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Electrophilicity Parameters for 2-Benzylidene-indan-1,3-diones – a systematic extension of the benzhydrylium based electrophilicity scale

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Table of Contents

1. Materials. DMSO (content of H_2O < 50 ppm) was used. Stock solutions of KO*t*Bu were prepared by dissolving the corresponding alkoxide salt in DMSO under a nitrogen atmosphere.

The 2-benzylidene-indan-1,3-diones **1a-d** were prepared according to a literature procedure:[S1] A solution of indan-1,3-dione (10 mmol) and the corresponding benzaldehyde (10 mmol) in absolute ethanol was treated with a few drops of piperidine and refluxed for 1h, until the product precipitated. It was filtered off and purified by repeated recrystallization from ethanol given rise to the products **1a-d** in about 80-90% yield. ^{1}H and ^{13}C NMR data were found to be in agreement with the literature values.

2. Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 400 (400 MHz, 100 MHz) and on a Bruker ARX 300 (300 MHz, 75 MHz) and a Varian Mercury 200 (200 MHz). Chemical shifts are expressed in ppm and refer to d_6-DMSO (δ_H = 2.49 ppm ,δ_c = 39.7 ppm) or to $CDCl_3$ (δ_H = 7.26 ppm ,δ_c = 77.00 ppm). The coupling constants are in Hz. Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet) and m (multiplet).

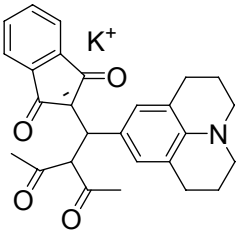
3. Products of the Reactions of 2-Benzylidene-indan-1,3-dione (1) with Carbanions (2)

Typical Procedure. If nothing else is quoted, the reactions were performed as NMR-experiments at room temperature (ca. 20 °C). Thus 1 equiv. of the carbanion **2** was added to 1 equiv. of 2-benzylidene-indan-1,3-dione **1** in d_6-DMSO (1 mL). For a better intermixture of the compounds the NMR tube was put into a ultrasound bath.

In all other cases the conditions for the reactions were not optimized for high yields and are described subsequently.

[S1] R. K. Behera and A. Nayak, *Indian J. Chem. B,* 1976, **14,** 223-224.

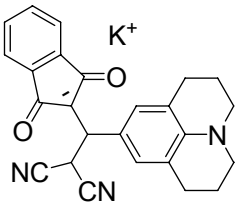
Reaction of 1a with 2d.



3ad

3ad: ^{1}H NMR (d_6-DMSO, 200 MHz): δ = 1.80 (quint, J = 5.0 Hz, 4 H), 1.91 (s, 3 H), 2.02 (s, 3H), 2.57 (t, J = 6.4 Hz, 4 H), 2.96 (t, J = 5.2 Hz, 4 H), 4.16 (d, J = 12.4 Hz, 1 H), 5.23 (d, J = 12.4 Hz, 1 H), 6.75 (s, 2 H), 6.88 (dd, ^{3}J = 5.0 Hz, ^{4}J = 3.0 Hz, 2H), 7.08 (dd, ^{3}J = 5.0 Hz, ^{4}J = 3.0 Hz, 2H).

Reaction of 1a with 2h.

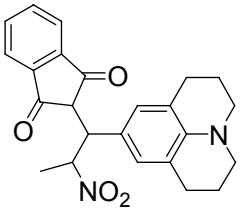


3ah

3ah: ^{1}H NMR (d_6-DMSO, 200 MHz): δ = 1.82 (quint, J = 5.2 Hz, 4 H), 2.60 (t, J = 6.4 Hz, 4 H), 3.02 (t, J = 5.4 Hz, 4 H), 3.98 (d, J = 11.6 Hz, 1 H), 5.76 (d, J = 11.6 Hz, 1 H), 6.82 (s, 2 H), 7.01 (dd, ^{3}J = 5.1 Hz, ^{4}J = 3.0 Hz, 2 H), 7.18 (dd, ^{3}J = 5.1 Hz, ^{4}J = 3.0 Hz, 2 H).

Reaction of 1a with 2l.

At room temperature (ca. 20 °C) nitroethane **2l-H** (90 µL, 1.3 mmol) was added to a stirred solution of freshly sublimated KO*t*Bu (137 mg, 1.22 mmol) in DMSO (5 mL). After 2 min of stirring, **1a** was added (304 mg, 0.924 mmol) to give a red clear solution. After 10 min, HCl conc. (1.5 mL) was added, and the mixture was poured into water (50 mL), giving rise to a purple precipitate. The solvent was removed, and the crude product was dried in the vacuum. Recrystallization from ethanol gave **3al** (227 mg, 61%) which was obtained as a mixture of diastereomers in the ratio 2:1.



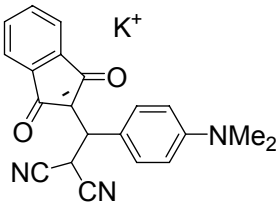
3al

3al: ^{1}H NMR ($CDCl_3$, 300 MHz): major product: δ = 1.72 – 1.86 (m, 7 H), 2.39 – 2.62 (m, 4 H), 2.92 (t, J = 6.0 Hz, 4 H), 3.34 (d, J = 4.1 Hz, 1 H), 3.88 (dd, ^{2}J = 11.4 Hz, ^{3}J = 4.1 Hz, 1 H), 5.63 – 5.75 (m, 1 H), 6.43 (s, 2 H), 7.72 – 7.91 (m, 4 H); minor product: δ = 1.39 (d, J = 6.9 Hz, 3 H), 1.72 – 1.86 (m, 4 H), 2.39 – 2.62 (m, 4 H), 3.01 (t, J = 5.7 Hz, 4 H), 3.20 (d, J = 3.6 Hz, 1 H), 3.79 (dd, J = 3.6 Hz, J = 11.4 Hz, 1 H), 5.63 – 5.75 (m, 1 H), 6.49 (s, 2 H), 7.72 – 7.91 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz): major product:

δ = 19.1 (q), 21.8 (t), 27.4 (t), 48.1 (d), 49.7 (t), 54.7 (d), 85.3 (d), 121.2 (s), 121.5 (s), 122.9 (d), 123.2 (d), 127.1 (d), 135.4 (d), 142.7 (s), 198.1 (s), 199.9

(s). minor product: δ = 19.3 (q), 21.6 (t), 27.5 (t), 47.9 (d), 49.7 (t), 55.6 (d), 84.0 (d), 121.5 (s), 121.6 (s), 122.8 (d), 123.3 (d), 127.6 (d), 135.6 (d), 142.3 (s), 198.0 (s), 199.4.

Reaction of 1b with 2h.

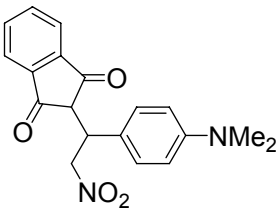


3bh

3bh: ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 2.85 (s, 6 H, NMe_2), 4.17 (d, J = 11.3 Hz, 1 H), 5.81 (d, J = 11.3 Hz, 1 H), 6.62 (d, J = 8.8 Hz, 2 H), 7.05 (dd, ^{3}J = 5.0 Hz, ^{4}J = 3.0 Hz, 2 H), 7.18 (dd, ^{3}J = 5.1 Hz, ^{4}J = 3.0 Hz, 2 H), 7.35 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 26.4, 39.9, 42.2, 101.6, 111.9, 114.6, 116.3, 128.4, 128.5, 129.5, 140.1, 149.2, 187.6.

Reaction of 1b with 2k.

