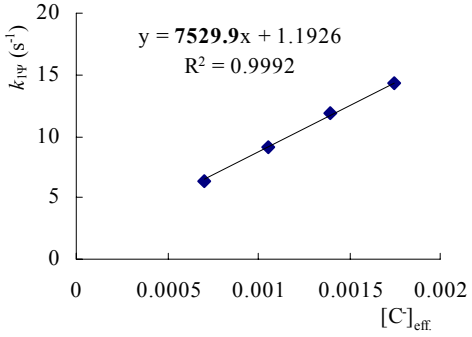
4.2. Nitroethyl anion (2b)

4.2.1. Rate constants

Reaction with $(pyr)_2CH^+BF_4^-$ (1a): $k_{2,C^-} = 7.53 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 610 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.99×10^{-2}	7.92×10^{-4}	7.70×10^{-4}	2.23×10^{-5}	7.00×10^{-4}	2.02×10^{-5}	7.35	6.38
6.99×10^{-2}	1.19×10^{-3}	1.15×10^{-3}	3.36×10^{-5}	1.05×10^{-3}	3.05×10^{-5}	1.06×10^1	9.18
6.99×10^{-2}	1.58×10^{-3}	1.54×10^{-3}	4.50×10^{-5}	1.40×10^{-3}	4.09×10^{-5}	1.38×10^1	1.18×10^1
6.99×10^{-2}	1.98×10^{-3}	1.92×10^{-3}	5.66×10^{-5}	1.75×10^{-3}	5.14×10^{-5}	1.67×10^1	1.43×10^1

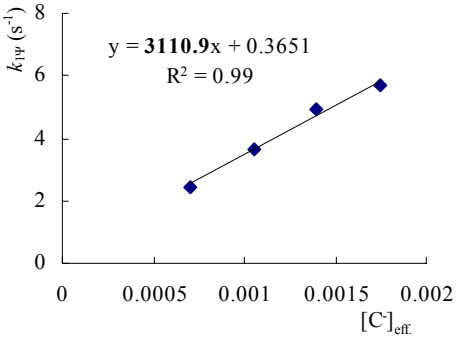


[a] Concentration of $(pyr)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.00 \times 10^2\ M^{-1}$.

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 3.11 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.99×10^{-2}	7.92×10^{-4}	7.70×10^{-4}	2.23×10^{-5}	7.00×10^{-4}	2.02×10^{-5}	2.77	2.45
6.99×10^{-2}	1.19×10^{-3}	1.15×10^{-3}	3.36×10^{-5}	1.05×10^{-3}	3.05×10^{-5}	4.15	3.68
6.99×10^{-2}	1.58×10^{-3}	1.54×10^{-3}	4.50×10^{-5}	1.40×10^{-3}	4.09×10^{-5}	5.54	4.90
6.99×10^{-2}	1.98×10^{-3}	1.92×10^{-3}	5.66×10^{-5}	1.75×10^{-3}	5.14×10^{-5}	6.48	5.67

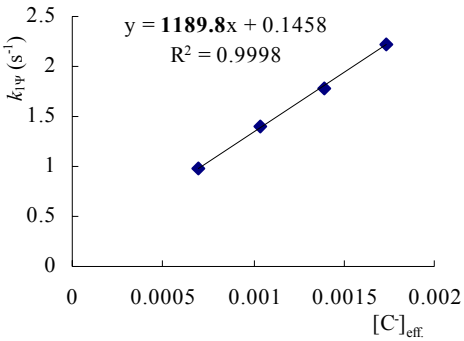


[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.02×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.00 \times 10^2\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 1.19 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

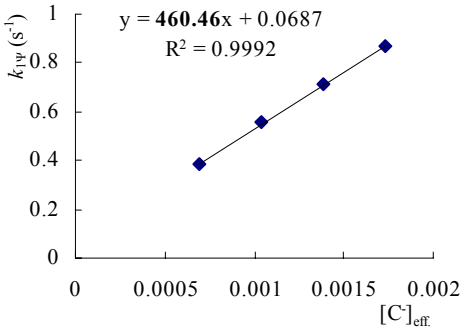
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.99×10^{-2}	7.87×10^{-4}	7.65×10^{-4}	2.21×10^{-5}	6.95×10^{-4}	2.01×10^{-5}	1.12	9.72
6.99×10^{-2}	1.18×10^{-3}	1.15×10^{-3}	3.33×10^{-5}	1.04×10^{-3}	3.03×10^{-5}	1.62	1.39
6.99×10^{-2}	1.57×10^{-3}	1.53×10^{-3}	4.47×10^{-5}	1.39×10^{-3}	4.06×10^{-5}	2.09	1.79
6.99×10^{-2}	1.97×10^{-3}	1.91×10^{-3}	5.62×10^{-5}	1.74×10^{-3}	5.11×10^{-5}	2.60	2.22



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.00 \times 10^2\ M^{-1}$.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): $k_{2,C^-} = 4.60 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

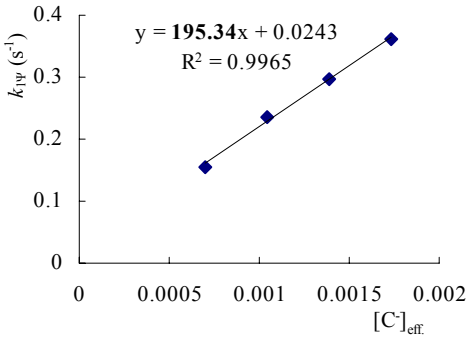
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.99×10^{-2}	7.87×10^{-4}	7.65×10^{-4}	2.21×10^{-5}	6.95×10^{-4}	2.01×10^{-5}	4.33×10^{-1}	3.83×10^{-1}
6.99×10^{-2}	1.18×10^{-3}	1.15×10^{-3}	3.33×10^{-5}	1.04×10^{-3}	3.03×10^{-5}	6.32×10^{-1}	5.56×10^{-1}
6.99×10^{-2}	1.57×10^{-3}	1.53×10^{-3}	4.47×10^{-5}	1.39×10^{-3}	4.06×10^{-5}	8.11×10^{-1}	7.10×10^{-1}
6.99×10^{-2}	1.97×10^{-3}	1.91×10^{-3}	5.62×10^{-5}	1.74×10^{-3}	5.11×10^{-5}	9.92×10^{-1}	8.65×10^{-1}



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.00 \times 10^2\ M^{-1}$.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): $k_{2,C^-} = 1.95 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

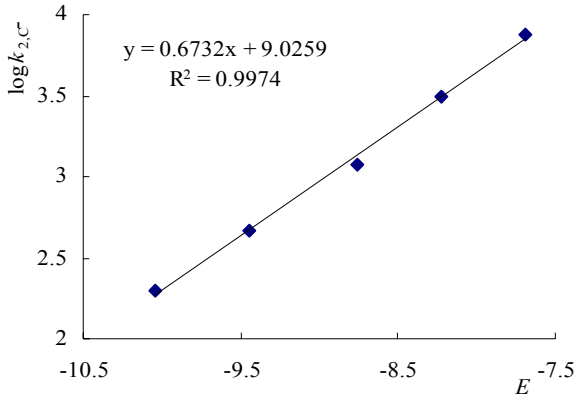
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.99×10^{-2}	7.87×10^{-4}	7.65×10^{-4}	2.21×10^{-5}	6.95×10^{-4}	2.01×10^{-5}	1.79×10^{-1}	1.55×10^{-1}
6.99×10^{-2}	1.18×10^{-3}	1.15×10^{-3}	3.33×10^{-5}	1.04×10^{-3}	3.03×10^{-5}	2.70×10^{-1}	2.35×10^{-1}
6.99×10^{-2}	1.57×10^{-3}	1.53×10^{-3}	4.47×10^{-5}	1.39×10^{-3}	4.06×10^{-5}	3.45×10^{-1}	2.97×10^{-1}
6.99×10^{-2}	1.97×10^{-3}	1.91×10^{-3}	5.62×10^{-5}	1.74×10^{-3}	5.11×10^{-5}	4.20×10^{-1}	3.61×10^{-1}



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.00×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.00 \times 10^2\ M^{-1}$.

4.2.2. Reactivity parameters: $N = 13.41$; $s = 0.67_3$

Reference electrophile			Rate constants	
	Name	E	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1a	$(pyr)_2CH^+$	-7.69	7.53×10^3	3.88
1b	$(thq)_2CH^+$	-8.22	3.11×10^3	3.49
1c	$(ind)_2CH^+$	-8.76	1.19×10^3	3.08
1d	$(jul)_2CH^+$	-9.45	4.60×10^2	2.66
1e	$(lil)_2CH^+$	-10.04	1.95×10^2	2.29

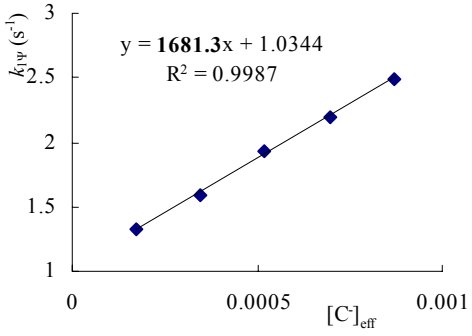


4.3. 2-Nitroprop-2-yl anion (2c)

4.3.1. Rate constants

Reaction with $(pyr)_2CH^+BF_4^-$ (1a): $k_{2,C^-} = 1.68 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 610 nm)

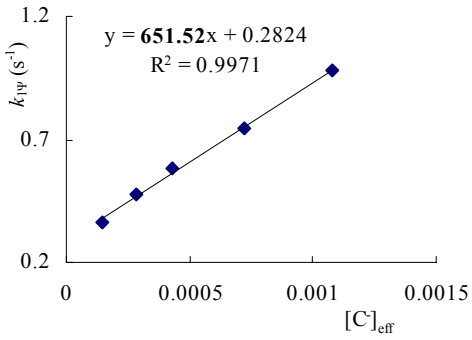
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
5.56×10^{-2}	1.91×10^{-4}	1.91×10^{-4}	6.42×10^{-7}	1.73×10^{-4}	5.83×10^{-7}	1.36	1.33
1.11×10^{-1}	3.83×10^{-4}	3.82×10^{-4}	6.43×10^{-7}	3.47×10^{-4}	5.84×10^{-7}	1.62	1.60
1.67×10^{-1}	5.74×10^{-4}	5.74×10^{-4}	6.43×10^{-7}	5.21×10^{-4}	5.85×10^{-7}	1.96	1.93
2.22×10^{-1}	7.66×10^{-4}	7.65×10^{-4}	6.43×10^{-7}	6.95×10^{-4}	5.85×10^{-7}	2.23	2.20
2.78×10^{-1}	9.57×10^{-4}	9.56×10^{-4}	6.43×10^{-7}	8.69×10^{-4}	5.85×10^{-7}	2.52	2.50



[a] Concentration of $(pyr)_2CH^+BF_4^-$ in reaction cell = 1.05×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.37 \times 10^3\ M^{-1}$.

