

Nucleophilicity of the bis(4-nitrophenyl)methyl anion

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**Dedicated to Professor Nouria Al-Awadi in recognition of her achievements for science in
Kuwait**

Abstract

Kinetics of the reactions of the bis(4-nitrophenyl)methyl anion **1** with quinone methides and other Michael acceptors have been measured in dimethyl sulfoxide solution at 20 °C. The second-order rate constants k_2 have been used to determine the nucleophilicity parameters $N = 19.9$ and $s = 0.67$ of **1** according to the linear free energy relationship $\log k(20\text{ °C}) = s(N + E)$.

Keywords: Kinetics, linear free energy relationship, nucleophilicity, intrinsic barriers

Introduction

In previous work, we have demonstrated that the rates of the reactions of carbocations and Michael acceptors with nucleophiles can be calculated by Equation 1,

$$\log k_2(20\text{ °C}) = s(N + E) \quad (1)$$

where E represents the reactivity of the electrophile, N is a nucleophilicity parameter and s is a nucleophile-specific slope parameter.¹⁻⁴

By using colored benzhydrylium ions and structurally related quinone methides as reference electrophiles, a comprehensive nucleophilicity scale has been developed, which includes a large variety of σ -, n - and π -nucleophiles. This scale allows us to compare the reactivities of different types of nucleophiles on the basis of the nucleophilicity parameters N and s .

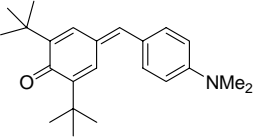
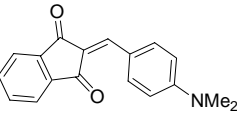
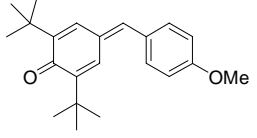
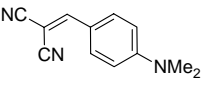
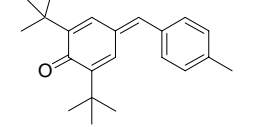
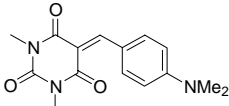
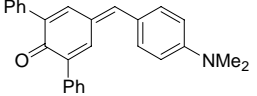
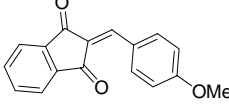
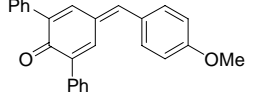
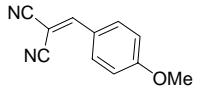
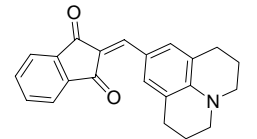
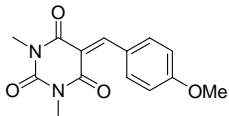
The fast characterization of a large number of nucleophiles became possible, because spectrophotometry provides an efficient tool to determine rate constants for the reactions of

nucleophiles with colored reference electrophiles on different time scales. An analogous characterization of synthetically important electrophiles, most of which are colorless, requires the availability of colored reference nucleophiles. In this investigation we have examined whether benzhydryl anions can be employed for this purpose.

The bis(4-nitrophenyl)methyl anion **1** has been reported to show an absorption maximum at 782 nm in a 95/5-mixture of DMSO and methanol (v/v).⁵ We now report on the kinetics of the additions of **1** to quinone methides in DMSO and show that the resulting nucleophilicity parameters *N* and *s* for **1** can be used to estimate the rates of reactions of **1** with other Michael acceptors.

Results

Table 1. Electrophilicity parameters *E* of the electrophiles **2a-l** and second-order rate constants *k*₂ (in L mol⁻¹ s⁻¹) for the reactions of **1** with **2a-k** in DMSO at 20 °C

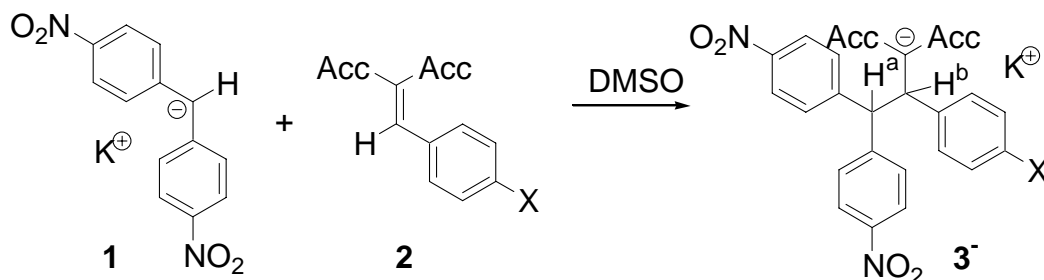
Electrophile	<i>E</i>	<i>k</i> ₂	Electrophile	<i>E</i>	<i>k</i> ₂
2a 	-17.29 ^a	6.36 × 10 ¹	2g 	-13.56 ^b	7.01 × 10 ³
2b 	-16.11 ^a	3.32 × 10 ²	2h 	-13.3 ^c	2.39 × 10 ³
2c 	-15.83 ^a	5.29 × 10 ²	2i 	-12.76 ^d	2.24 × 10 ⁴ 2.33 × 10 ⁴ ^e
2d 	-13.39 ^a	2.99 × 10 ⁴	2j 	-11.32 ^b	3.54 × 10 ⁵
2e 	-12.18 ^a	1.46 × 10 ⁵	2k 	-10.8 ^c	1.81 × 10 ⁵
2f 	-14.68 ^b	8.79 × 10 ²	2l 	-10.37 ^d	too fast

^a From ref. 6. ^b From ref. 7. ^c From ref. 8. ^d From ref. 9. ^e Pseudo-first-order conditions using **1** as the compound in excess.