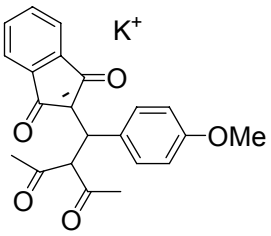
At room temperature (ca. 20 °C) nitromethane **2k**-**H** (80 µL, 1.5 mmol) was added to a stirred solution of freshly sublimated KO*t*Bu (167 mg ,1.49 mmol) in DMSO (5 mL). After addition of **1b** (336 mg, 1.21 mmol) the mixture was stirred for 10 min giving rise to a clear red solution. The mixture was diluted with conc. HCl (1.5 mL) and water (50 mL). The yellow suspension was extracted with EtOAc (3 × 50 mL), and the organic layer was separated and dried with $MgSO_4$. The solvent was removed, and the crude orange product was dried in the vacuum. Recrystallization from ethanol yielded **3bk** (325 mg, 79%) which was obtained as an enantiomeric mixture.



3bk

3bk: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.81 (s, 6 H), 3.39 (d, J = 3.8 Hz, 1 H), 4.33 (dt, ^{3}J = 7.7 Hz, ^{3}J = 3.9 Hz, 1 H), 5.03 (dd, ^{2}J = 13.3 Hz, ^{3}J = 7.4 Hz, 1 H), 5.31 (dd, ^{2}J = 13.3 Hz, ^{3}J = 8.5 Hz, 1H), 6.46 (d, J = 9.0 Hz, 2 H), 7.00 (d, J = 9.0 Hz, 2 H), 7.71 – 7.91 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 40.4 (d), 41.7 (q), 55.8 (d), 77.0 (t), 112.6 (d), 122.6 (d), 123.3 (d), 123.5 (d), 129.4 (d), 135.9 (d), 135.9 (d), 142.7 (s), 150.2 (s), 198.1 (s), 199.7 (s).

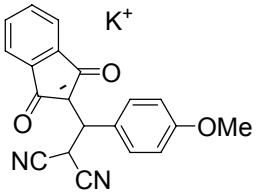
Reaction of 1c with 2d.



3cd

3cd: ^{1}H NMR (d_6-DMSO, 200 MHz): δ = 1.87 (s, 3 H), 2.07 (s, 3 H), 3.66 (s, 3 H, OMe), 4.34 (d, J = 12.2 Hz, 1 H), 5.28 (d, J = 12.2 Hz, 1 H), 6.71 (d, J = 8.4 Hz, 2 H), 6.92 (dd, ^{3}J = 4.8 Hz, ^{4}J = 3.0 Hz, 2 H), 7.11 (dd, ^{3}J = 4.8 Hz, ^{4}J = 3.0 Hz, 2 H), 7.37 (d, J = 8.6 Hz, 2 H).

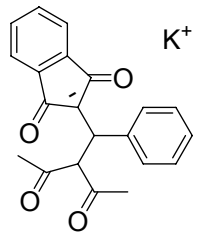
Reaction of 1c with 2h.



3ch

3ch: ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 3.72 (s, 3 H, OMe), 4.24 (d, J = 11.6 Hz, 1 H), 5.85 (d, J = 11.2 Hz, 1 H), 6.83 (d, J = 8.8 Hz, 2 H), 7.06 (dd, ^{3}J = 5.1 Hz, ^{4}J = 3.0 Hz, 2 H), 7.19 (dd, ^{3}J = 5.1 Hz, ^{4}J = 3.0 Hz, 2 H), 7.47 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 26.3, 42.1, 54.7, 101.2, 113.3, 114.5, 116.4, 128.6, 128.9, 133.9, 140.0, 157.9, 187.6.

Reaction of 1d with 2d.



3dd

3dd: ^{1}H NMR (d_6-DMSO, 200 MHz): δ = 1.88 (s, 3 H), 2.08 (s, 3 H), 4.40 (d, J = 12.3 Hz, 1 H), 5.35 (d, J = 12.3 Hz, 1 H), 6.91 – 7.46 (m, 9 H). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 28.3, 30.0, 40.8, 70.1, 104.2, 115.7, 124.6, 127.2, 127.8, 128.1, 140.5, 145.1, 187.5, 203.2, 204.1.

4. Reactivities of 2-Benzylidene-indan-1,3-diones in DMSO

4.1 General

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

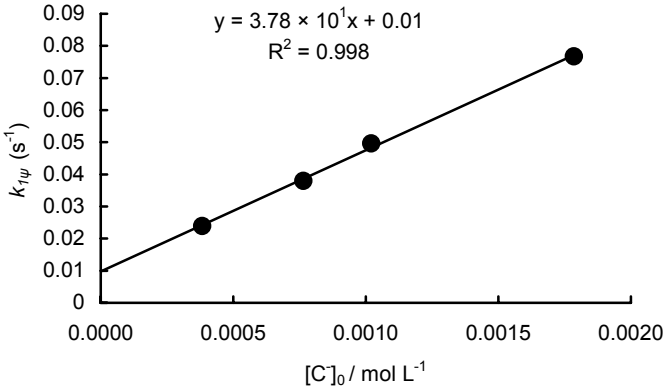
The temperature of the solutions during all kinetic studies was kept constant (20 ± 0.1°C) by using a circulating bath thermostat. DMSO with a content of H_2O < 50 ppm was used for the kinetic experiments.

For the evaluation of the kinetic experiments the stopped-flow spectrophotometer systems Hi-Tech SF-61DX2 or Applied Photophysics SX.18MV-R were used. Rate constants k_{obs} (s^{-1}) were obtained by fitting the single exponential $A_t = A_0\exp(-k_{obs}t) + C$ to the observed time-dependent carbocation absorbance (averaged from at least 3 kinetic runs for each nucleophile concentration). For the stopped-flow experiments 2 stock solutions were used: A solution of the 2-benzylidene-indan-1,3-dione **1a-d** in DMSO and a solution of the carbanion **2**, generated by the deprotonation of the CH acidic compound with 1.05 equivalents of KO*t*Bu in DMSO, respectively, or by adding the corresponding isolated potassium salt into a solution of DMSO.

4.2 Kinetics of the Reactions of Carbanions with 1a

Reaction of **1a** with dimedone **2b** (stopped-flow, 490 nm, 20 °C)

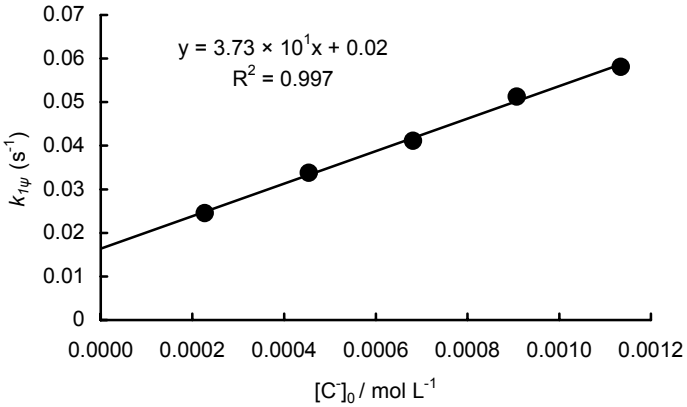
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.74×10^{-5}	3.82×10^{-4}	2.39×10^{-2}
1.74×10^{-5}	7.65×10^{-4}	3.80×10^{-2}
1.74×10^{-5}	1.02×10^{-3}	4.96×10^{-2}
1.74×10^{-5}	1.78×10^{-3}	7.67×10^{-2}



k_2 =3.78 × 10^1 $Lmol^{-1}s^{-1}$

Reaction of **1a** with 4-cyano-benzylnitronate **2c** (stopped-flow, 520 nm, 20 °C)