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 6.52 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

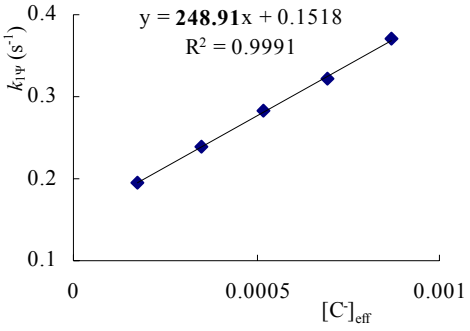
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
5.56×10^{-2}	1.58×10^{-4}	1.58×10^{-4}	5.31×10^{-7}	1.44×10^{-4}	4.83×10^{-7}	3.67×10^{-1}	3.60×10^{-1}
5.56×10^{-2}	3.17×10^{-4}	3.16×10^{-4}	1.06×10^{-6}	2.87×10^{-4}	9.68×10^{-7}	4.90×10^{-1}	4.75×10^{-1}
5.56×10^{-2}	4.75×10^{-4}	4.74×10^{-4}	1.60×10^{-6}	4.31×10^{-4}	1.46×10^{-6}	6.04×10^{-1}	5.82×10^{-1}
5.56×10^{-2}	7.92×10^{-4}	7.90×10^{-4}	2.68×10^{-6}	7.18×10^{-4}	2.44×10^{-6}	7.84×10^{-1}	7.46×10^{-1}
5.56×10^{-2}	1.19×10^{-3}	1.18×10^{-3}	4.06×10^{-6}	1.08×10^{-3}	3.69×10^{-6}	1.04	9.80×10^{-1}



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.37 \times 10^3\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 2.49 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

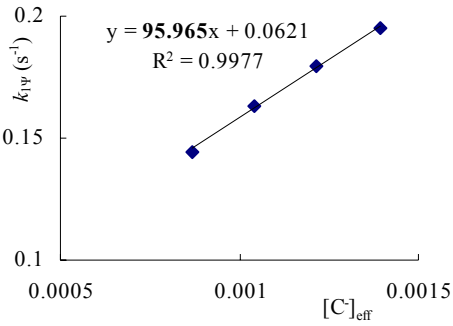
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
5.56×10^{-2}	1.91×10^{-4}	1.91×10^{-4}	6.42×10^{-7}	1.73×10^{-4}	5.83×10^{-7}	1.98×10^{-1}	1.94×10^{-1}
1.11×10^{-1}	3.83×10^{-4}	3.82×10^{-4}	6.43×10^{-7}	3.47×10^{-4}	5.84×10^{-7}	2.44×10^{-1}	2.40×10^{-1}
1.67×10^{-1}	5.74×10^{-4}	5.74×10^{-4}	6.43×10^{-7}	5.21×10^{-4}	5.85×10^{-7}	2.86×10^{-1}	2.82×10^{-1}
2.22×10^{-1}	7.66×10^{-4}	7.65×10^{-4}	6.43×10^{-7}	6.95×10^{-4}	5.85×10^{-7}	3.26×10^{-1}	3.22×10^{-1}
2.78×10^{-1}	9.57×10^{-4}	9.56×10^{-4}	6.43×10^{-7}	8.69×10^{-4}	5.85×10^{-7}	3.74×10^{-1}	3.70×10^{-1}



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.37 \times 10^3\ M^{-1}$.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): $k_{2,C^-} = 9.60 \times 10^1\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

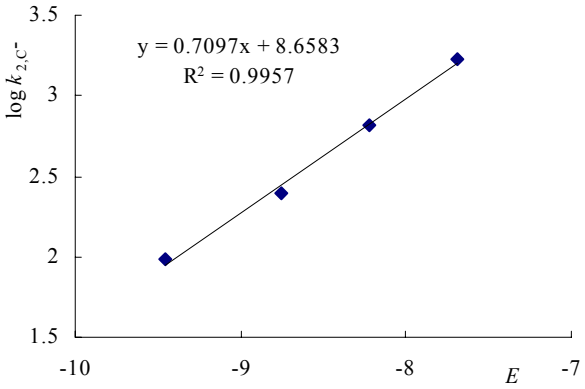
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
2.78×10^{-1}	9.57×10^{-4}	9.56×10^{-4}	6.43×10^{-7}	8.69×10^{-4}	5.85×10^{-7}	1.46×10^{-1}	1.45×10^{-1}
3.33×10^{-1}	1.15×10^{-3}	1.15×10^{-3}	6.43×10^{-7}	1.04×10^{-3}	5.85×10^{-7}	1.64×10^{-1}	1.63×10^{-1}
3.89×10^{-1}	1.34×10^{-3}	1.34×10^{-3}	6.43×10^{-7}	1.22×10^{-3}	5.85×10^{-7}	1.81×10^{-1}	1.80×10^{-1}
4.44×10^{-1}	1.53×10^{-3}	1.53×10^{-3}	6.43×10^{-7}	1.39×10^{-3}	5.85×10^{-7}	1.96×10^{-1}	1.95×10^{-1}



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.02×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 5.37 \times 10^3\ M^{-1}$.

4.3.2. Reactivity parameters: *N* = 12.20; *s* = 0.71

Reference electrophile			Rate constants	
	Name	*E*	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1a	$(pyr)_2CH^+$	-7.69	1.68×10^3	3.23
1b	$(thq)_2CH^+$	-8.22	6.52×10^2	2.81
1c	$(ind)_2CH^+$	-8.76	2.49×10^2	2.40
1d	$(jul)_2CH^+$	-9.45	9.60×10^1	1.98

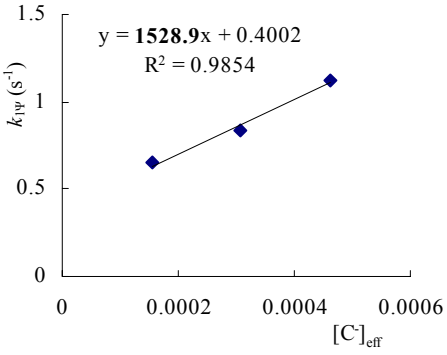


4.4. Phenylnitromethyl anion (2d)

4.4.1. Rate constants

Reaction with $(pyr)_2CH^+BF_4^-$ (1a): $k_{2,C^-} = 1.53 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 610 nm)

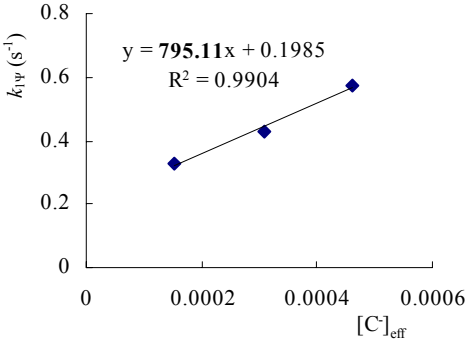
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.38×10^{-2}	1.69×10^{-4}	1.69×10^{-4}	1.72×10^{-7}	1.54×10^{-4}	1.57×10^{-7}	6.59×10^{-1}	6.52×10^{-1}
8.76×10^{-2}	3.39×10^{-4}	3.39×10^{-4}	1.73×10^{-7}	3.08×10^{-4}	1.57×10^{-7}	8.45×10^{-1}	8.38×10^{-1}
1.31×10^{-1}	5.08×10^{-4}	5.08×10^{-4}	1.73×10^{-7}	4.62×10^{-4}	1.57×10^{-7}	1.13	1.12



[a] Concentration of $(pyr)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 2.25 \times 10^4\ M^{-1}$.

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 7.95 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

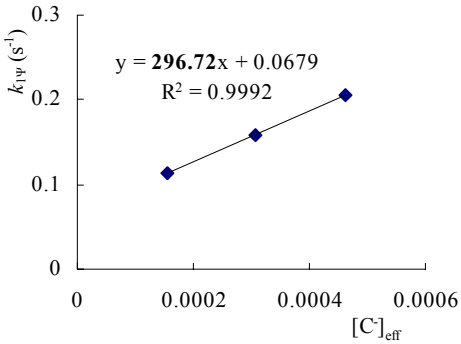
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.38×10^{-2}	1.69×10^{-4}	1.69×10^{-4}	1.72×10^{-7}	1.54×10^{-4}	1.57×10^{-7}	3.30×10^{-1}	3.28×10^{-1}
8.76×10^{-2}	3.39×10^{-4}	3.39×10^{-4}	1.73×10^{-7}	3.08×10^{-4}	1.57×10^{-7}	4.32×10^{-1}	4.29×10^{-1}
1.31×10^{-1}	5.08×10^{-4}	5.08×10^{-4}	1.73×10^{-7}	4.62×10^{-4}	1.57×10^{-7}	5.75×10^{-1}	5.73×10^{-1}



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 2.25 \times 10^4\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 2.97 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

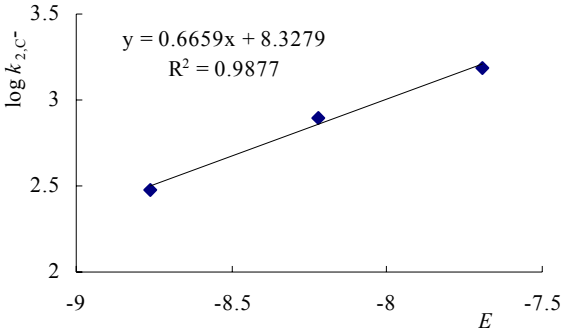
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.38×10^{-2}	1.69×10^{-4}	1.69×10^{-4}	1.72×10^{-7}	1.54×10^{-4}	1.57×10^{-7}	1.15×10^{-1}	1.14×10^{-1}
8.76×10^{-2}	3.39×10^{-4}	3.39×10^{-4}	1.73×10^{-7}	3.08×10^{-4}	1.57×10^{-7}	1.59×10^{-1}	1.58×10^{-1}
1.31×10^{-1}	5.08×10^{-4}	5.08×10^{-4}	1.73×10^{-7}	4.62×10^{-4}	1.57×10^{-7}	2.07×10^{-1}	2.06×10^{-1}



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 2.25 \times 10^4\ M^{-1}$.