Reaction products

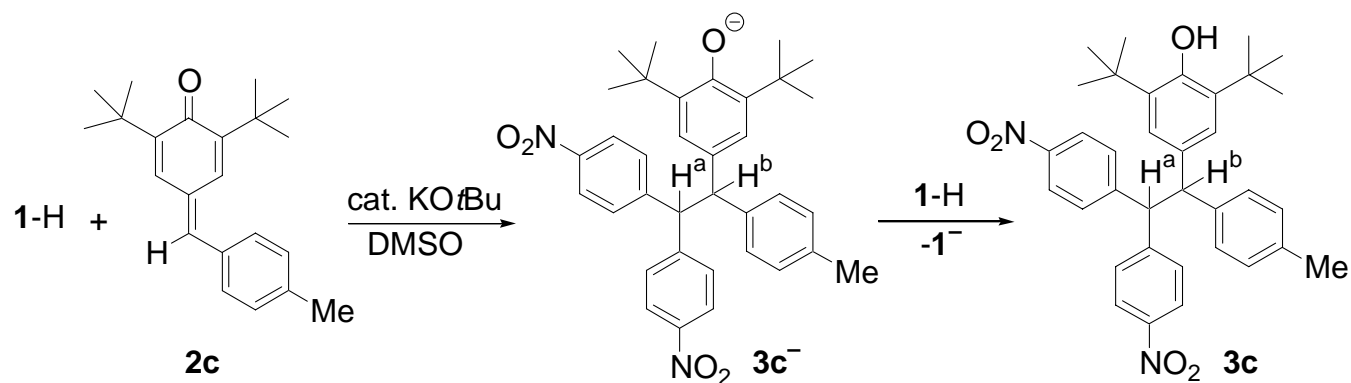
Because the nucleophile **1** can be expected to react analogously with all electrophiles **2** which were studied kinetically (Table 1), reaction products have only been identified for some representative substrates as listed in Table 2.

The anionic adducts **3⁻** obtained by mixing equimolar amounts of the electrophiles **2** and the potassium salt of the carbanion **1** in *d*₆-DMSO solutions were investigated by ¹H NMR spectroscopy (Scheme 1). Their neutral analogues which were supposed to be formed by protonation of **3⁻** with aqueous HCl decomposed to the starting materials.



Scheme 1. Reactions of the potassium salt **1** with the electrophiles **2** in DMSO (Acc = electron-withdrawing group).

In the case of the reaction of the quinone methide **2c** with **1** we succeeded in isolating the phenol **3c** by using catalytic amounts of KO*t*-Bu for the deprotonation of the CH acid **1-H**. The pK_{aH} value of the addition product **3c⁻** can be estimated to be $(pK_{aH} > 16)^{10}$ higher than that of the CH acid **1-H** ($pK_a = 15.1$)¹¹, so that **3c⁻** functions as internal base during the reaction (Scheme 2).



Scheme 2. Reaction of **1-H** with **2c** by using catalytic amounts of KO^tBu.

Evidence for the formation of the reaction products **3⁻** and **3** is given by their ¹H NMR spectra (Table 2) which show characteristic doublets for H^a ($\delta = 4.64\text{--}6.05$ ppm) and H^b ($\delta = 3.88\text{--}5.10$ ppm).

Table 2. Characterized adducts **3⁻** or **3c** and some characteristic ¹H NMR chemical shifts and coupling constants

Reactants	Adduct	$\delta(\text{H}^{\text{a}})/\text{ppm}$	$\delta(\text{H}^{\text{b}})/\text{ppm}$	J_{ab}/Hz
1 2c	3c	4.86	4.58	12.2
1 2h	3h⁻	4.64	3.88	12.5
1 2j	3j⁻	5.82	4.63	12.6
1 2l	3l⁻	6.05	5.10	12.6

Kinetic investigations

The kinetic investigations were performed in dimethyl sulfoxide solution at 20 °C by using conventional UV-vis spectroscopy with fiber optics or the stopped-flow technique. All reactions reported in this paper followed second-order kinetics, first-order with respect to the nucleophile concentration and first-order with respect to the electrophile concentration. For the kinetic experiments the bis(4-nitrophenyl)methyl anion **1** was either generated freshly by deprotonating the corresponding CH acid **1-H** with 1.05 equivalents of KO^{*t*}-Bu, or the isolated potassium salt of **1** was employed.

In general, the reactions of the colored nucleophile **1** with the colored electrophiles **2a-k** were carried out under pseudo-first-order conditions by using an excess of the electrophiles **2a-k**. The rates were determined photometrically by following the decrease of the absorbance of the nucleophile **1** at its absorption maximum (Figure 1).

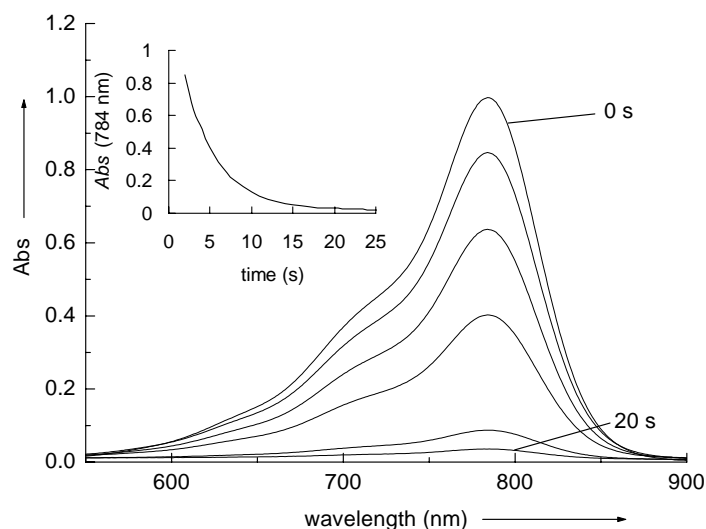


Figure 1. UV-vis-spectroscopic monitoring of the reaction of the bis(4-nitrophenyl)methyl anion **1** (2.16×10^{-5} mol L⁻¹) with the quinone methide **2c** (4.83×10^{-4} mol L⁻¹) at 784 nm in DMSO at 20 °C.