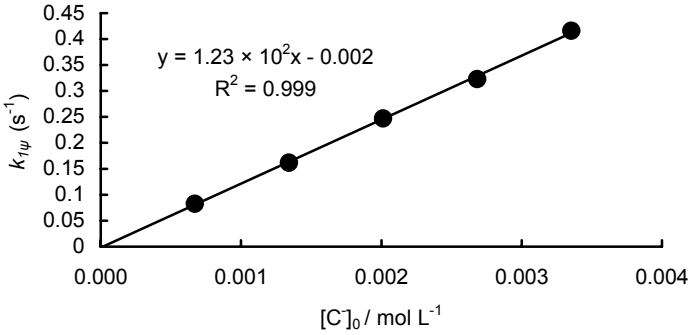
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.64×10^{-5}	2.27×10^{-4}	2.45×10^{-2}
3.64×10^{-5}	4.54×10^{-4}	3.38×10^{-2}
3.64×10^{-5}	6.81×10^{-4}	4.11×10^{-2}
3.64×10^{-5}	9.08×10^{-4}	5.13×10^{-2}
3.64×10^{-5}	1.13×10^{-3}	5.81×10^{-2}



k_2 = 3.73 × 10^1 $Lmol^{-1}s^{-1}$

Reaction of **1a** with the potassium salt of acetylacetone **2d** (stopped-flow, 500 nm, 20 °C)

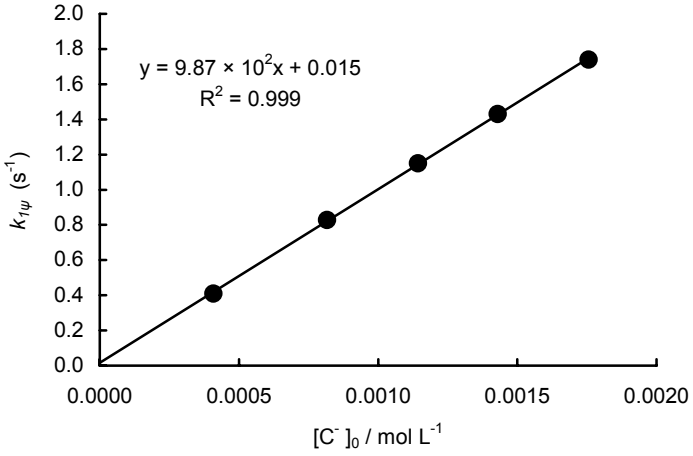
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
4.14×10^{-5}	6.71×10^{-4}	8.34×10^{-2}
4.14×10^{-5}	1.34×10^{-3}	1.62×10^{-1}
4.14×10^{-5}	2.01×10^{-3}	2.48×10^{-1}
4.14×10^{-5}	2.68×10^{-3}	3.23×10^{-1}
4.14×10^{-5}	3.36×10^{-3}	4.17×10^{-1}



$k_2 = 1.23 \times 10^2\ \mathrm{L mol^{-1} s^{-1}}$

Reaction of **1a** with the potassium salt of ethylacetylacetate **2e** (stopped-flow, 500 nm, 20 °C)

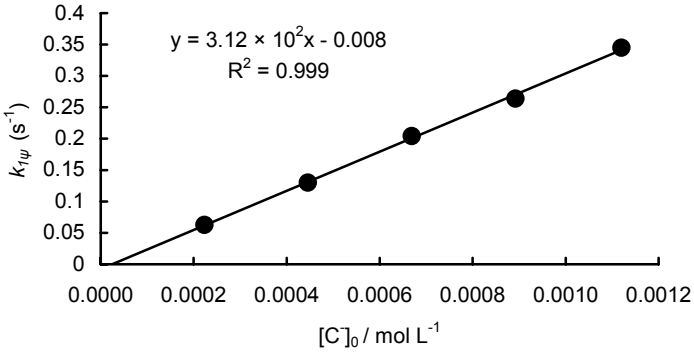
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.93×10^{-5}	4.08×10^{-4}	4.10×10^{-1}
2.93×10^{-5}	8.17×10^{-4}	8.28×10^{-1}
2.93×10^{-5}	1.14×10^{-3}	1.15
2.93×10^{-5}	1.43×10^{-3}	1.43
2.93×10^{-5}	1.76×10^{-3}	1.74



$k_2 = 9.87 \times 10^2\ \mathrm{L mol^{-1} s^{-1}}$

Reaction of **1a** with benzyltriflinate **2f** (stopped-flow, 500 nm, 20 °C)

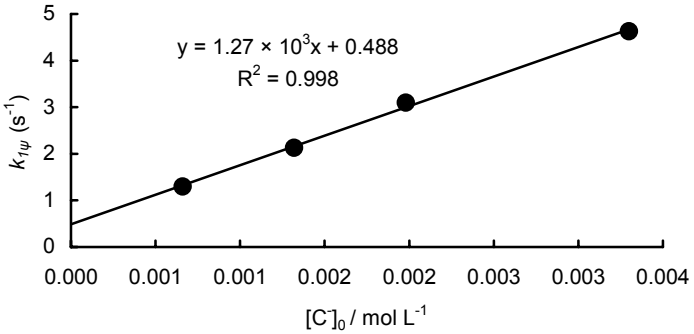
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.74×10^{-5}	2.23×10^{-4}	6.29×10^{-2}
2.74×10^{-5}	4.46×10^{-4}	1.30×10^{-1}
2.74×10^{-5}	6.69×10^{-4}	2.04×10^{-1}
2.74×10^{-5}	8.92×10^{-4}	2.64×10^{-1}
2.74×10^{-5}	1.12×10^{-3}	3.45×10^{-1}



$k_2 = 3.12 \times 10^2$ $Lmol^{-1}s^{-1}$

Reaction of **1a** with the potassium salt of malononitrile **2h** (stopped-flow, 500 nm, 20 °C)

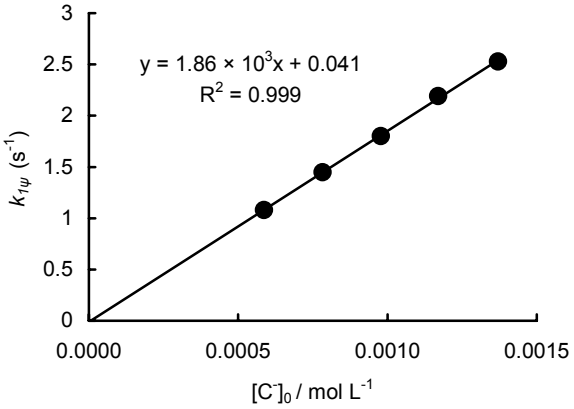
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
4.14×10^{-5}	1.32×10^{-3}	2.13
4.14×10^{-5}	1.98×10^{-3}	3.10
4.14×10^{-5}	2.64×10^{-3}	4.29
4.14×10^{-5}	3.30×10^{-3}	4.63



$k_2 = 1.27 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1a** with ethyl cyanoacetate **2i** (stopped-flow, 500 nm, 20 °C)