4.4.2. Reactivity parameters: $N = 12.51$; $s = 0.66_6$

Reference electrophile			Rate constants	
	Name	E	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1a	$(pyr)_2CH^+$	-7.69	1.53×10^3	3.18
1b	$(thq)_2CH^+$	-8.22	7.95×10^2	2.90
1c	$(ind)_2CH^+$	-8.76	2.97×10^2	2.47

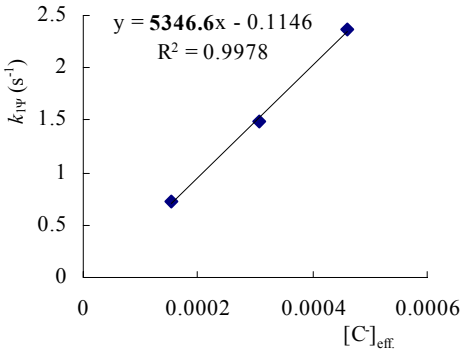


4.5. (*p*-Tolyl)nitromethyl anion (2e)

4.5.1. Rate constants

Reaction with $(pyr)_2CH^+BF_4^-$ (1a): $k_{2,C^-} = 5.35 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 610 nm)

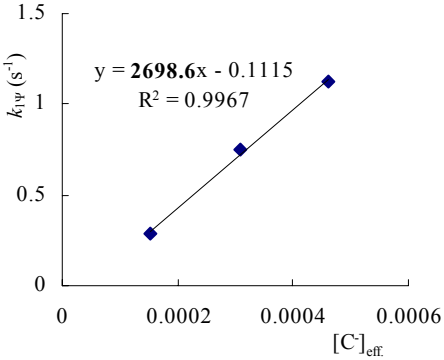
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.23×10^{-2}	1.69×10^{-4}	1.69×10^{-4}	3.22×10^{-7}	1.54×10^{-4}	2.92×10^{-7}	7.43×10^{-1}	7.29×10^{-1}
1.25×10^{-1}	3.39×10^{-4}	3.38×10^{-4}	3.21×10^{-7}	3.08×10^{-4}	2.92×10^{-7}	1.50	1.49
1.87×10^{-1}	5.08×10^{-4}	5.08×10^{-4}	3.22×10^{-7}	4.62×10^{-4}	2.93×10^{-7}	2.39	2.38



[a] Concentration of $(pyr)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 8.46 \times 10^3\ M^{-1}$.

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 2.70 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

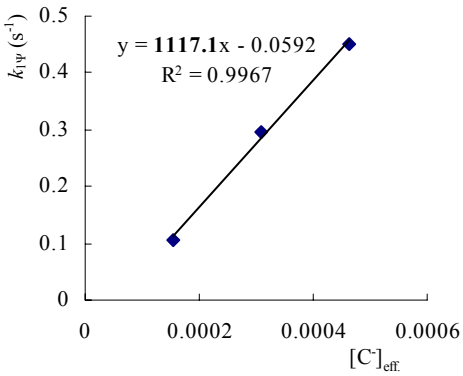
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.23×10^{-2}	1.69×10^{-4}	1.69×10^{-4}	3.22×10^{-7}	1.54×10^{-4}	2.92×10^{-7}	2.94×10^{-1}	2.89×10^{-1}
1.25×10^{-1}	3.39×10^{-4}	3.38×10^{-4}	3.21×10^{-7}	3.08×10^{-4}	2.92×10^{-7}	7.51×10^{-1}	7.46×10^{-1}
1.87×10^{-1}	5.08×10^{-4}	5.08×10^{-4}	3.22×10^{-7}	4.62×10^{-4}	2.93×10^{-7}	1.13	1.12



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 8.46 \times 10^3\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 1.12 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

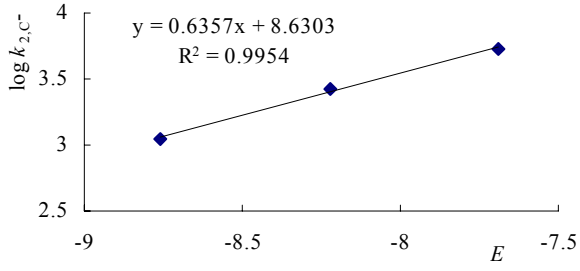
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.23×10^{-2}	1.69×10^{-4}	1.69×10^{-4}	3.22×10^{-7}	1.54×10^{-4}	2.92×10^{-7}	1.09×10^{-1}	1.07×10^{-1}
1.25×10^{-1}	3.39×10^{-4}	3.38×10^{-4}	3.21×10^{-7}	3.08×10^{-4}	2.92×10^{-7}	2.98×10^{-1}	2.96×10^{-1}
1.87×10^{-1}	5.08×10^{-4}	5.08×10^{-4}	3.22×10^{-7}	4.62×10^{-4}	2.93×10^{-7}	4.53×10^{-1}	4.51×10^{-1}



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = = 8.46 \times 10^3\ M^{-1}$.

4.5.2. Reactivity parameters: *N* = 13.58; *s* = 0.636

Reference electrophile			Rate constants	
	Name	*E*	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1a	$(pyr)_2CH^+$	-7.69	5.35×10^3	3.73
1b	$(thq)_2CH^+$	-8.22	2.70×10^3	3.43
1c	$(ind)_2CH^+$	-8.76	1.12×10^3	3.05

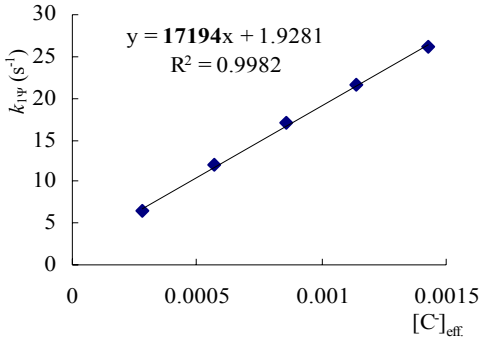


4.6. (*p*-Nitrophenyl)nitromethyl anion (2f)

4.6.1. Rate constants

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 1.72 \times 10^4\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

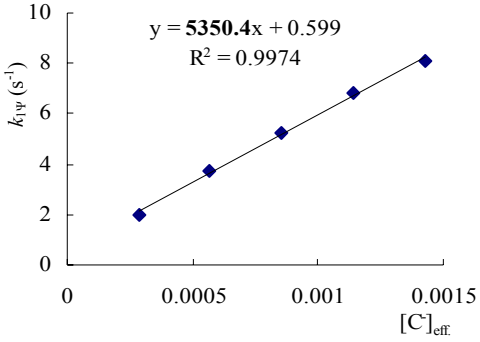
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.37×10^{-4}	3.14×10^{-4}	3.13×10^{-4}	9.59×10^{-7}	2.84×10^{-4}	8.72×10^{-7}	6.45	6.44
8.73×10^{-4}	6.27×10^{-4}	6.26×10^{-4}	9.64×10^{-7}	5.69×10^{-4}	8.76×10^{-7}	1.20×10^1	1.20×10^1
1.31×10^{-3}	9.41×10^{-4}	9.40×10^{-4}	9.66×10^{-7}	8.54×10^{-4}	8.78×10^{-7}	1.69×10^1	1.69×10^1
1.75×10^{-3}	1.25×10^{-3}	1.25×10^{-3}	9.67×10^{-7}	1.14×10^{-4}	8.79×10^{-7}	2.17×10^1	2.17×10^1
2.18×10^{-3}	1.57×10^{-3}	1.57×10^{-3}	9.67×10^{-7}	1.42×10^{-4}	8.79×10^{-7}	2.61×10^1	2.61×10^1



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.02×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = = 2.63 \times 10^6\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 5.35 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

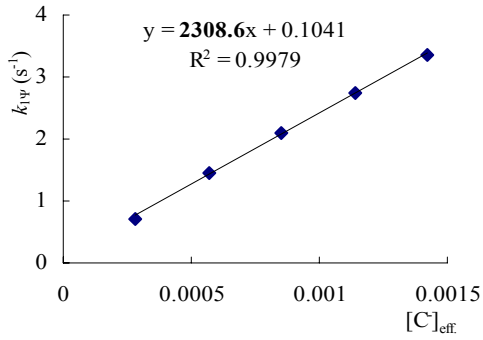
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.37×10^{-4}	3.14×10^{-4}	3.13×10^{-4}	9.59×10^{-7}	2.84×10^{-4}	8.72×10^{-7}	2.00	1.99
8.73×10^{-4}	6.27×10^{-4}	6.26×10^{-4}	9.64×10^{-7}	5.69×10^{-4}	8.76×10^{-7}	3.74	3.73
1.31×10^{-3}	9.41×10^{-4}	9.40×10^{-4}	9.66×10^{-7}	8.54×10^{-4}	8.78×10^{-7}	5.25	5.24
1.75×10^{-3}	1.25×10^{-3}	1.25×10^{-3}	9.67×10^{-7}	1.14×10^{-4}	8.79×10^{-7}	6.81	6.81
2.18×10^{-3}	1.57×10^{-3}	1.57×10^{-3}	9.67×10^{-7}	1.42×10^{-4}	8.79×10^{-7}	8.09	8.08