Because the concentrations of the electrophiles were thus kept almost constant throughout the reactions, an exponential decay of the nucleophile absorbance at 782 nm resulted (Equation 2) from which the first-order rate constants k_{obs} were derived by least-squares fitting of the single-exponential $A_t = A_0 \exp(-k_{\text{obs}}t) + C$.

$$-d[\mathbf{1}]/dt = -dA/dt = k_{\text{obs}} [\mathbf{1}] \quad (2)$$

Plots of k_{obs} versus the concentrations of the electrophile $[\mathbf{2}]_0$ gave straight lines with the slopes k_2 as shown for one example in Figure 2 and for all other kinetic experiments in the Experimental Section. All second-order rate constants k_2 ($\text{L mol}^{-1} \text{s}^{-1}$) for the reactions of **1** with **2a-k** are listed in Table 1.

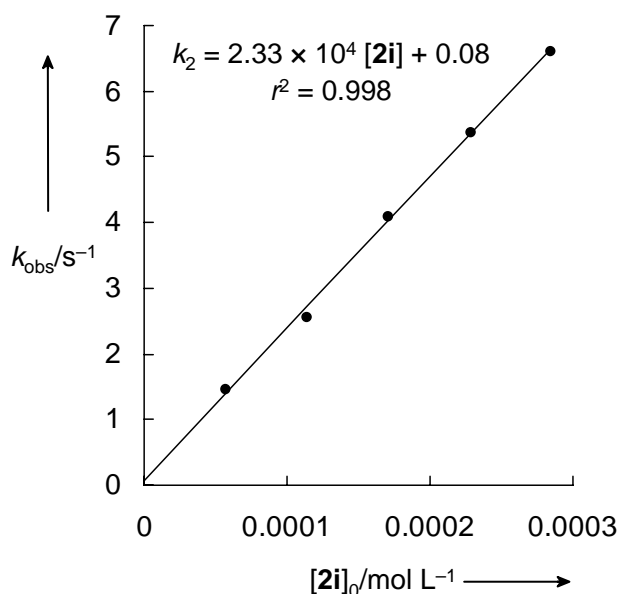


Figure 2. Determination of the second-order rate constant $k_2 = 2.33 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ for the reaction of **1** with **2i** in DMSO at 20 °C.

The reaction of **1** with **2i** was also studied under pseudo-first order conditions with an excess of the bis(4-nitrophenyl)methyl anion **1**; the resulting second-order rate constant differed by 3% from the value obtained with an excess of **2i**.

With one exception, all reactions proceeded quantitatively. Only the reaction of **1** with benzylidenemalononitrile **2h** was incomplete, and the absorbance at the end of the reaction decreased with increasing concentration of **2h** (Figure 3).

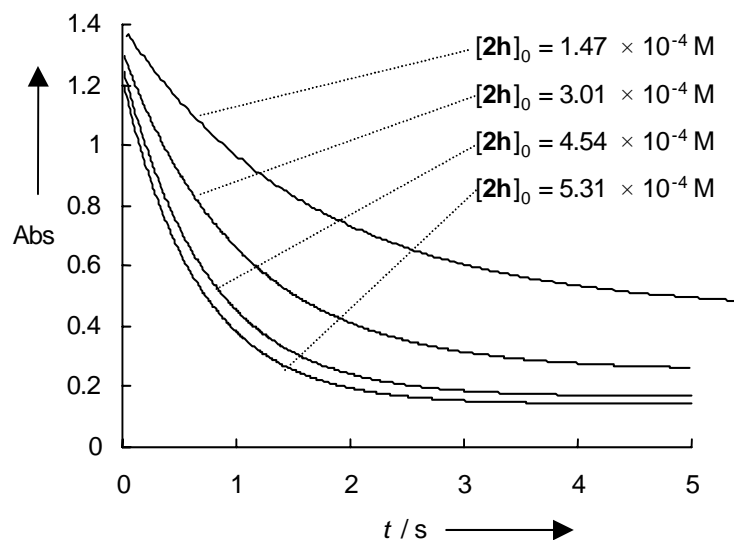


Figure 3. Plot of the absorbance ($\lambda = 783$ nm) versus t for the reversible reaction of **2h** with **1** ($c_0 = 4.86 \times 10^{-5}$ M) at different initial concentrations of **2h** in DMSO (20 °C).

Because the molar absorption coefficient of **1** is known ($97000 \text{ L mol}^{-1} \text{ cm}^{-1}$)⁵ we were able to determine the equilibrium constant K as $(61022 \pm 2570) \text{ L mol}^{-1}$ corresponding to a reaction free energy of $\Delta_r G^0 = -26.8 \text{ kJ mol}^{-1}$ (Experimental Section).

Discussion

When the rate constants ($\log k_2$) for the reactions of **1** with the reference electrophiles **2a-e** were plotted against their electrophilicity parameters E , a straight line is obtained (Figure 4), the slope of which yields the nucleophile-specific parameter s , whereas the intercept with the abscissa corresponds to the negative value of the nucleophilicity parameter N of **1**. The fact that all data points for the reference electrophiles are exactly on the correlation line indicates the applicability of Equation 1.

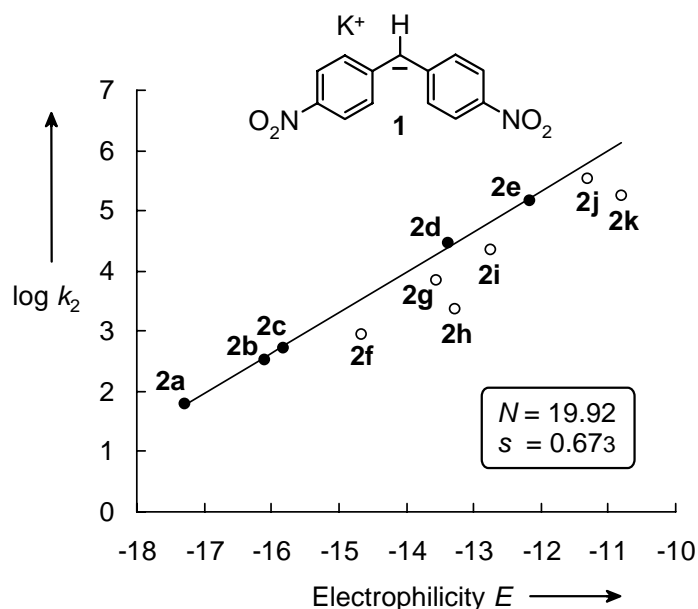


Figure 4. Plot of $\log k_2$ for the reaction of the bis(4-nitrophenyl)methyl anion **1** with the reference electrophiles **2a-e** and the Michael acceptors **2f-k** in DMSO at 20 °C (Table 1) versus the corresponding electrophilicity parameters E (Table 1). Because compounds **2f-k** are not (yet) considered as reference electrophiles, as defined in ref. 1a, the rate constants characterized by open symbols were not used for the construction of the correlation line and for the determination of the nucleophilicity parameters of **1**.