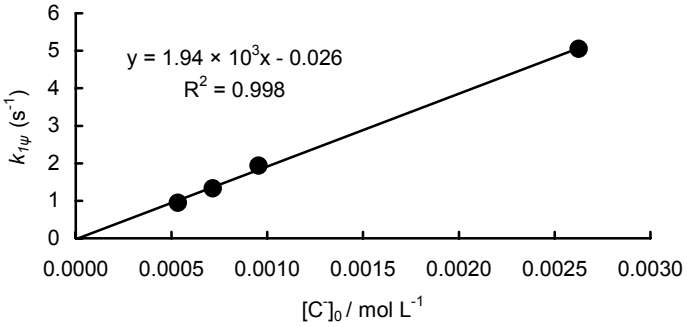
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.93×10^{-5}	5.87×10^{-4}	1.08
2.93×10^{-5}	7.83×10^{-4}	1.45
2.93×10^{-5}	9.78×10^{-4}	1.80
2.93×10^{-5}	1.17×10^{-3}	2.19
2.93×10^{-5}	1.37×10^{-3}	2.53



$k_2 = 1.86 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1a** with 2-nitropropane **2j** (stopped-flow, 500 nm, 20 °C)

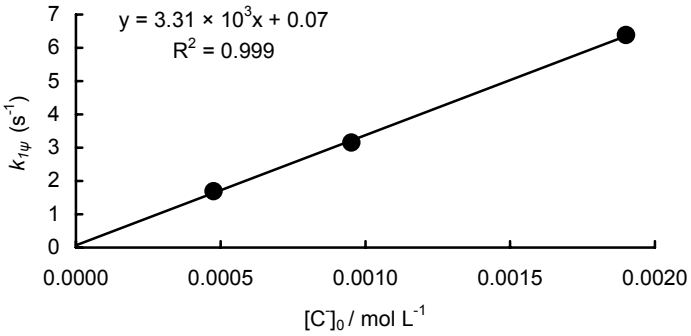
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.03×10^{-5}	5.33×10^{-4}	9.58×10^{-1}
3.03×10^{-5}	7.16×10^{-4}	1.33
3.03×10^{-5}	9.55×10^{-4}	1.94
3.03×10^{-5}	2.63×10^{-3}	5.05



$k_2 = 1.94 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1a** with nitromethane **2k** (stopped-flow, 500 nm, 20 °C)

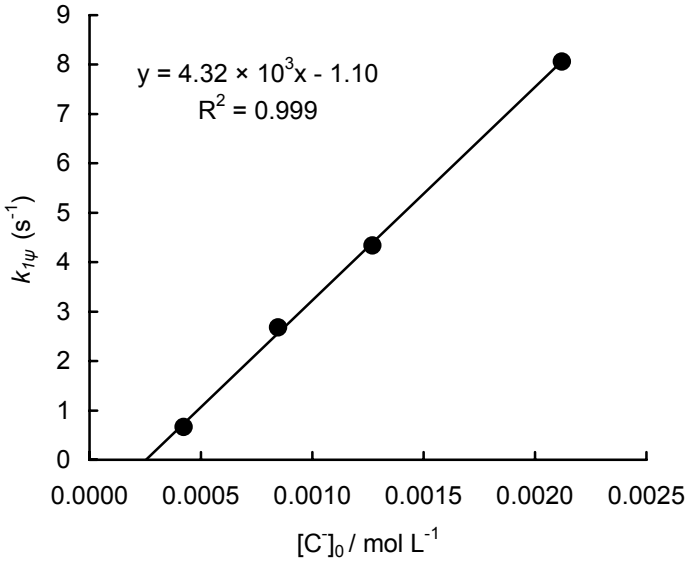
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.75×10^{-5}	4.76×10^{-4}	1.69
1.75×10^{-5}	9.52×10^{-4}	3.15
1.75×10^{-5}	1.90×10^{-3}	6.38



$k_2 = 3.31 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1a** with nitroethane **2l** (stopped-flow, 500 nm, 20 °C)

$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.64×10^{-5}	4.23×10^{-4}	6.66×10^{-1}
3.64×10^{-5}	8.46×10^{-4}	2.68
3.64×10^{-5}	1.27×10^{-3}	4.34
3.64×10^{-5}	2.12×10^{-3}	8.06

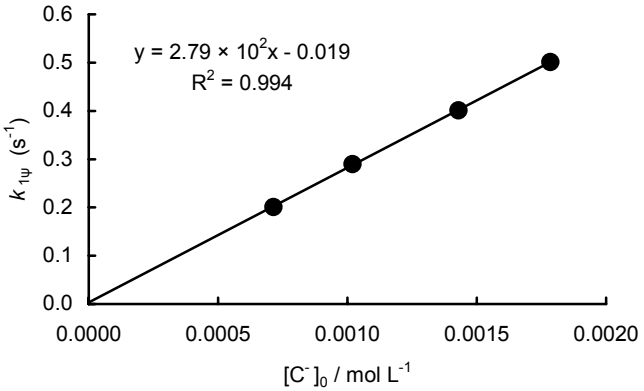


$k_2 = 4.32 \times 10^3$ $Lmol^{-1}s^{-1}$

4.3 Kinetics of the Reactions of Carbanions with **1b**

Reaction of **1b** with the potassium salt of dimedone **2b** (stopped-flow, 490 nm, 20 °C)

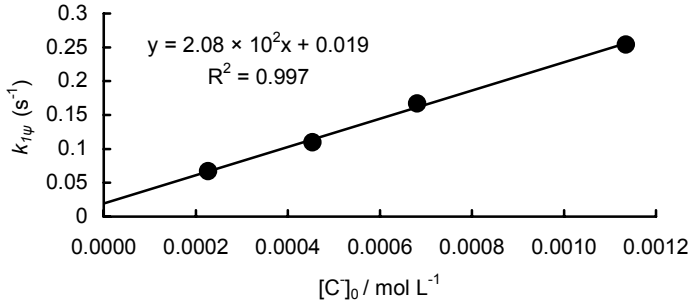
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.80×10^{-5}	7.14×10^{-4}	2.01×10^{-1}
1.80×10^{-5}	1.02×10^{-3}	2.89×10^{-1}
1.80×10^{-5}	1.43×10^{-3}	4.02×10^{-1}
1.80×10^{-5}	1.79×10^{-3}	5.01×10^{-1}



$k_2 = 2.79 \times 10^2$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with 4-cyano-benzylnitronate **2c** (stopped-flow, 520 nm, 20 °C)

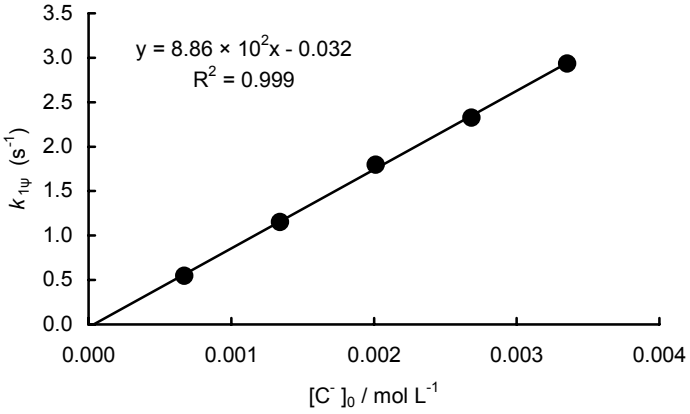
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.89×10^{-5}	2.27×10^{-4}	6.70×10^{-2}
2.89×10^{-5}	4.54×10^{-4}	1.11×10^{-1}
2.89×10^{-5}	6.81×10^{-4}	1.67×10^{-1}
2.89×10^{-5}	1.13×10^{-3}	2.54×10^{-1}



$k_2 = 2.08 \times 10^2$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with the potassium salt of acetylacetate **2d** (stopped-flow, 500 nm, 20 °C)