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = = 2.63 \times 10^6\ M^{-1}$.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): $k_{2,C^-} = 2.31 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

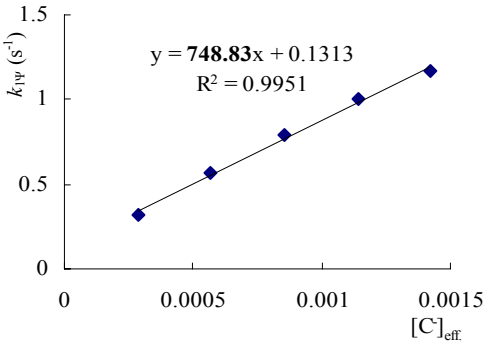
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.37×10^{-4}	3.14×10^{-4}	3.13×10^{-4}	9.59×10^{-7}	2.84×10^{-4}	8.72×10^{-7}	7.04×10^{-1}	7.02×10^{-1}
8.73×10^{-4}	6.27×10^{-4}	6.26×10^{-4}	9.64×10^{-7}	5.69×10^{-4}	8.76×10^{-7}	1.47	1.47
1.31×10^{-3}	9.41×10^{-4}	9.40×10^{-4}	9.66×10^{-7}	8.54×10^{-4}	8.78×10^{-7}	2.12	2.11
1.75×10^{-3}	1.25×10^{-3}	1.25×10^{-3}	9.67×10^{-7}	1.14×10^{-4}	8.79×10^{-7}	2.75	2.75
2.18×10^{-3}	1.57×10^{-3}	1.57×10^{-3}	9.67×10^{-7}	1.42×10^{-4}	8.79×10^{-7}	3.35	3.35



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = = 2.63 \times 10^6\ M^{-1}$.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): $k_{2,C^-} = 7.49 \times 10^2\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

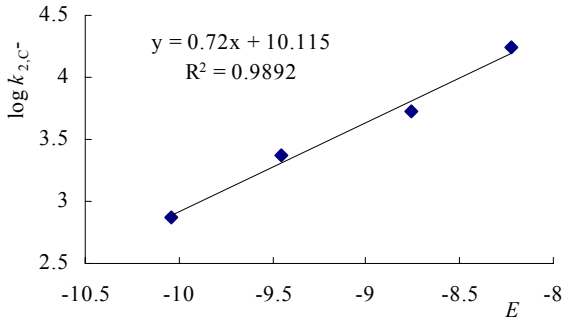
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.37×10^{-4}	3.14×10^{-4}	3.13×10^{-4}	9.59×10^{-7}	2.84×10^{-4}	8.72×10^{-7}	3.20×10^{-1}	3.19×10^{-1}
8.73×10^{-4}	6.27×10^{-4}	6.26×10^{-4}	9.64×10^{-7}	5.69×10^{-4}	8.76×10^{-7}	5.72×10^{-1}	5.71×10^{-1}
1.31×10^{-3}	9.41×10^{-4}	9.40×10^{-4}	9.66×10^{-7}	8.54×10^{-4}	8.78×10^{-7}	7.95×10^{-1}	7.94×10^{-1}
1.75×10^{-3}	1.25×10^{-3}	1.25×10^{-3}	9.67×10^{-7}	1.14×10^{-4}	8.79×10^{-7}	1.00	1.00
2.18×10^{-3}	1.57×10^{-3}	1.57×10^{-3}	9.67×10^{-7}	1.42×10^{-4}	8.79×10^{-7}	1.17	1.17



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.00×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 2.63 \times 10^6\ M^{-1}$.

4.6.2. Reactivity parameters: N = 14.05; s = 0.72

Reference electrophile			Rate constants	
	Name	E	$k_{2,C}$- ($M^{-1}s^{-1}$)	log $k_{2,C}$-
1b	$(thq)_2CH^+$	-8.22	1.72×10^4	4.24
1c	$(ind)_2CH^+$	-8.76	5.35×10^3	3.73
1d	$(jul)_2CH^+$	-9.45	2.31×10^3	3.36
1e	$(lil)_2CH^+$	-10.04	7.49×10^3	2.87

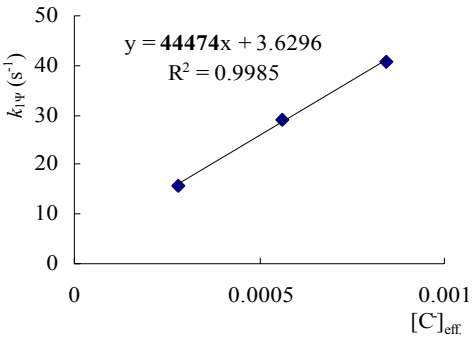


4.7. (*m*-Nitrophenyl)nitromethyl anion (2g)

4.7.1. Rate constants

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C}$- = 4.45×10^4 $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

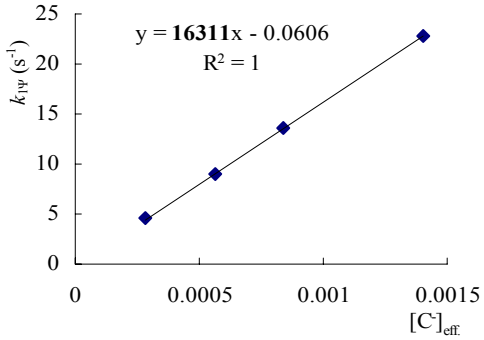
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.40×10^{-4}	3.10×10^{-4}	3.07×10^{-4}	2.21×10^{-6}	2.79×10^{-4}	2.01×10^{-6}	1.58×10^1	1.58×10^1
8.80×10^{-4}	6.19×10^{-4}	6.17×10^{-4}	2.24×10^{-6}	5.61×10^{-4}	2.03×10^{-6}	2.92×10^1	2.91×10^1
1.32×10^{-3}	9.29×10^{-4}	9.26×10^{-4}	2.25×10^{-6}	8.42×10^{-4}	2.04×10^{-6}	4.08×10^1	4.08×10^1



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.02×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 1.05×10^6 M^{-1}.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C}$- =1.63×10^4 $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

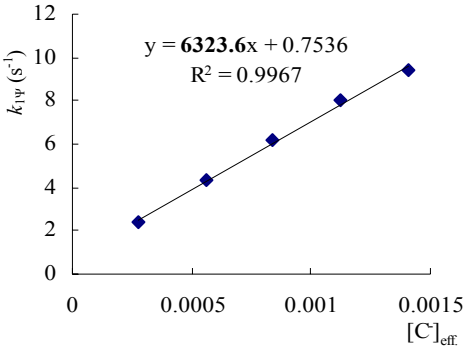
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.40×10^{-4}	3.10×10^{-4}	3.07×10^{-4}	2.21×10^{-6}	2.79×10^{-4}	2.01×10^{-6}	4.57	4.55
8.80×10^{-4}	6.19×10^{-4}	6.17×10^{-4}	2.24×10^{-6}	5.61×10^{-4}	2.03×10^{-6}	9.05	9.04
1.32×10^{-3}	9.29×10^{-4}	9.26×10^{-4}	2.25×10^{-6}	8.42×10^{-4}	2.04×10^{-6}	1.37×10^1	1.36×10^1
2.20×10^{-3}	1.55×10^{-3}	1.55×10^{-3}	2.25×10^{-6}	1.40×10^{-4}	2.05×10^{-6}	2.29×10^1	2.29×10^1



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 1.05×10^6 M^{-1}.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): $k_{2,C^-} = 6.32 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

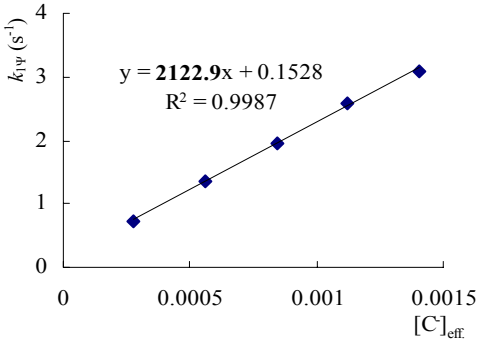
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.40×10^{-4}	3.10×10^{-4}	3.07×10^{-4}	2.21×10^{-6}	2.79×10^{-4}	2.01×10^{-6}	2.37	2.36
8.80×10^{-4}	6.19×10^{-4}	6.17×10^{-4}	2.24×10^{-6}	5.61×10^{-4}	2.03×10^{-6}	4.38	4.38
1.32×10^{-3}	9.29×10^{-4}	9.26×10^{-4}	2.25×10^{-6}	8.42×10^{-4}	2.04×10^{-6}	6.21	6.20
1.76×10^{-3}	1.24×10^{-3}	1.24×10^{-3}	2.25×10^{-6}	1.12×10^{-4}	2.05×10^{-6}	8.01	8.00
2.20×10^{-3}	1.55×10^{-3}	1.55×10^{-3}	2.25×10^{-6}	1.40×10^{-4}	2.05×10^{-6}	9.45	9.44



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 1.05 \times 10^6\ M^{-1}$.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): $k_{2,C^-} = 2.12 \times 10^3\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

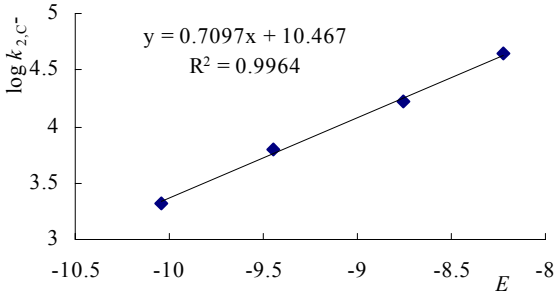
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.40×10^{-4}	3.10×10^{-4}	3.07×10^{-4}	2.21×10^{-6}	2.79×10^{-4}	2.01×10^{-6}	7.28×10^{-1}	7.26×10^{-1}
8.80×10^{-4}	6.19×10^{-4}	6.17×10^{-4}	2.24×10^{-6}	5.61×10^{-4}	2.03×10^{-6}	1.35	1.35
1.32×10^{-3}	9.29×10^{-4}	9.26×10^{-4}	2.25×10^{-6}	8.42×10^{-4}	2.04×10^{-6}	1.95	1.95
1.76×10^{-3}	1.24×10^{-3}	1.24×10^{-3}	2.25×10^{-6}	1.12×10^{-4}	2.05×10^{-6}	2.59	2.58
2.20×10^{-3}	1.55×10^{-3}	1.55×10^{-3}	2.25×10^{-6}	1.40×10^{-4}	2.05×10^{-6}	3.10	3.09



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.00×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 1.05 \times 10^6\ M^{-1}$.