It is obvious, however, that the reactions of the bis(4-nitrophenyl)methyl anion **1** with the Michael acceptors **2f-k** proceed more slowly than expected on the basis of their electrophilicity parameters E . While we do not yet know why all rate constants for **2f-k** are below the correlation line, it should be emphasized that all deviations are smaller than 1 order of magnitude and thus are within the previously postulated confidence limit of Equation 1.^{2d}

Possibly the deviations are due to steric effects, because the Michael acceptors **2f-k** are sterically more congested at the reaction center than the quinone methides **2a-e** which were used as reference compounds for determining N and s of **1**. Because of the two phenyl groups at the carbanionic center, the bis(4-nitrophenyl)methyl anion **1** might be more sensitive to steric shielding of the electrophiles than the carbanions used for the determination of the E -parameters of **2a-k**. However, the particularly strong deviation of the sterically nonshielded benzylidenemalononitriles **2h** and **2k** contradicts this explanation.

The availability of rate and equilibrium constants for the reaction of **1** with **2h** allows us to calculate the intrinsic barrier $\Delta G_0^\ddagger = 65.5 \text{ kJ mol}^{-1}$ by substituting $\Delta G^\ddagger = 52.8 \text{ kJ mol}^{-1}$ and $\Delta_r G^0 = -26.8 \text{ kJ mol}^{-1}$ into the Marcus Equation¹² (3) where the work term has been omitted.

$$\Delta G^\ddagger = \Delta G_0^\ddagger + 0.5\Delta_r G^0 + [(\Delta_r G^0)^2/16\Delta G_0^\ddagger] \quad (3)$$

As mentioned above, the reaction of **1** with **2h** is the only one of the series listed in Table 1 which proceeds incompletely. Despite its unfavorable equilibrium constant, **2h** reacts with similar rate or even faster than several other electrophiles of Table 1 which is indicative of a particularly low intrinsic barrier of the reaction of **2h**. This finding is in accord with previous observations of Bernasconi that reactions to benzylidene malonitriles have lower intrinsic barriers than olefins activated by alkoxy carbonyl or nitro groups.¹³

The title compound **1** can be considered as a phenylog of *p*-nitrophenylnitronate **4**. Figure 5 shows that separation of the nitro group from the carbanionic center by a phenylene group (cf. **4** with **1**) causes an increase of *N* by 3 units. With an *N* parameter of 19.9 the nucleophilicity of anion **1** in DMSO is comparable to those of the nitromethyl anion¹⁴ and the malononitrile anion in the same solvent⁶ and thus ranks among the most reactive carbanions so far characterized in our nucleophilicity scales.¹

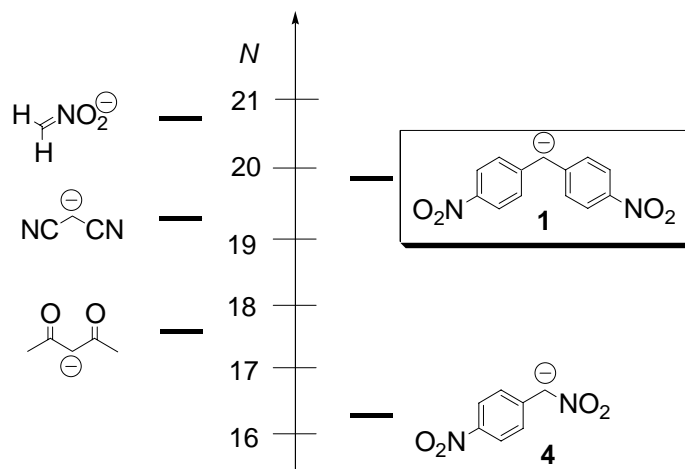


Figure 5. Comparison of the nucleophilicities of typical carbanions in DMSO.

Conclusions

With this investigation we have integrated another colored nucleophile in our comprehensive nucleophilicity scale. The fair correlation depicted in Figure 3 suggests that **1** might be applicable for the determination of the electrophilicities of colorless electrophiles by UV-vis spectroscopy.

Experimental Section

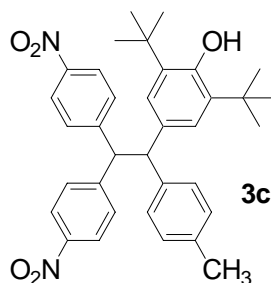
General Procedures. DMSO (content of H_2O < 50 ppm) was used. Stock solutions of $\text{KO}t\text{-Bu}$ were prepared by adding the potassium salt to DMSO under a nitrogen atmosphere. ^1H NMR

spectra were recorded on a Varian Mercury 200 (200 MHz) and on a Bruker AMX 400 (400 MHz). Chemical shifts are expressed in ppm and refer to Me₄Si ($\delta_{\text{H}} = 0.00$ ppm). The coupling constants are given in Hz. The melting point was determined on a Büchi B-540 instrument and is uncorrected. The yields correspond to isolated products without optimization of the work-up. Abbreviations used are s (singlet), d (doublet). The mass spectrum was measured with a Finnigan MAT 95 Q.

Preparation of the potassium salt of bis(4-nitrophenyl)methane (1)

A solution of **1-H** (2.58 g, 10.0 mmol) in THF (160 mL) was added dropwise within 15 min to a solution of potassium ethoxide (840 mg, 10.0 mmol) in EtOH/THF (60 mL / 40 mL) at 0 °C. The solution was concentrated by evaporation to 100 mL in vacuum. Then, toluene (20 mL) was added and evaporation was continued to give a precipitate of dark-blue crystals. After addition of toluene (20 mL) the mixture was filtered and the crystals were washed with two 10 mL portions of toluene. The product was dried in vacuum at 10^{-5} mbar yielding 2.8 g of **1** (94%).