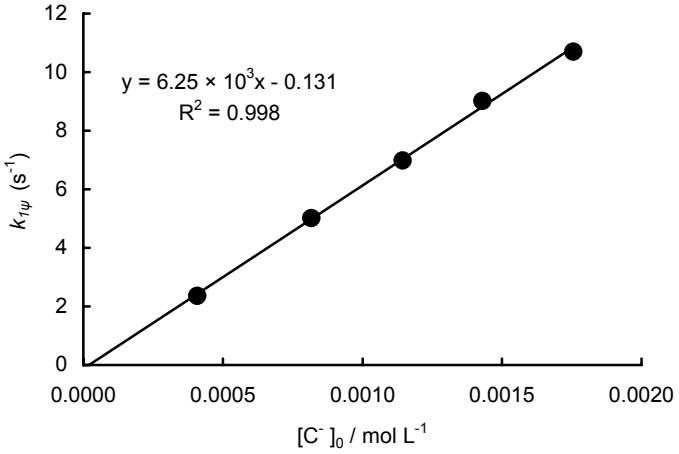
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
4.92×10^{-5}	6.71×10^{-4}	5.50×10^{-1}
4.92×10^{-5}	1.34×10^{-3}	1.15
4.92×10^{-5}	2.01×10^{-3}	1.80
4.92×10^{-5}	2.68×10^{-3}	2.33
4.92×10^{-5}	3.36×10^{-3}	2.94



$k_2 = 8.86 \times 10^2$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with the potassium salt of ethyl acetylacetate **2e** (stopped-flow, 500 nm, 20 °C)

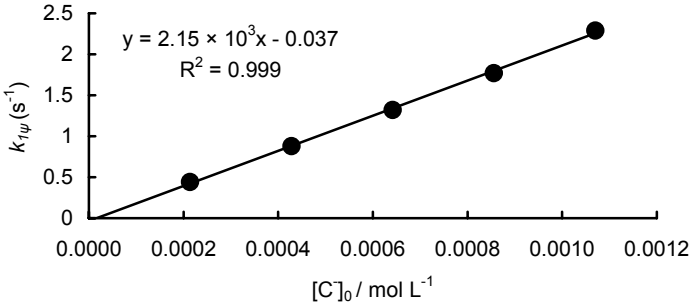
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.92×10^{-5}	4.08×10^{-4}	2.36
2.92×10^{-5}	8.17×10^{-4}	5.02
2.92×10^{-5}	1.14×10^{-3}	6.98
2.92×10^{-5}	1.43×10^{-3}	9.02
2.92×10^{-5}	1.76×10^{-3}	10.7



$k_2 = 6.25 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with benzyltriflinate **2f** (stopped-flow, 500 nm, 20 °C)

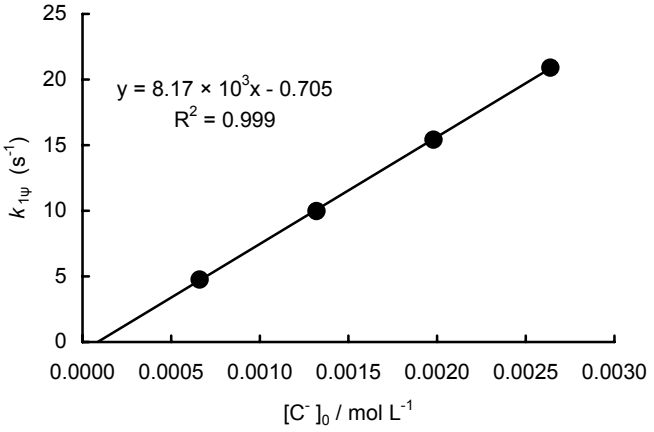
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.64×10^{-5}	2.14×10^{-4}	4.36×10^{-1}
3.64×10^{-5}	4.28×10^{-4}	8.81×10^{-1}
3.64×10^{-5}	6.42×10^{-4}	1.32
3.64×10^{-5}	8.56×10^{-4}	1.77
3.64×10^{-5}	1.07×10^{-3}	2.29



$k_2 = 2.15 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with the potassium salt of malononitrile **2h** (stopped-flow, 500 nm, 20 °C)

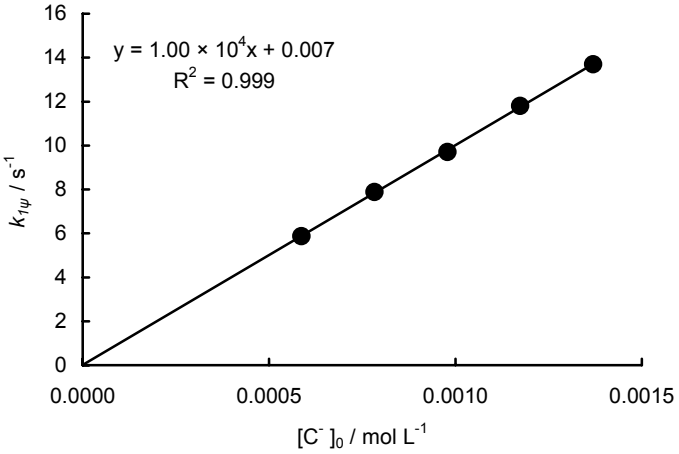
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
4.92×10^{-5}	6.60×10^{-4}	4.76
4.92×10^{-5}	1.32×10^{-3}	9.98
4.92×10^{-5}	1.98×10^{-3}	1.54×10^{1}
4.92×10^{-5}	2.64×10^{-3}	2.09×10^{1}



$k_2 = 8.17 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with the potassium salt of ethyl cyanoacetate **2i** (stopped-flow, 500 nm, 20 °C)

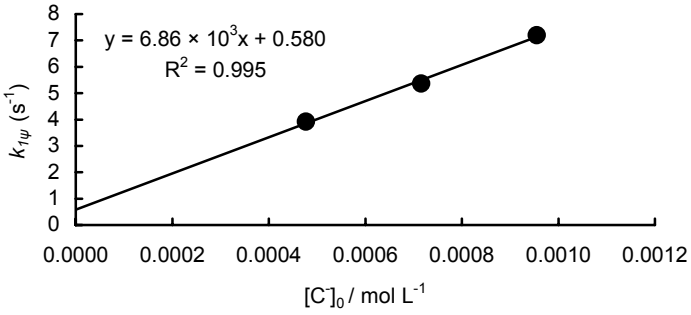
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.82×10^{-5}	5.87×10^{-4}	5.87
2.82×10^{-5}	7.83×10^{-4}	7.89
2.82×10^{-5}	9.78×10^{-4}	9.70
2.82×10^{-5}	1.17×10^{-3}	1.18×10^{1}
2.82×10^{-5}	1.37×10^{-3}	1.37×10^{1}



$k_2 = 1.00 \times 10^4$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with 2-nitropropane **2j** (stopped-flow, 500 nm, 20 °C)

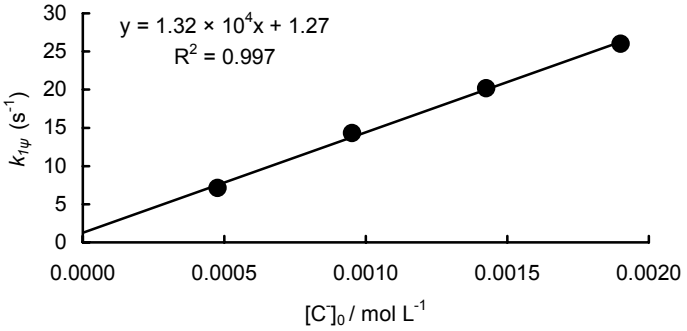
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.69×10^{-5}	4.77×10^{-4}	3.92
3.69×10^{-5}	7.16×10^{-4}	5.36
3.69×10^{-5}	9.55×10^{-4}	7.22