4.7.2. Reactivity parameters: $N = 14.75$; $s = 0.71$

Reference electrophile			Rate constants	
	Name	E	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1b	$(thq)_2CH^+$	-8.22	4.45×10^4	4.65
1c	$(ind)_2CH^+$	-8.76	1.63×10^4	4.21
1d	$(jul)_2CH^+$	-9.45	6.32×10^3	3.80
1e	$(lil)_2CH^+$	-10.04	2.12×10^3	3.33



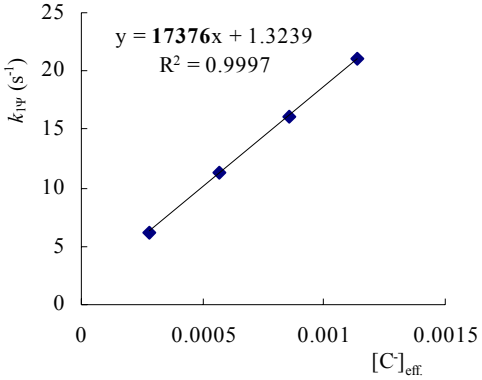
4.8. (*p*-Cyanophenyl)nitromethyl anion (2h)

4.8.1. Rate constants

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 1.74 \times 10^4\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
2.04×10^{-3}	3.14×10^{-4}	3.12×10^{-4}	1.88×10^{-6}	2.84×10^{-4}	1.71×10^{-6}	6.19	6.16
4.08×10^{-3}	6.28×10^{-4}	6.26×10^{-4}	1.89×10^{-6}	5.69×10^{-4}	1.72×10^{-6}	1.14×10^{1}	1.14×10^{1}
6.12×10^{-3}	9.42×10^{-4}	9.40×10^{-4}	1.89×10^{-6}	8.55×10^{-4}	1.72×10^{-6}	1.62×10^{1}	1.61×10^{1}
8.16×10^{-3}	1.26×10^{-3}	1.25×10^{-3}	1.89×10^{-6}	1.14×10^{-3}	1.72×10^{-6}	2.11×10^{1}	2.11×10^{1}

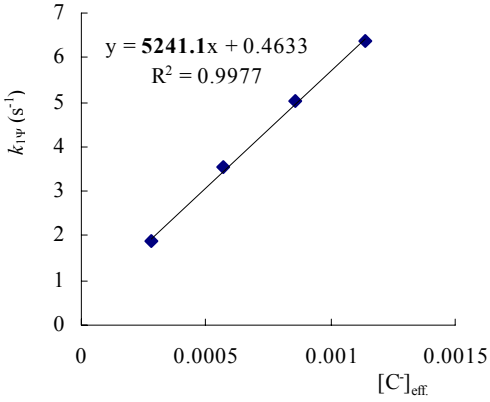


[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 9.60 \times 10^4\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 5.24 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
2.04×10^{-3}	3.14×10^{-4}	3.12×10^{-4}	1.88×10^{-6}	2.84×10^{-4}	1.71×10^{-6}	1.88	1.87
4.08×10^{-3}	6.28×10^{-4}	6.26×10^{-4}	1.89×10^{-6}	5.69×10^{-4}	1.72×10^{-6}	3.54	3.53
6.12×10^{-3}	9.42×10^{-4}	9.40×10^{-4}	1.89×10^{-6}	8.55×10^{-4}	1.72×10^{-6}	5.03	5.02
8.16×10^{-3}	1.26×10^{-3}	1.25×10^{-3}	1.89×10^{-6}	1.14×10^{-3}	1.72×10^{-6}	6.37	6.36

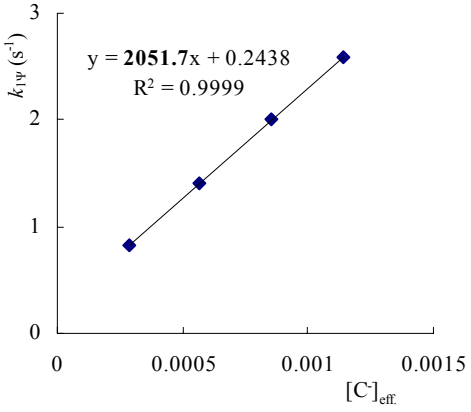


[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 9.60 \times 10^4\ M^{-1}$.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): $k_{2,C^-} = 2.05 \times 10^3\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
2.04×10^{-3}	3.14×10^{-4}	3.12×10^{-4}	1.88×10^{-6}	2.84×10^{-4}	1.71×10^{-6}	8.32×10^{-1}	8.28×10^{-1}
4.08×10^{-3}	6.28×10^{-4}	6.26×10^{-4}	1.89×10^{-6}	5.69×10^{-4}	1.72×10^{-6}	1.41	1.40
6.12×10^{-3}	9.42×10^{-4}	9.40×10^{-4}	1.89×10^{-6}	8.55×10^{-4}	1.72×10^{-6}	2.01	2.01
8.16×10^{-3}	1.26×10^{-3}	1.25×10^{-3}	1.89×10^{-6}	1.14×10^{-3}	1.72×10^{-6}	2.58	2.58

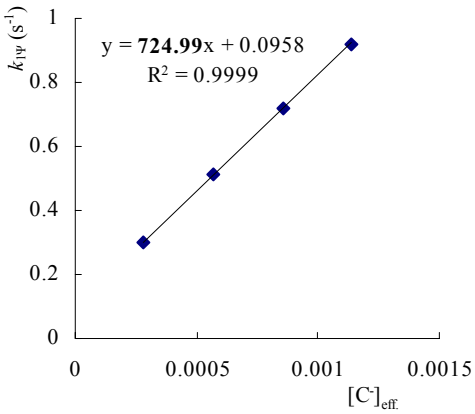


[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.02×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 9.60 \times 10^4\ M^{-1}$.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): $k_{2,C^-} = 7.25 \times 10^2\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

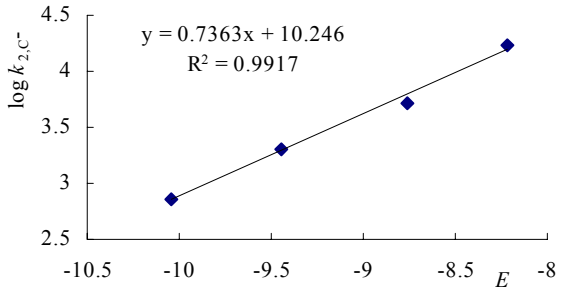
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
2.04×10^{-3}	3.14×10^{-4}	3.12×10^{-4}	1.88×10^{-6}	2.84×10^{-4}	1.71×10^{-6}	3.01×10^{-1}	2.99×10^{-1}
4.08×10^{-3}	6.28×10^{-4}	6.26×10^{-4}	1.89×10^{-6}	5.69×10^{-4}	1.72×10^{-6}	5.13×10^{-1}	5.11×10^{-1}
6.12×10^{-3}	9.42×10^{-4}	9.40×10^{-4}	1.89×10^{-6}	8.55×10^{-4}	1.72×10^{-6}	7.20×10^{-1}	7.18×10^{-1}
8.16×10^{-3}	1.26×10^{-3}	1.25×10^{-3}	1.89×10^{-6}	1.14×10^{-3}	1.72×10^{-6}	9.22×10^{-1}	9.20×10^{-1}



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.02×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 9.60 \times 10^4\ M^{-1}$.

4.8.2. Reactivity parameters: $N = 13.92$; $s = 0.73_6$

Reference electrophile			Rate constants	
	Name	E	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1b	$(thq)_2CH^+$	-8.22	1.74×10^4	4.24
1c	$(ind)_2CH^+$	-8.76	5.24×10^3	3.72
1d	$(jul)_2CH^+$	-9.45	2.05×10^3	3.31
1e	$(lil)_2CH^+$	-10.04	7.25×10^2	2.86



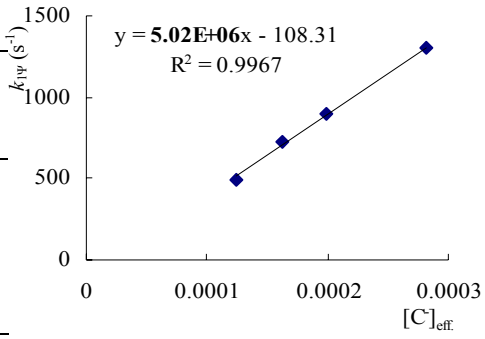
4.9. Ethyl cyanoacetate anion (2i)

4.9.1. Rate constants

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 5.02 \times 10^6\ M^{-1}s^{-1}$