4-[2,2-Bis(4-nitrophenyl)-1-*p*-tolyl-ethyl]-2,6-di-*tert*-butylphenol (3c). To a solution of **1-H** (52 mg, 0.20 mmol) and KO*t*-Bu (4.0 mg, 36 μ mol) in DMSO (2 mL) a solution of quinone methide **2c** (62 mg, 0.20 mmol) in CH₂Cl₂ (3 mL) was added at ambient temperature. After stirring for 5 min the mixture was poured into 1% aqueous HCl (20 mL) at 0 °C. The product was extracted with CH₂Cl₂, the extract dried with Na₂SO₄, and purified by column chromatography on silica gel with hexane/ethyl acetate as eluent. Crystallization from hexane yielded **3c** (85 mg, 75%), mp 193-195 °C.

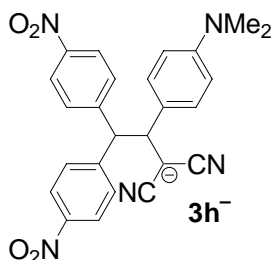


3c: ¹H NMR (CDCl₃, 200 MHz): δ = 1.24 (s, 18 H), 2.21 (s, 3 H), 4.58 (d, $J = 12.2$ Hz, 1 H), 4.86 (d, $J = 12.2$ Hz, 1 H), 4.95 (s, 1 H, OH), 6.75 (s, 2 H), 6.94–6.98 (m, 2 H), 7.05–7.10 (m, 2 H), 7.12–7.18 (m, 2 H), 7.33–7.39 (m, 2 H), 7.93–7.99 (m, 2 H), 7.99–8.05 (m, 2 H). MS (EI, 70eV) m/z (%): 564 (M⁺-H₂), 309 (100), 293 (91), 265 (39), 251 (66). Anal. Calcd. For C₃₅H₃₈N₂O₅: H 6.76 C 74.18 N 4.94% Found: H 6.69 C 74.00 N 4.98%

General procedure. Reaction of 1 with Michael acceptors

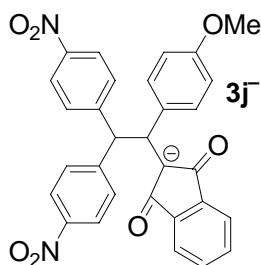
The reactions of **1** with different Michael acceptors were followed by ¹H NMR spectroscopy in *d*₆-DMSO. Equimolar amounts of **1** and **2** in *d*₆-DMSO were mixed in an NMR tube and homogenized in an ultrasound bath.

Reaction of 1 with 2h



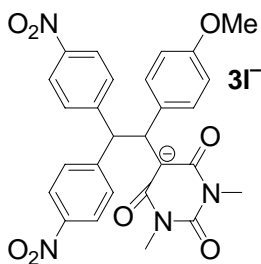
3h⁻: ¹H NMR (*d*₆-DMSO, 200 MHz): δ = 2.76 (s, 6 H), 3.88 (d, *J* = 12.5 Hz, 1 H), 4.64 (d, *J* = 12.5 Hz, 1 H), 6.47 (d, *J* = 8.5 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 7.59–7.70 (m, 4 H), 7.81 (d, *J* = 8.5 Hz, 2 H), 8.14 (d, *J* = 8.5 Hz, 2 H).

Reaction of 1 with 2j



3j⁻: ¹H NMR (*d*₆-DMSO, 200 MHz): δ = 3.58 (s, 3 H), 4.63 (d, *J* = 12.6 Hz, 1 H), 5.82 (d, *J* = 12.6 Hz, 1 H), 6.59 (d, *J* = 8.5 Hz, 2 H), 7.12 (d, *J* = 8.9 Hz, 2 H), 7.36–7.71 (m, 6 H), 7.89–7.95 (m, 6 H).

Reaction of 1 with 2l



3l⁻: ¹H NMR (*d*₆-DMSO, 400 MHz): δ = 2.89 (s, 3 H), 2.98 (s, 3 H), 3.59 (s, 3 H), 5.10 (d, *J* = 12.6 Hz, 1 H), 6.05 (d, *J* = 12.6 Hz, 1 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.9 Hz, 2 H), 7.65 (d, *J* = 8.9 Hz, 2 H), 7.95 (d, *J* = 8.8 Hz, 2 H), 8.00 (d, *J* = 8.8 Hz, 2 H).

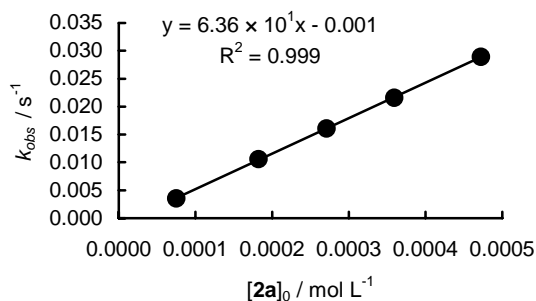
Kinetics in DMSO at 20 °C

The rates of slow reactions ($\tau_{1/2} > 10$ s) were determined by using a J&M TIDAS diode array spectrophotometer which was controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fibre optic cables and standard SMA connectors. The temperature of the solutions of all kinetic experiments was kept constant (20 ± 0.2 °C) by using a circulating bath thermostat and was monitored with a thermo-coupling probe inserted into the reaction mixture. In these experiments three stock solutions were used: A stock solution of the electrophile in DMSO, the CH acid in DMSO and a solution of base. The stock solutions of KO t -Bu were prepared as mentioned above.