$k_2 = 6.86 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with nitromethane **2k** (stopped-flow, 500 nm, 20 °C)

$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.75×10^{-5}	4.76×10^{-4}	7.14
1.75×10^{-5}	9.52×10^{-4}	1.43×10^{1}
1.75×10^{-5}	1.43×10^{-3}	2.02×10^{1}
1.75×10^{-5}	1.90×10^{-3}	2.60×10^{1}

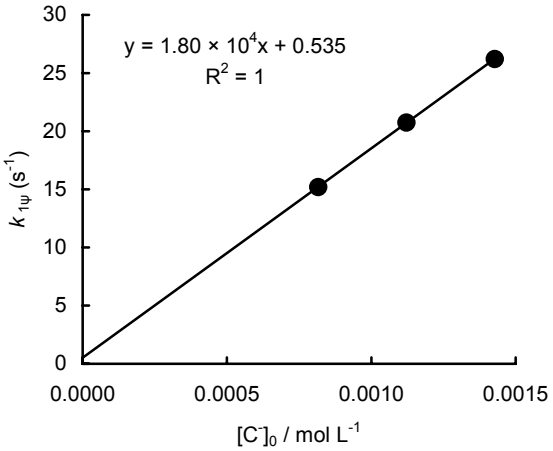


$k_2 = 1.32 \times 10^4$ $Lmol^{-1}s^{-1}$

4.4 Kinetics of the Reactions of Carbanions with **1c**

Reaction of **1c** with the potassium salt of dimedone **2b** (stopped-flow, 390 nm, 20 °C)

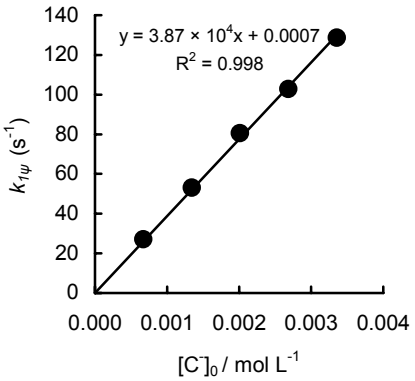
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.79×10^{-5}	8.16×10^{-4}	1.52×10^{1}
1.79×10^{-5}	1.12×10^{-3}	2.08×10^{1}
1.79×10^{-5}	1.43×10^{-3}	2.62×10^{1}



$k_2 = 1.80 \times 10^4$ $Lmol^{-1}s^{-1}$

Reaction of **1c** with the potassium salt of acetylacetone **2d** (stopped-flow, 380 nm, 20 °C)

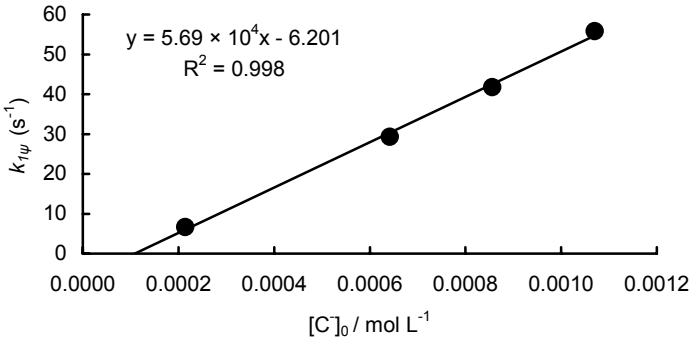
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
5.16×10^{-5}	6.71×10^{-4}	2.71×10^{1}
5.16×10^{-5}	1.34×10^{-3}	5.31×10^{1}
5.16×10^{-5}	2.01×10^{-3}	8.06×10^{1}
5.16×10^{-5}	2.68×10^{-3}	1.03×10^{2}
5.16×10^{-5}	3.36×10^{-3}	1.29×10^{2}



$k_2 = 3.87 \times 10^4$ $Lmol^{-1}s^{-1}$

Reaction of **1c** with benzyltriflinate **2f** (stopped-flow, 400 nm, 20 °C)

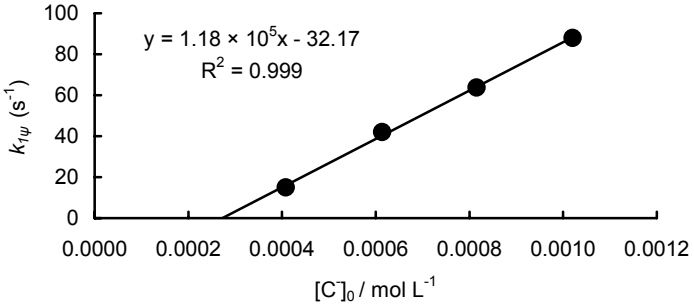
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.78×10^{-5}	2.14×10^{-4}	6.69
3.78×10^{-5}	6.42×10^{-4}	2.93×10^{1}
3.78×10^{-5}	8.56×10^{-4}	4.18×10^{1}
3.78×10^{-5}	1.07×10^{-3}	5.58×10^{1}



$k_2 = 5.69 \times 10^4$ $Lmol^{-1}s^{-1}$

Reaction of **1c** with 4-methylbenzyltriflinate **2g** (stopped-flow, 400 nm, 20 °C)

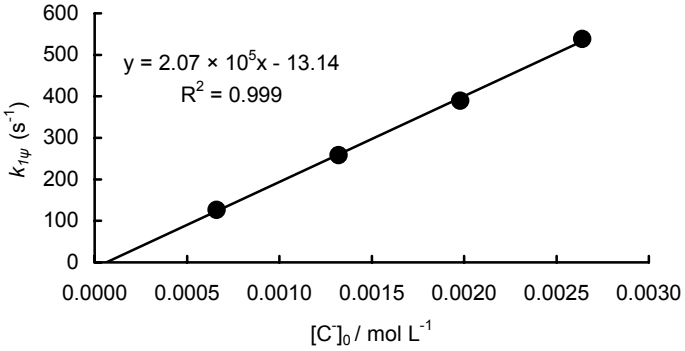
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.78×10^{-5}	4.08×10^{-4}	1.50×10^{1}
3.78×10^{-5}	6.12×10^{-4}	4.20×10^{1}
3.78×10^{-5}	8.16×10^{-4}	6.38×10^{1}
3.78×10^{-5}	1.02×10^{-3}	8.79×10^{1}



$k_2 = 1.18 \times 10^5$ $Lmol^{-1}s^{-1}$

Reaction of **1c** with the potassium salt of malononitrile **2h** (stopped-flow, 380 nm, 20 °C)

$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
5.16×10^{-5}	6.60×10^{-4}	1.27×10^{2}
5.16×10^{-5}	1.32×10^{-3}	2.59×10^{2}
5.16×10^{-5}	1.98×10^{-3}	3.89×10^{2}
5.16×10^{-5}	2.64×10^{-3}	5.38×10^{2}