(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

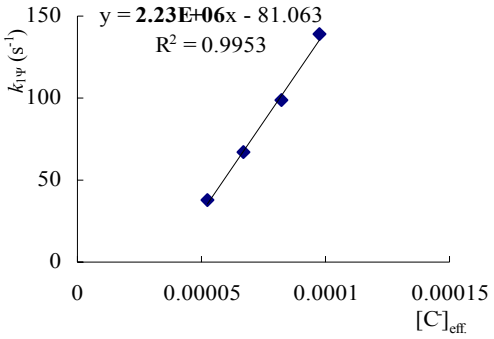
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
1.41×10^{-1}	1.78×10^{-4}	1.38×10^{-4}	4.08×10^{-5}	1.25×10^{-4}	3.71×10^{-5}	4.98×10^2	4.98×10^2
1.69×10^{-1}	2.23×10^{-4}	1.79×10^{-4}	4.42×10^{-5}	1.63×10^{-4}	4.02×10^{-5}	7.30×10^2	7.29×10^2
1.87×10^{-1}	2.68×10^{-4}	2.19×10^{-4}	4.87×10^{-5}	1.99×10^{-4}	4.43×10^{-5}	9.00×10^2	8.99×10^2
2.81×10^{-1}	3.57×10^{-4}	3.11×10^{-4}	4.61×10^{-5}	2.83×10^{-4}	4.19×10^{-5}	1.30×10^3	1.30×10^3



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 5.00×10^{-6} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 2.40 \times 10^1\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): k_{2,C^-} =2.23 × 10⁶ $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

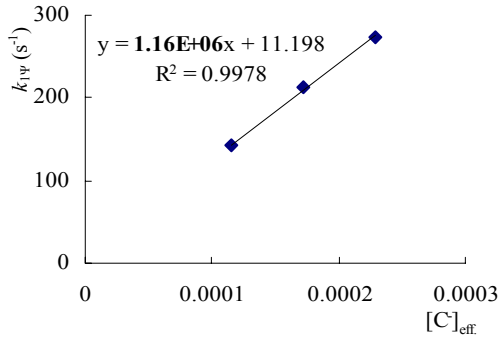
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
7.03×10^{-2}	9.18×10^{-5}	5.76×10^{-5}	3.42×10^{-5}	5.24×10^{-5}	3.11×10^{-5}	3.81×10^{1}	3.78×10^{1}
8.43×10^{-2}	1.10×10^{-4}	7.37×10^{-5}	3.65×10^{-5}	6.70×10^{-5}	3.31×10^{-5}	6.68×10^{1}	6.65×10^{1}
9.84×10^{-2}	1.29×10^{-4}	9.03×10^{-5}	3.83×10^{-5}	8.21×10^{-5}	3.48×10^{-5}	9.86×10^{1}	9.84×10^{1}
1.12×10^{-1}	1.47×10^{-4}	1.07×10^{-4}	3.97×10^{-5}	9.74×10^{-5}	3.61×10^{-5}	1.39×10^{2}	1.39×10^{2}



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 5.00 × 10^{-6} M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 2.40 × 10^1 M^{-1}.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): k_{2,C^-} = 1.16 × 10⁶ $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

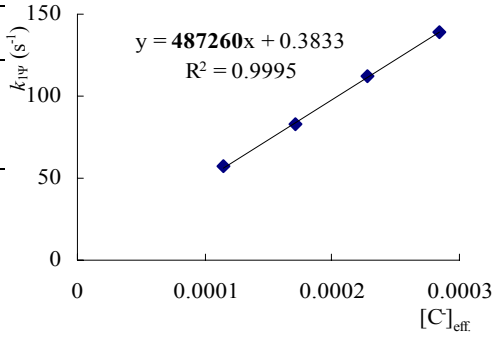
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
2.81×10^{-2}	3.13×10^{-4}	1.26×10^{-4}	1.87×10^{-4}	1.14×10^{-4}	1.70×10^{-4}	1.43×10^{2}	1.42×10^{2}
2.81×10^{-2}	4.70×10^{-4}	1.89×10^{-4}	2.81×10^{-4}	1.71×10^{-4}	2.56×10^{-4}	2.14×10^{2}	2.14×10^{2}
2.81×10^{-2}	6.27×10^{-4}	2.51×10^{-4}	3.76×10^{-4}	2.28×10^{-4}	3.41×10^{-4}	2.75×10^{2}	2.74×10^{2}



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.01 × 10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 2.40 × 10^1 M^{-1}.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): k_{2,C^-} = 4.87 × 10⁵ $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

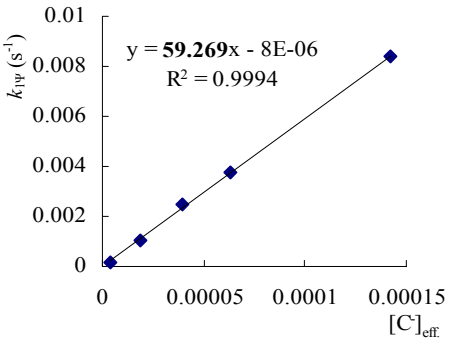
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
2.81×10^{-2}	3.13×10^{-4}	1.26×10^{-4}	1.87×10^{-4}	1.14×10^{-4}	1.70×10^{-4}	5.70×10^{1}	5.68×10^{1}
2.81×10^{-2}	4.70×10^{-4}	1.89×10^{-4}	2.81×10^{-4}	1.71×10^{-4}	2.56×10^{-4}	8.31×10^{1}	8.28×10^{1}
2.81×10^{-2}	6.27×10^{-4}	2.51×10^{-4}	3.76×10^{-4}	2.28×10^{-4}	3.41×10^{-4}	1.12×10^{2}	1.12×10^{2}
2.81×10^{-2}	7.84×10^{-4}	3.14×10^{-4}	4.70×10^{-4}	2.85×10^{-4}	4.27×10^{-4}	1.40×10^{2}	1.39×10^{2}



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.00 × 10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 2.40 × 10^1 M^{-1}.

Reaction with tolQM (1f): k_{2,C^-} = 5.93 × 10¹ $M^{-1}s^{-1}$
(at 20 °C, in MeOH; J&M, detection at 365 nm)

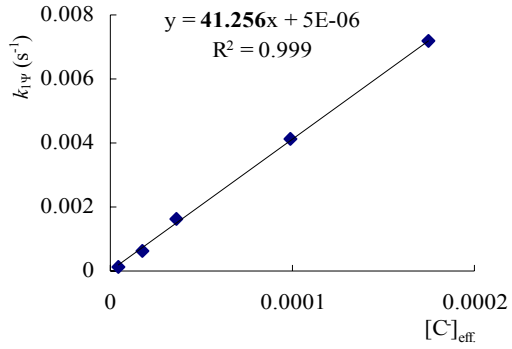
Concentrations[a] (M)			Rates	
$[C^-]_o$	$[C^-]_{eff}$	$[MeO^-]_{eff}$	k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
4.31×10^{-4}	4.39E-06	4.27×10^{-4}	4.25×10^{-4}	1.64×10^{-4}
9.00×10^{-4}	1.86E-05	8.81×10^{-4}	1.61×10^{-3}	1.07×10^{-3}
1.32×10^{-3}	3.94E-05	1.28×10^{-3}	3.23×10^{-3}	2.45×10^{-3}
1.69×10^{-3}	6.34E-05	1.62×10^{-3}	4.77×10^{-3}	3.78×10^{-3}
2.58×10^{-3}	1.43×10^{-4}	2.44×10^{-3}	9.89×10^{-3}	8.40×10^{-3}



[a] Concentration of tolQM in reaction cell = 1.00 × 10^{-5} M; $[C^-]_{eff}$ and $[MeO^-]_{eff}$ were calculated based on K_{CH} = 2.40 × 10^1 M^{-1}.

Reaction with aniQM (1g): $k_{2,C^-} = 4.13 \times 10^1\ M^{-1}s^{-1}$
(at 20 °C, in MeOH; J&M, detection at 385 nm)

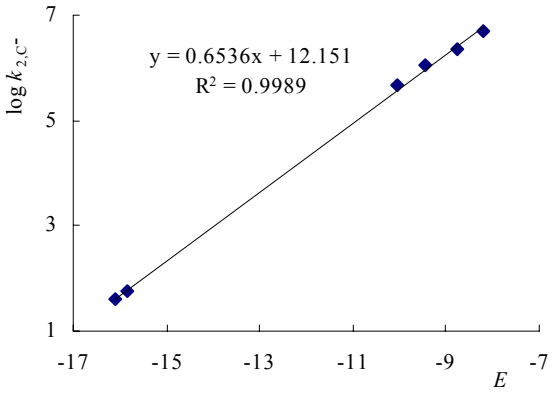
Concentrations[a] (M)			Rates	
$[C^-]_o$	$[C^-]_{eff}$	$[MeO^-]_{eff}$	k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
4.10×10^{-4}	3.98×10^{-6}	4.06×10^{-4}	3.26×10^{-4}	1.25×10^{-4}
8.69×10^{-4}	1.74×10^{-5}	8.52×10^{-4}	1.05×10^{-3}	6.27×10^{-4}
1.27×10^{-3}	3.65×10^{-5}	1.23×10^{-3}	2.26×10^{-3}	1.65×10^{-3}
2.13×10^{-3}	9.93×10^{-5}	2.03×10^{-3}	5.16×10^{-3}	4.15×10^{-3}
2.87×10^{-3}	1.75×10^{-4}	2.70×10^{-3}	8.50×10^{-3}	7.16×10^{-3}



[a] Concentration of aniQM in reaction cell = 1.00×10^{-5} M; $[C^-]_{eff}$ and $[MeO^-]_{eff}$ were calculated based on $K_{CH} = 2.40 \times 10^1\ M^{-1}$.