For the evaluation of fast kinetics ($\tau_{1/2} < 10$ s) the stopped flow spectrophotometer systems Hi-Tech SF-61DX2 or Applied Photophysics SX.18MV-R were used. Rate constants were obtained by fitting the single exponential $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ to the observed time-dependent carbanion absorbance (averaged from at least 4 kinetic runs for each electrophile concentration). For the stopped flow experiments two stock solutions were used: A solution of the electrophile in DMSO and a solution of the carbanion, generated by the deprotonation of the CH acid with 1.05 equiv. of KO t -Bu the preparation of which was described above.

Reaction of **2a** with **1** (J&M, 783 nm, 20 °C)

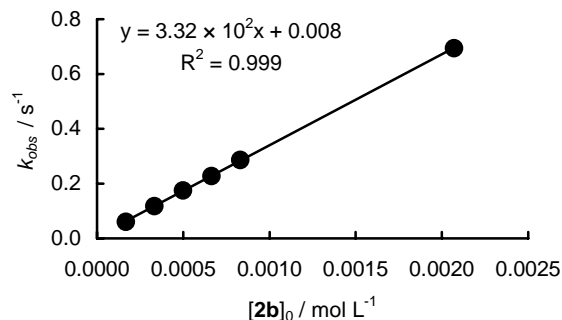
$[\mathbf{2a}]_0 / \text{mol L}^{-1}$	$[\mathbf{C}^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
7.50×10^{-5}	9.92×10^{-6}	3.53×10^{-3}
1.82×10^{-4}	1.05×10^{-5}	1.06×10^{-2}
2.71×10^{-4}	1.04×10^{-5}	1.61×10^{-2}
3.59×10^{-4}	1.04×10^{-5}	2.16×10^{-2}
4.72×10^{-4}	1.09×10^{-5}	2.89×10^{-2}



$$k_2 = 6.36 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2b** with **1** (J&M, 783 nm, 20 °C)

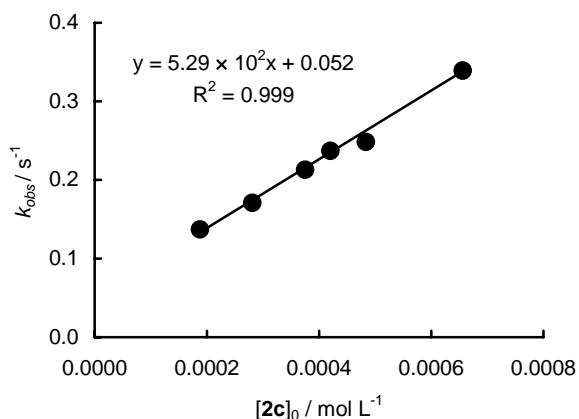
$[\mathbf{2b}]_0 / \text{mol L}^{-1}$	$[\mathbf{C}^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.66×10^{-4}	1.91×10^{-5}	6.04×10^{-2}
3.32×10^{-4}	1.91×10^{-5}	1.18×10^{-1}
4.98×10^{-4}	1.91×10^{-5}	1.76×10^{-1}
6.64×10^{-4}	1.91×10^{-5}	2.28×10^{-1}
8.30×10^{-4}	1.91×10^{-5}	2.86×10^{-1}
2.07×10^{-3}	2.29×10^{-5}	6.95×10^{-1}



$$k_2 = 3.32 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2c** with **1** (J&M, 783 nm, 20 °C)

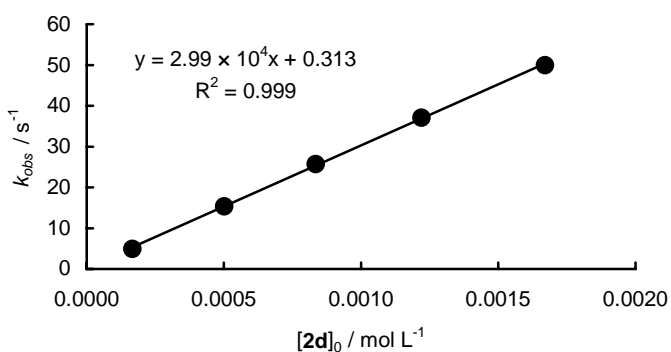
$[2c]_0 / \text{mol L}^{-1}$	$[C^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.88×10^{-4}	2.35×10^{-5}	1.37×10^{-1}
2.81×10^{-4}	2.35×10^{-5}	1.71×10^{-1}
3.75×10^{-4}	2.35×10^{-5}	2.13×10^{-1}
4.20×10^{-4}	2.35×10^{-5}	2.37×10^{-1}
4.83×10^{-4}	2.16×10^{-5}	2.48×10^{-1}
6.56×10^{-4}	2.35×10^{-5}	3.39×10^{-1}



$$k_2 = 5.29 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2d** with **1** (stopped-flow, 783 nm, 20 °C)

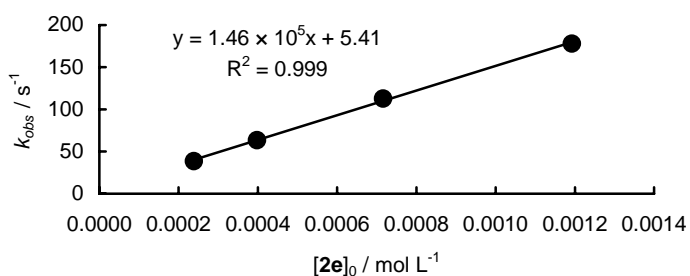
$[2d]_0 / \text{mol L}^{-1}$	$[C^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.67×10^{-4}	2.29×10^{-5}	4.97
5.01×10^{-4}	2.29×10^{-5}	1.54×10^1
8.34×10^{-4}	2.29×10^{-5}	2.57×10^1
1.22×10^{-3}	2.29×10^{-5}	3.71×10^1
1.67×10^{-3}	2.29×10^{-5}	5.00×10^1



$$k_2 = 2.99 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2e** with **1** (stopped-flow, 783 nm, 20 °C)