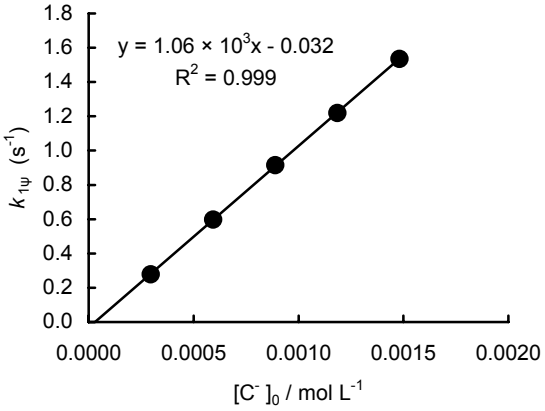


$k_2 = 2.07 \times 10^5$ $Lmol^{-1}s^{-1}$

4.5 Kinetics of the Reactions of Carbanions with **1d**

Reaction of **1d** with the potassium salt of Meldrum`s acid **2a** (stopped-flow, 364 nm, 20 °C)

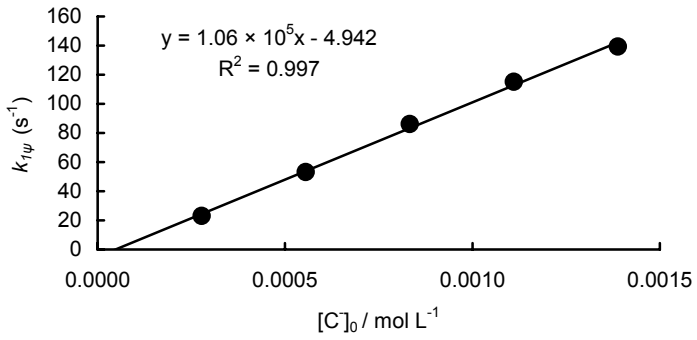
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.13×10^{-5}	2.96×10^{-4}	2.79×10^{-1}
2.13×10^{-5}	5.93×10^{-4}	5.97×10^{-1}
2.13×10^{-5}	8.89×10^{-4}	9.15×10^{-1}
2.13×10^{-5}	1.19×10^{-3}	1.22
2.13×10^{-5}	1.48×10^{-3}	1.54



$k_2 = 1.06 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1d** with the potassium salt of dimedone **2b** (stopped-flow, 390 nm, 20 °C)

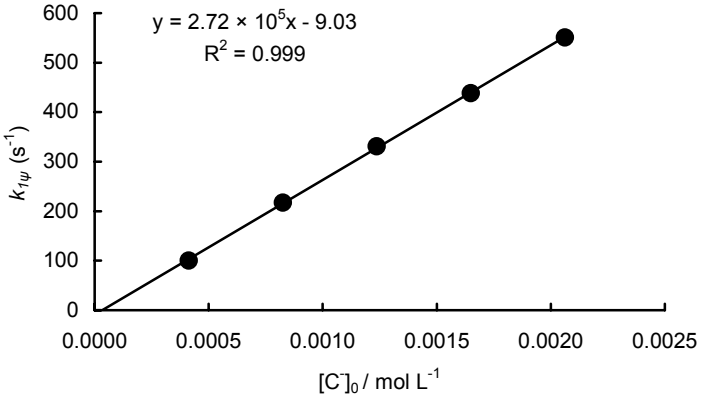
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.13×10^{-5}	2.78×10^{-4}	2.32×10^{1}
2.13×10^{-5}	5.55×10^{-4}	5.31×10^{1}
2.13×10^{-5}	8.33×10^{-4}	8.61×10^{1}
2.13×10^{-5}	1.11×10^{-3}	1.15×10^{2}
2.13×10^{-5}	1.39×10^{-3}	1.39×10^{2}



$k_2 = 1.06 \times 10^5$ $Lmol^{-1}s^{-1}$

Reaction of **1d** with the potassium salt of acetylacetone **2d** (stopped-flow, 364 nm, 20 °C)

$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.13×10^{-5}	4.12×10^{-4}	1.00×10^{2}
2.13×10^{-5}	8.25×10^{-4}	2.17×10^{2}
2.13×10^{-5}	1.24×10^{-3}	3.31×10^{2}
2.13×10^{-5}	1.65×10^{-3}	4.38×10^{2}
2.13×10^{-5}	2.06×10^{-3}	5.51×10^{2}

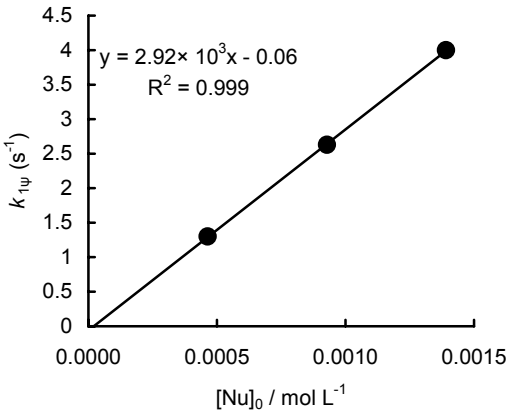


$k_2 = 2.72 \times 10^5\ \mathrm{Lmol^{-1}s^{-1}}$

4.6 Kinetics of the Reactions of Ar_2CH^+ with Piperidine in DMSO/water (50/50 v,v)

Reaction of $(lil)_2CH^+$ (**1h**) with piperidine (stopped-flow, 620 nm, 20 °C)

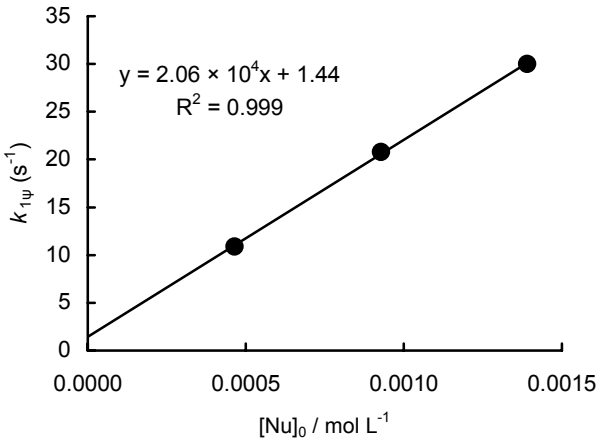
$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.03×10^{-5}	4.64×10^{-4}	1.30
1.03×10^{-5}	9.28×10^{-4}	2.63
1.03×10^{-5}	1.39×10^{-3}	4.00



$k_2 = 2.92 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of $(ind)_2CH^+$ (**1l**) with piperidine (stopped-flow, 620 nm, 20 °C)

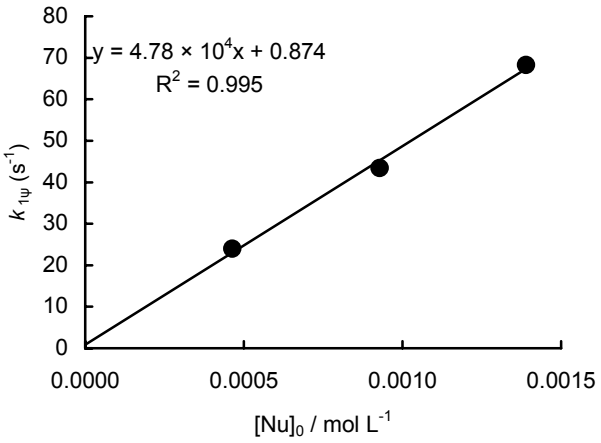
$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.27×10^{-5}	4.64×10^{-4}	1.09×10^1
1.27×10^{-5}	9.28×10^{-4}	2.08×10^1
1.27×10^{-5}	1.39×10^{-3}	3.00×10^1



$k_2 = 2.06 \times 10^4$ $Lmol^{-1}s^{-1}$

Reaction of $(thq)_2CH^+$ (**1m**) with piperidine (stopped-flow, 620 nm, 20 °C)