4.9.2. Reactivity parameters: *N* = 18.59; *s* = 0.654

Reference electrophile			Rate constants	
	Name	*E*	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1b	$(thq)_2CH^+$	-8.22	5.02×10^6	6.70
1c	$(ind)_2CH^+$	-8.76	2.23×10^6	6.35
1d	$(jul)_2CH^+$	-9.45	1.16×10^6	6.06
1e	$(lil)_2CH^+$	-10.04	4.87×10^5	5.69
1f	$tol(tBu)_2QM$	-15.83	5.90×10^1	1.77
1g	$ani(tBu)_2QM$	-16.11	4.20×10^1	1.62

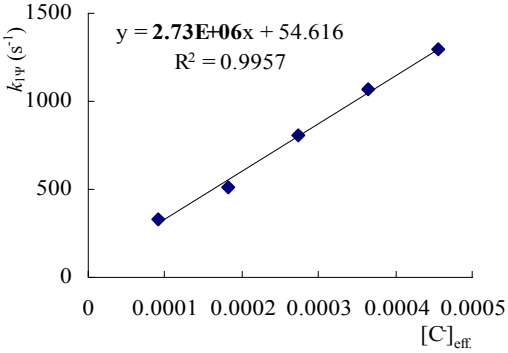


4.10. Dimethyl malonate anion (2j)

4.10.1. Rate constants

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 2.73 \times 10^6\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

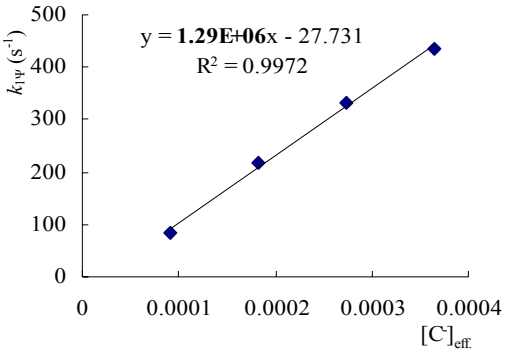
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
8.71×10^{-1}	3.57×10^{-4}	1.01×10^{-4}	2.56×10^{-4}	9.14×10^{-5}	2.33×10^{-4}	3.33×10^2	3.29×10^2
8.71×10^{-1}	7.14×10^{-4}	2.01×10^{-4}	5.13×10^{-4}	1.83×10^{-4}	4.66×10^{-4}	5.18×10^2	5.11×10^2
8.71×10^{-1}	1.07×10^{-3}	3.01×10^{-4}	7.69×10^{-4}	2.74×10^{-4}	6.99×10^{-4}	8.16×10^2	8.05×10^2
8.71×10^{-1}	1.43×10^{-3}	4.02×10^{-4}	1.03×10^{-3}	3.65×10^{-4}	9.32×10^{-4}	1.08×10^3	1.07×10^3
8.71×10^{-1}	1.78×10^{-3}	5.02×10^{-4}	1.28×10^{-3}	4.57×10^{-4}	1.17×10^{-3}	1.31×10^3	1.30×10^3



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 5.00×10^{-6} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 4.50 \times 10^{-1}\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): k_{2,C^-} =1.29 × 10⁶ $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

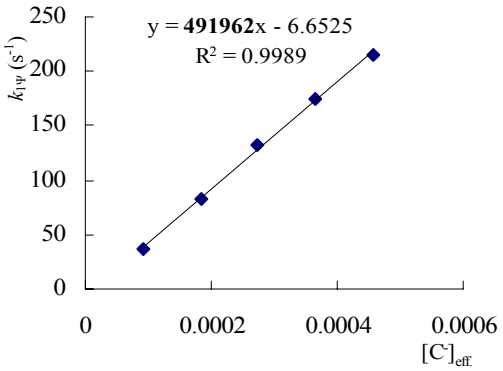
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
8.71×10^{-1}	3.57×10^{-4}	1.01×10^{-4}	2.56×10^{-4}	9.14×10^{-5}	2.33×10^{-4}	8.43×10^{1}	8.26×10^{1}
8.71×10^{-1}	7.14×10^{-4}	2.01×10^{-4}	5.13×10^{-4}	1.83×10^{-4}	4.66×10^{-4}	2.20×10^{2}	2.16×10^{2}
8.71×10^{-1}	1.07×10^{-3}	3.01×10^{-4}	7.69×10^{-4}	2.74×10^{-4}	6.99×10^{-4}	3.36×10^{2}	3.31×10^{2}
8.71×10^{-1}	1.43×10^{-3}	4.02×10^{-4}	1.03×10^{-3}	3.65×10^{-4}	9.32×10^{-4}	4.44×10^{2}	4.37×10^{2}



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 5.00 × 10⁻⁶ M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 4.50 × 10⁻¹ M^{-1}.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): k_{2,C^-} = 4.92 × 10⁵ $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

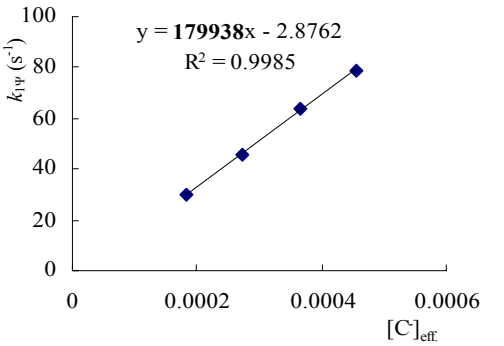
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
8.71×10^{-1}	3.57×10^{-4}	1.01×10^{-4}	2.56×10^{-4}	9.14×10^{-5}	2.33×10^{-4}	3.72×10^{1}	3.66×10^{1}
8.71×10^{-1}	7.14×10^{-4}	2.01×10^{-4}	5.13×10^{-4}	1.83×10^{-4}	4.66×10^{-4}	8.40×10^{1}	8.28×10^{1}
8.71×10^{-1}	1.07×10^{-3}	3.01×10^{-4}	7.69×10^{-4}	2.74×10^{-4}	6.99×10^{-4}	1.33×10^{2}	1.32×10^{2}
8.71×10^{-1}	1.43×10^{-3}	4.02×10^{-4}	1.03×10^{-3}	3.65×10^{-4}	9.32×10^{-4}	1.77×10^{2}	1.74×10^{2}
8.71×10^{-1}	1.78×10^{-3}	5.02×10^{-4}	1.28×10^{-3}	4.57×10^{-4}	1.17×10^{-3}	2.18×10^{2}	2.15×10^{2}



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.01 × 10⁻⁵ M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 4.50 × 10⁻¹ M^{-1}.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): k_{2,C^-} = 1.80 × 10⁵ $M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

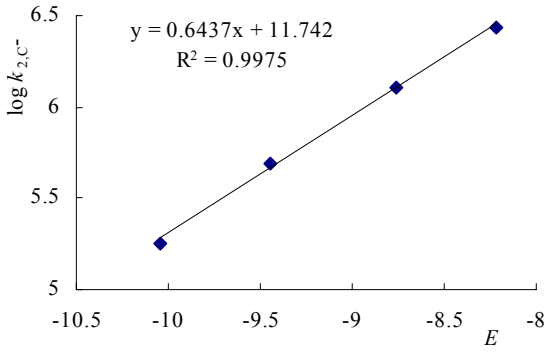
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
8.71×10^{-1}	7.14×10^{-4}	2.01×10^{-4}	5.13×10^{-4}	1.83×10^{-4}	4.66×10^{-4}	3.08×10^{1}	3.03×10^{1}
8.71×10^{-1}	1.07×10^{-3}	3.01×10^{-4}	7.69×10^{-4}	2.74×10^{-4}	6.99×10^{-4}	4.64×10^{1}	4.56×10^{1}
8.71×10^{-1}	1.43×10^{-3}	4.02×10^{-4}	1.03×10^{-3}	3.65×10^{-4}	9.32×10^{-4}	6.50×10^{1}	6.39×10^{1}
8.71×10^{-1}	1.78×10^{-3}	5.02×10^{-4}	1.28×10^{-3}	4.57×10^{-4}	1.17×10^{-3}	8.03×10^{1}	7.89×10^{1}



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.00 × 10⁻⁵ M, $[C^-]$ and $[MeO^-]$ were calculated based on K_{CH} = 4.50 × 10⁻¹ M^{-1}.

4.10.2. Reactivity parameters: *N* = 18.24; *s* = 0.64₄

Reference electrophile			Rate constants	
	Name	*E*	k_{2,C^-} ($M^{-1}s^{-1}$)	log k_{2,C^-}
1b	$(thq)_2CH^+$	-8.22	2.73×10^{6}	6.44
1c	$(ind)_2CH^+$	-8.76	1.29×10^{6}	6.11
1d	$(jul)_2CH^+$	-9.45	4.92×10^{5}	5.69
1e	$(lil)_2CH^+$	-10.04	1.80×10^{5}	5.26

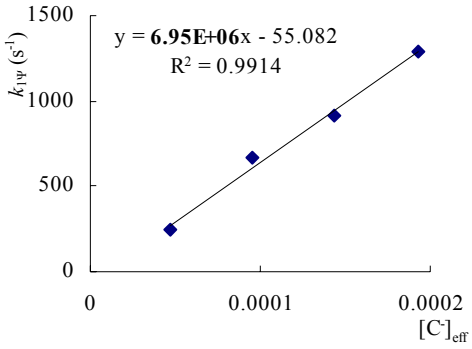


4.11. Malodinitrile anion (2k)

4.11.1. Rate constants

Reaction with $(thq)_2CH^+BF_4^-$ (1b): $k_{2,C^-} = 6.95 \times 10^6\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 618 nm)

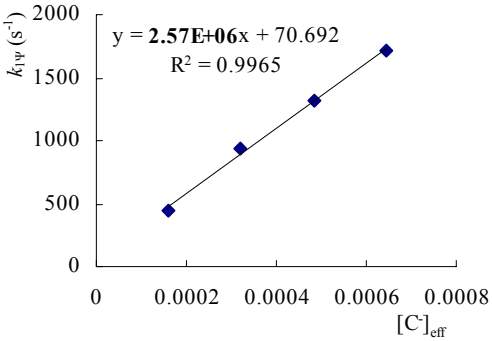
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
4.15×10^{-2}	5.35×10^{-5}	5.15×10^{-5}	2.07×10^{-6}	4.68×10^{-5}	1.88×10^{-6}	2.41×10^2	2.41×10^2
8.30×10^{-2}	1.07×10^{-4}	1.05×10^{-4}	2.11×10^{-6}	9.54×10^{-5}	1.92×10^{-6}	6.65×10^2	6.65×10^2
1.24×10^{-1}	1.61×10^{-4}	1.58×10^{-4}	2.13×10^{-6}	1.44×10^{-4}	1.93×10^{-6}	9.17×10^2	9.17×10^2
1.66×10^{-1}	2.14×10^{-4}	2.12×10^{-4}	2.13×10^{-6}	1.93×10^{-4}	1.94×10^{-6}	1.28×10^3	1.28×10^3



[a] Concentration of $(thq)_2CH^+BF_4^-$ in reaction cell = 5.00×10^{-6} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 6.00 \times 10^2\ M^{-1}$.