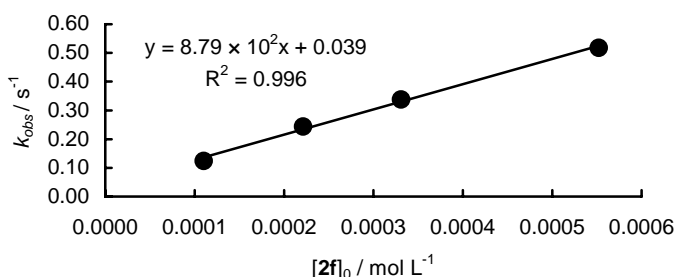
$[2e]_0 / \text{mol L}^{-1}$	$[C^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
2.38×10^{-4}	2.16×10^{-5}	3.87×10^1
3.97×10^{-4}	2.16×10^{-5}	6.35×10^1
7.15×10^{-4}	2.16×10^{-5}	1.13×10^2
1.19×10^{-3}	2.16×10^{-5}	1.78×10^2



$$k_2 = 1.46 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2f** with **1** (stopped-flow, 700 nm, 20 °C)

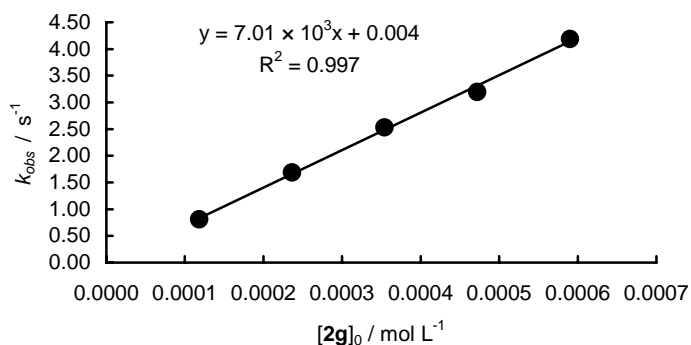
$[\mathbf{2f}]_0 / \text{mol L}^{-1}$	$[\mathbf{C}^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.10×10^{-4}	1.21×10^{-5}	1.25×10^{-1}
2.21×10^{-4}	1.21×10^{-5}	2.44×10^{-1}
3.31×10^{-4}	1.21×10^{-5}	3.38×10^{-1}
5.52×10^{-4}	1.21×10^{-5}	5.18×10^{-1}



$$k_2 = 8.79 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2g** with **1** (stopped-flow, 700 nm, 20 °C)

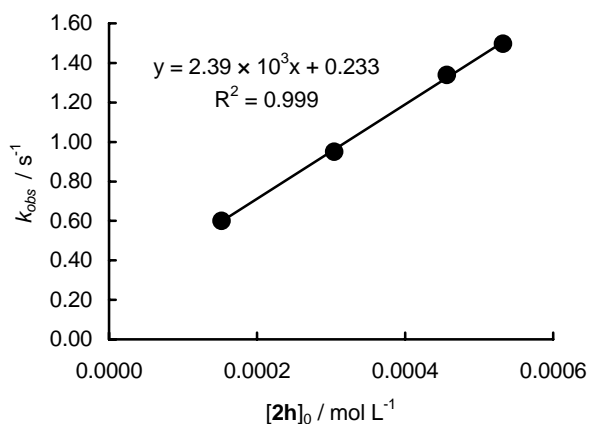
$[\mathbf{2g}]_0 / \text{mol L}^{-1}$	$[\mathbf{C}^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.18×10^{-4}	1.06×10^{-5}	8.10×10^{-1}
2.36×10^{-4}	1.06×10^{-5}	1.69
3.54×10^{-4}	1.06×10^{-5}	2.54
4.72×10^{-4}	1.06×10^{-5}	3.20
5.90×10^{-4}	1.06×10^{-5}	4.19



$$k_2 = 7.01 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2h** with **1** (stopped-flow, 783 nm, 20 °C)

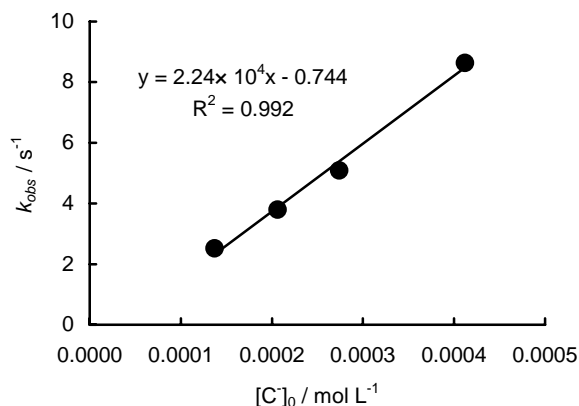
$[\mathbf{2h}]_0 / \text{mol L}^{-1}$	$[\mathbf{C}^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.47×10^{-4}	4.86×10^{-5}	6.00×10^{-1}
3.01×10^{-4}	4.86×10^{-5}	9.52×10^{-1}
4.54×10^{-4}	4.86×10^{-5}	1.34
5.31×10^{-4}	4.86×10^{-5}	1.50



$$k_2 = 2.39 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2i** with **1** (stopped-flow, 470 nm, 20 °C)

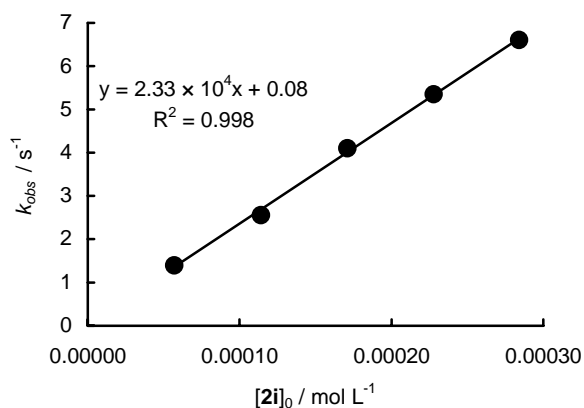
$[2i]_0 / \text{mol L}^{-1}$	$[C^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.22×10^{-5}	1.37×10^{-4}	2.52
1.22×10^{-5}	2.06×10^{-4}	3.80
1.22×10^{-5}	2.74×10^{-4}	5.09
1.22×10^{-5}	4.12×10^{-4}	8.64



$$k_2 = 2.24 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2i** with **1** (stopped-flow, 700 nm, 20 °C)