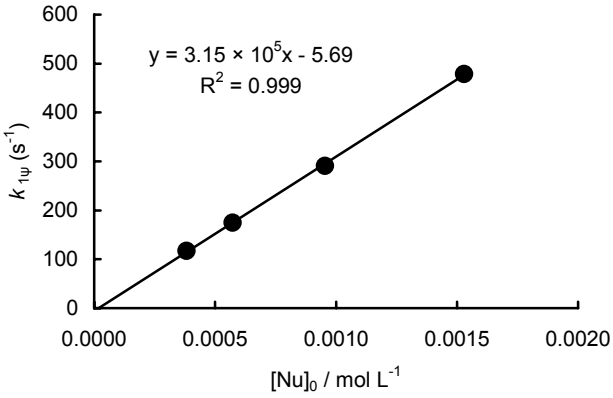
$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.33×10^{-5}	4.64×10^{-4}	2.40×10^{1}
1.33×10^{-5}	9.28×10^{-4}	4.34×10^{1}
1.33×10^{-5}	1.39×10^{-3}	6.83×10^{1}



$k_2 = 4.78 \times 10^4$ $Lmol^{-1}s^{-1}$

Reaction of $(dma)_2CH^+$ (**1n**) with piperidine (stopped-flow, 620 nm, 20 °C)

$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.30×10^{-6}	3.82×10^{-4}	1.17×10^{2}
2.30×10^{-6}	5.73×10^{-4}	1.75×10^{2}
2.30×10^{-6}	9.55×10^{-4}	2.91×10^{2}
2.30×10^{-6}	1.53×10^{-3}	4.79×10^{2}

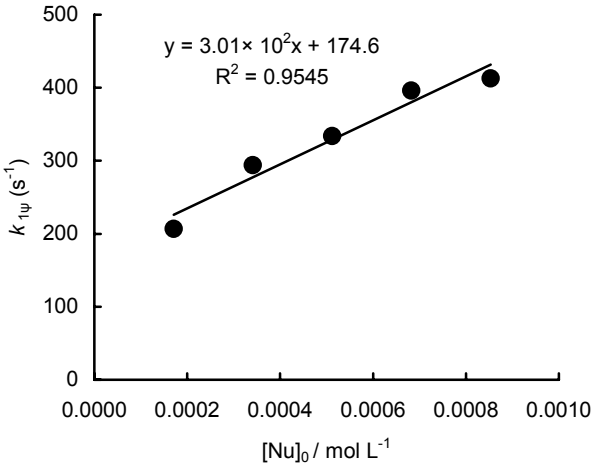


$k_2 = 3.15 \times 10^5$ $Lmol^{-1}s^{-1}$

4.7 Kinetics of the Reactions of Amines with **1d** in DMSO

Reaction of **1d** with piperidine in DMSO (stopped-flow, 341 nm, 20 °C)

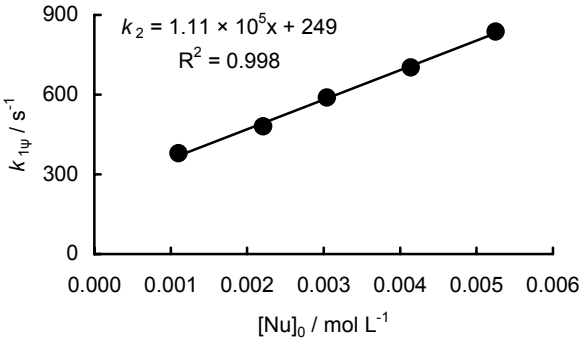
$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
3.37×10^{-5}	1.71×10^{-4}	2.07×10^{2}
3.37×10^{-5}	3.41×10^{-4}	2.94×10^{2}
3.37×10^{-5}	5.12×10^{-4}	3.34×10^{2}
3.37×10^{-5}	6.82×10^{-4}	3.96×10^{2}
3.37×10^{-5}	8.53×10^{-4}	4.13×10^{2}



$k_2 = 3.01 \times 10^{2}\ \mathrm{Lmol^{-1}s^{-1}}$

Reaction of **1d** with morpholine in DMSO (stopped-flow, 346 nm, 20 °C)

$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
5.32×10^{-5}	5.25×10^{-3}	837
5.32×10^{-5}	4.14×10^{-3}	703
5.32×10^{-5}	3.04×10^{-3}	589
5.32×10^{-5}	2.21×10^{-3}	481
5.32×10^{-5}	1.10×10^{-3}	379

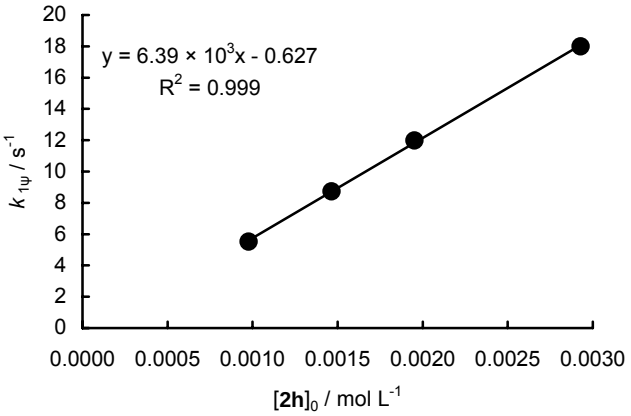


$k_2 = 1.11 \times 10^{5}\ \mathrm{Lmol^{-1}s^{-1}}$

4.8 Kinetics of the Reactions of Malononitrile Anion **2h** with **1a** and **1b** in DMSO/H_2O (50/50 v,v)

Reaction of **1a** with malononitrile anion **2h** (stopped-flow, 529 nm, 20 °C)

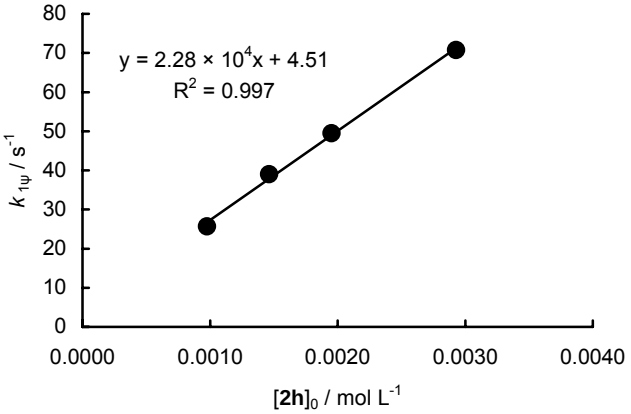
$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
1.06×10^{-4}	9.76×10^{-4}	5.52
1.06×10^{-4}	1.46×10^{-3}	8.73
1.06×10^{-4}	1.95×10^{-3}	1.20×10^{1}
1.06×10^{-4}	2.93×10^{-3}	1.80×10^{1}



$k_2 = 6.39 \times 10^3$ $Lmol^{-1}s^{-1}$

Reaction of **1b** with malononitrile anion **2h** (stopped-flow, 491 nm, 20 °C)

$[E]_0$ / mol L^{-1}	$[C^-]_0$ / mol L^{-1}	$k_{1\psi}$ / s^{-1}
2.36×10^{-4}	9.76×10^{-4}	2.57×10^{1}
2.36×10^{-4}	1.46×10^{-3}	3.90×10^{1}
2.36×10^{-4}	1.95×10^{-3}	4.95×10^{1}
2.36×10^{-4}	2.93×10^{-3}	7.07×10^{1}



$k_2 = 2.28 \times 10^4$ $Lmol^{-1}s^{-1}$