Reaction with $(ind)_2CH^+BF_4^-$ (1c): $k_{2,C^-} = 2.57 \times 10^6\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 615 nm)

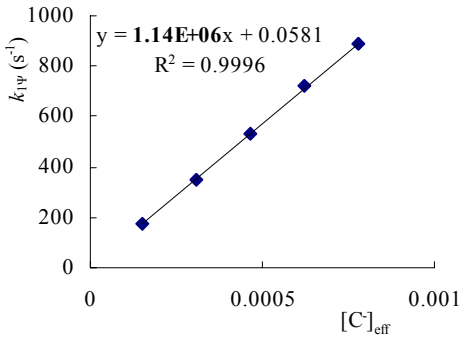
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
8.30×10^{-2}	1.78×10^{-4}	1.75×10^{-4}	3.52×10^{-6}	1.59×10^{-4}	3.20×10^{-6}	4.50×10^2	4.50×10^2
1.66×10^{-1}	3.57×10^{-4}	3.53×10^{-4}	3.56×10^{-6}	3.21×10^{-4}	3.23×10^{-6}	9.40×10^2	9.40×10^2
2.49×10^{-1}	5.35×10^{-4}	5.32×10^{-4}	3.57×10^{-6}	4.83×10^{-4}	3.24×10^{-6}	1.32×10^3	1.32×10^3
3.32×10^{-1}	7.14×10^{-4}	7.10×10^{-4}	3.57×10^{-6}	6.46×10^{-4}	3.25×10^{-6}	1.72×10^3	1.71×10^3



[a] Concentration of $(ind)_2CH^+BF_4^-$ in reaction cell = 5.00×10^{-6} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 6.00 \times 10^2\ M^{-1}$.

Reaction with $(jul)_2CH^+BF_4^-$ (1d): $k_{2,C^-} = 1.14 \times 10^6\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 632 nm)

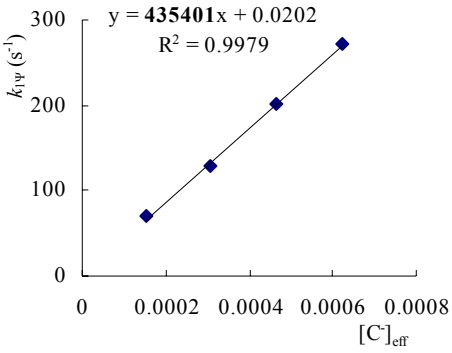
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.81×10^{-2}	1.72×10^{-4}	1.68×10^{-4}	4.11×10^{-6}	1.52×10^{-4}	3.74×10^{-6}	1.77×10^2	1.77×10^2
1.36×10^{-1}	3.44×10^{-4}	3.39×10^{-4}	4.16×10^{-6}	3.08×10^{-4}	3.78×10^{-6}	3.49×10^2	3.49×10^2
2.04×10^{-1}	5.15×10^{-4}	5.11×10^{-4}	4.18×10^{-6}	4.65×10^{-4}	3.80×10^{-6}	5.29×10^2	5.29×10^2
2.72×10^{-1}	6.87×10^{-4}	6.83×10^{-4}	4.19×10^{-6}	6.21×10^{-4}	3.81×10^{-6}	7.19×10^2	7.19×10^2
3.40×10^{-1}	8.59×10^{-4}	8.55×10^{-4}	4.19×10^{-6}	7.77×10^{-4}	3.81×10^{-6}	8.86×10^2	8.86×10^2



[a] Concentration of $(jul)_2CH^+BF_4^-$ in reaction cell = 1.01×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 6.00 \times 10^2\ M^{-1}$.

Reaction with $(lil)_2CH^+BF_4^-$ (1e): $k_{2,C^-} = 4.35 \times 10^5\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 629 nm)

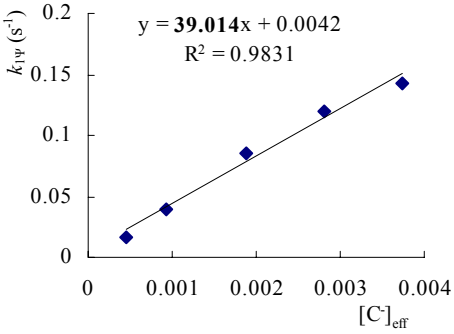
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
6.81×10^{-2}	1.72×10^{-4}	1.68×10^{-4}	4.11×10^{-6}	1.52×10^{-4}	3.74×10^{-6}	7.02×10^{1}	7.02×10^{1}
1.36×10^{-1}	3.44×10^{-4}	3.39×10^{-4}	4.16×10^{-6}	3.08×10^{-4}	3.78×10^{-6}	1.29×10^{2}	1.29×10^{2}
2.04×10^{-1}	5.15×10^{-4}	5.11×10^{-4}	4.18×10^{-6}	4.65×10^{-4}	3.80×10^{-6}	2.02×10^{2}	2.02×10^{2}
2.55×10^{-1}	6.87×10^{-4}	6.83×10^{-4}	4.47×10^{-6}	6.20×10^{-4}	4.06×10^{-6}	2.72×10^{2}	2.72×10^{2}



[a] Concentration of $(lil)_2CH^+BF_4^-$ in reaction cell = 1.00×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 6.00 \times 10^2\ M^{-1}$.

Reaction with tolQM (1f): $k_{2,C^-} = 3.90 \times 10^1\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 365 nm)

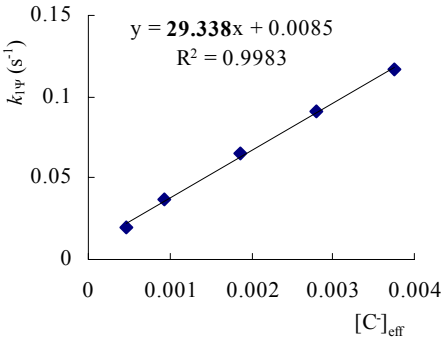
Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
1.63×10^{-1}	5.15×10^{-4}	5.10×10^{-4}	5.23×10^{-6}	4.64×10^{-4}	4.76×10^{-6}	1.67×10^{-2}	1.67×10^{-2}
3.26×10^{-1}	1.03×10^{-3}	1.03×10^{-3}	5.26×10^{-6}	9.32×10^{-4}	4.78×10^{-6}	4.00×10^{-2}	4.00×10^{-2}
6.52×10^{-1}	2.06×10^{-3}	2.06×10^{-3}	5.27×10^{-6}	1.87×10^{-3}	4.79×10^{-6}	8.48×10^{-2}	8.48×10^{-2}
9.78×10^{-1}	3.09×10^{-3}	3.09×10^{-3}	5.28×10^{-6}	2.81×10^{-3}	4.80×10^{-6}	1.20×10^{-1}	1.20×10^{-1}
1.30	4.12×10^{-3}	4.12×10^{-3}	5.28×10^{-6}	3.74×10^{-3}	4.80×10^{-6}	1.43×10^{-1}	1.43×10^{-1}



[a] Concentration of tolQM in reaction cell = 1.00×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 6.00 \times 10^2\ M^{-1}$.

Reaction with aniQM (1g): $k_{2,C^-} = 2.93 \times 10^1\ M^{-1}s^{-1}$
(at 20 °C, in 91 % MeOH/9 % MeCN; stopped-flow, detection at 385 nm)

Concentrations[a] (M)						Rates	
In syringes				In reaction cell		k_{obs} (s^{-1})	$k_{1\Psi}$ (s^{-1})
$[CH]_o$	$[MeO^-]_o$	$[C^-]$	$[MeO^-]$	$[C^-]_{eff}$	$[MeO^-]_{eff}$		
1.63×10^{-1}	5.15×10^{-4}	5.10×10^{-4}	5.23×10^{-6}	4.64×10^{-4}	4.76×10^{-6}	2.00×10^{-2}	2.00×10^{-2}
3.26×10^{-1}	1.03×10^{-3}	1.03×10^{-3}	5.26×10^{-6}	9.32×10^{-4}	4.78×10^{-6}	3.69×10^{-2}	3.69×10^{-2}
6.52×10^{-1}	2.06×10^{-3}	2.06×10^{-3}	5.27×10^{-6}	1.87×10^{-3}	4.79×10^{-6}	6.50×10^{-2}	6.50×10^{-2}
9.78×10^{-1}	3.09×10^{-3}	3.09×10^{-3}	5.28×10^{-6}	2.81×10^{-3}	4.80×10^{-6}	9.15×10^{-2}	9.15×10^{-2}
1.30	4.12×10^{-3}	4.12×10^{-3}	5.28×10^{-6}	3.74×10^{-3}	4.80×10^{-6}	1.17×10^{-1}	1.17×10^{-1}



[a] Concentration of aniQM in reaction cell = 1.00×10^{-5} M, $[C^-]$ and $[MeO^-]$ were calculated based on $K_{CH} = 6.00 \times 10^2\ M^{-1}$.

4.11.2. Reactivity parameters: N = 18.21; s = 0.68[6]

Reference electrophile			Rate constants	
	Name	E	$k_{2,C}$- ($M^{-1}s^{-1}$)	log $k_{2,C}$-
1b	$(thq)_2CH^+$	-8.22	6.95×10^6	6.84
1c	$(ind)_2CH^+$	-8.76	2.57×10^6	6.41
1d	$(jul)_2CH^+$	-9.45	1.14×10^6	6.06
1e	$(lil)_2CH^+$	-10.04	4.35×10^5	5.64
1f	tolQM	-15.83	3.90×10^1	1.59
1g	aniQM	-16.11	2.93×10^1	1.47