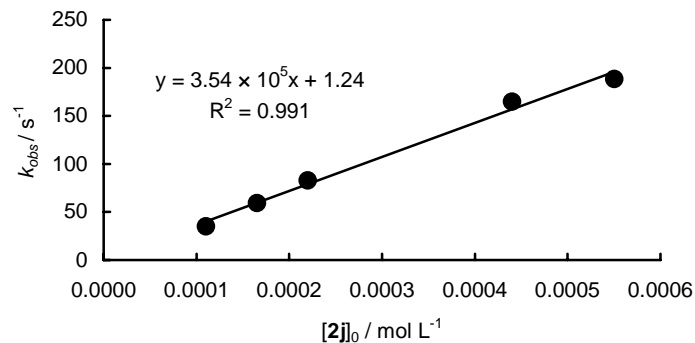
$[2i]_0 / \text{mol L}^{-1}$	$[C^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
5.70×10^{-5}	1.18×10^{-5}	1.46
1.14×10^{-4}	1.18×10^{-5}	2.57
1.71×10^{-4}	1.18×10^{-5}	4.10
2.28×10^{-4}	1.18×10^{-5}	5.38
2.84×10^{-4}	1.18×10^{-5}	6.62



$$k_2 = 2.33 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2j** with **1** (stopped-flow, 700 nm, 20 °C)

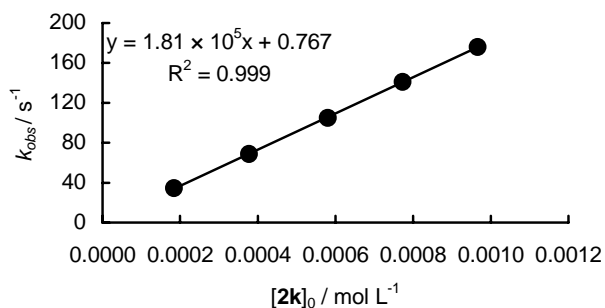
$[2j]_0 / \text{mol L}^{-1}$	$[C^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.10×10^{-4}	1.10×10^{-5}	3.52×10^1
1.65×10^{-4}	1.10×10^{-5}	5.95×10^1
2.20×10^{-4}	1.10×10^{-5}	8.30×10^1
4.40×10^{-4}	1.10×10^{-5}	1.65×10^2
5.50×10^{-4}	1.10×10^{-5}	1.89×10^2



$$k_2 = 3.54 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$$

Reaction of **2k** with **1** (stopped-flow, 783 nm, 20 °C)

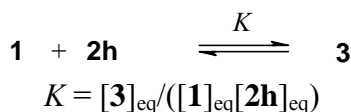
$[\mathbf{2k}]_0 / \text{mol L}^{-1}$	$[\mathbf{C}^-]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
1.84×10^{-4}	1.89×10^{-5}	3.46×10^1
3.77×10^{-4}	1.89×10^{-5}	6.88×10^1
5.80×10^{-4}	1.89×10^{-5}	1.05×10^2
7.73×10^{-4}	1.89×10^{-5}	1.41×10^2
9.66×10^{-4}	1.89×10^{-5}	1.76×10^2



$$k_2 = 1.81 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$$

Equilibrium constant for the reaction of **1** with **2h**

While all reactions of carbanion **1** with electrophiles **2** investigated in this work proceeded with quantitative formation of the addition products, reversible adduct formation was observed for the combination with the benzylidenemalononitrile **2h**. The equilibrium constant K of this reaction was calculated on the basis of the equilibrium concentrations of **1** which were determined photometrically using the stopped-flow technique (Table 3). For that, different amounts of **2h** were mixed with solutions of **1** in DMSO. When the equilibrium was reached, the absorbance of the solution was determined photometrically at the absorbance maximum of **1** at 784 nm (Figure 2).



Assuming the validity of Beer-Lambert's law and that the initial concentrations of **1** and **2h** are $[\mathbf{1}]_0$ and $[\mathbf{2h}]_0$, their equilibrium concentrations are $[\mathbf{1}]_{\text{eq}} = Abs/\epsilon$ (path length $d = 1$ cm) and $[\mathbf{2h}]_{\text{eq}} = [\mathbf{2h}]_0 - [\mathbf{1}]_{\text{eq}}$. The equilibrium concentration of **3** can be calculated as $[\mathbf{3}]_{\text{eq}} = [\mathbf{1}]_0 - [\mathbf{1}]_{\text{eq}}$.

Table 3 shows that higher concentrations of **2h** increase the degree of conversion of the bis-(4-nitrophenyl)methyl anion **1**. The equilibrium constant K calculated as the ratio of the rate constants for the forward and the backward reactions equals 10257 L mol^{-1} . This value is much smaller than the one derived from the concentrations of reactants and products in Table 3.

Table 3. Initial and equilibrium concentrations of **1**, **2h** and **3** for the determination of the equilibrium constant K of the reaction of **1** with **2h**. $\varepsilon(\mathbf{1}) = 97000 \text{ L mol}^{-1}\text{cm}^{-1}$ (from ref. 5), $[\mathbf{1}]_0 = 4.86 \times 10^{-5} \text{ mol L}^{-1}$

$[\mathbf{2h}]_0$ (M)	<i>Abs</i>	$[\mathbf{1}]_{\text{eq}}$ (M)	$[\mathbf{2h}]_{\text{eq}}$ (M)	$[\mathbf{3}]_{\text{eq}}$ (M)	K (L mol ⁻¹)
1.52×10^{-4}	0.450	4.64×10^{-6}	1.47×10^{-4}	4.40×10^{-5}	6.43×10^4
3.04×10^{-4}	0.254	2.62×10^{-6}	3.01×10^{-4}	4.60×10^{-5}	5.83×10^4
4.56×10^{-4}	0.167	1.72×10^{-6}	4.54×10^{-4}	4.69×10^{-5}	5.99×10^4
5.32×10^{-4}	0.144	1.44×10^{-6}	5.31×10^{-4}	4.72×10^{-5}	6.16×10^4

$$K = 61022 \pm 2570 \text{ L mol}^{-1}.$$

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