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 $\log k(20 \, ^\circ\text{C}) = s(N + E)$.

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,

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

where $E$ represents the reactivity of the electrophile, $N$ is a nucleophilicity parameter and $s$ is a nucleophile-specific slope parameter.\textsuperscript{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 $\sigma$-, $n$- and $\pi$-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 \(\text{L mol}^{-1} \text{s}^{-1}\)) for the reactions of 1 with 2a-k in DMSO at 20 °C

<table>
<thead>
<tr>
<th>Electrophile</th>
<th>(E)</th>
<th>(k_2)</th>
<th>Electrophile</th>
<th>(E)</th>
<th>(k_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>-17.29</td>
<td>(6.36 \times 10^1)</td>
<td>2g</td>
<td>-13.56</td>
<td>(7.01 \times 10^3)</td>
</tr>
<tr>
<td>2b</td>
<td>-16.11</td>
<td>(3.32 \times 10^2)</td>
<td>2h</td>
<td>-13.3</td>
<td>(2.39 \times 10^3)</td>
</tr>
<tr>
<td>2c</td>
<td>-15.83</td>
<td>(5.29 \times 10^2)</td>
<td>2i</td>
<td>-12.76</td>
<td>(2.24 \times 10^4)</td>
</tr>
<tr>
<td>2d</td>
<td>-13.39</td>
<td>(2.99 \times 10^4)</td>
<td>2j</td>
<td>-11.32</td>
<td>(3.54 \times 10^5)</td>
</tr>
<tr>
<td>2e</td>
<td>-12.18</td>
<td>(1.46 \times 10^5)</td>
<td>2k</td>
<td>-10.8</td>
<td>(1.81 \times 10^5)</td>
</tr>
<tr>
<td>2f</td>
<td>-14.68</td>
<td>(8.79 \times 10^2)</td>
<td>2l</td>
<td>-10.37</td>
<td>too fast</td>
</tr>
</tbody>
</table>

\(a\) 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 d₆-DMSO solutions were investigated by¹H 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.

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{Acc Acc} \\
\text{H} & \quad \text{K}^+ \\
\text{NO}_2 &
\end{align*}
\]
\[
\begin{align*}
1 & + \\
\text{K} & \quad \text{Acc Acc} \\
\text{H} & \quad \text{X} \\
\text{NO}_2 & 3^- \\
\text{DMSO} &
\end{align*}
\]

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 KOr-Bu for the deprotonation of the CH acid 1-H. The pKₐH value of the addition product 3c⁻ can be estimated to be (pKₐH > 16)¹⁰ higher than that of the CH acid 1-H (pKₐ = 15.1)¹¹, so that 3c⁻ functions as internal base during the reaction (Scheme 2).

\[
\begin{align*}
\text{O} & \quad \text{cat. KOrBu} \\
\text{O} & \quad \text{DMSO} \\
\text{Me} &
\end{align*}
\]
\[
\begin{align*}
1-H & + \\
\text{cat. KOrBu} & \quad \text{DMSO} \\
\text{1-H} & \quad \text{-1⁻} \\
\text{NO}_2 & 3c \\
\text{Me} &
\end{align*}
\]

Scheme 2. Reaction of 1-H with 2c by using catalytic amounts of KOrBu.
Evidence for the formation of the reaction products $3^-$ and $3$ is given by their $^1$H NMR spectra (Table 2) which show characteristic doublets for $H^a$ ($\delta = 4.64–6.05$ ppm) and $H^b$ ($\delta = 3.88–5.10$ ppm).

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

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Adduct</th>
<th>$\delta$(H$^a$)/ppm</th>
<th>$\delta$(H$^b$)/ppm</th>
<th>$J_{ab}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2c</td>
<td>3c</td>
<td>4.86</td>
<td>4.58</td>
</tr>
<tr>
<td>1</td>
<td>2h</td>
<td>3h$^-$</td>
<td>4.64</td>
<td>3.88</td>
</tr>
<tr>
<td>1</td>
<td>2j</td>
<td>3j$^-$</td>
<td>5.82</td>
<td>4.63</td>
</tr>
<tr>
<td>1</td>
<td>2l</td>
<td>3l$^-$</td>
<td>6.05</td>
<td>5.10</td>
</tr>
</tbody>
</table>

**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$\text{t}$-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](image-url)
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 $k_{\text{obs}}$ were derived by least-squares fitting of the single-exponential $A_t = A_0 \exp(-k_{\text{obs}}t) + C$.

$$-\frac{d[1]}{dt} = -\frac{dA}{dt} = k_{\text{obs}}[1]$$  \hspace{1cm} (2)

Plots of $k_{\text{obs}}$ versus the concentrations of the electrophile $[2]_0$ 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 $k_2$ (L mol$^{-1}$ s$^{-1}$) for the reactions of 1 with 2a-k are listed in Table 1.

![Figure 2](image.png)

Figure 2. Determination of the second-order rate constant $k_2 = 2.33 \times 10^4$ L mol$^{-1}$ 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 benzyldienemalononitrile 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 ($97000$ L mol$^{-1}$ cm$^{-1}$)$^5$ we were able to determine the equilibrium constant $K$ as $(61022\pm2570)$ L mol$^{-1}$ corresponding to a reaction free energy of $\Delta_r G^0 = –26.8$ 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 $\Delta G_0^\ddagger = 65.5$ kJ mol⁻¹ by substituting $\Delta G^\ddagger = 52.8$ kJ mol⁻¹ and $\Delta_r G^0 = -26.8$ kJ mol⁻¹ into the Marcus Equation¹² (3) where the work term has been omitted.

$$\Delta G^\ddagger = \Delta G_0^\ddagger + 0.5\Delta_r G^0 + [(\Delta_r G^0)^2/16\Delta G_0^\ddagger]$$  (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 malononitriles have lower intrinsic barriers than olefins activated by alkoxycarbonyl or nitro groups.\textsuperscript{13}

The title compound 1 can be considered as a phenylog of \textit{p}-nitrophenyl nitronate 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 \textit{N} by 3 units. With an \textit{N} parameter of 19.9 the nucleophilicity of anion 1 in DMSO is comparable to those of the nitromethyl anion\textsuperscript{14} and the malononitrile anion in the same solvent\textsuperscript{6} and thus ranks among the most reactive carbanions so far characterized in our nucleophilicity scales.\textsuperscript{1}

![Figure 5](image_url)

\textbf{Figure 5.} Comparison of the nucleophilicities of typical carbanions in DMSO.

\section*{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.

\section*{Experimental Section}

\textbf{General Procedures.} DMSO (content of H\textsubscript{2}O < 50 ppm) was used. Stock solutions of KO\textsubscript{t}-Bu were prepared by adding the potassium salt to DMSO under a nitrogen atmosphere. \textsuperscript{1}H 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 (δ_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 KOt-Bu (4.0 mg, 36 µmol) 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](image)

**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 d₆-DMSO. Equimolar amounts of 1 and 2 in d₆-DMSO were mixed in an NMR tube and homogenized in an ultrasound bath.

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**Reaction of 1 with 2h**

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{NMe}_2 \\
\text{CN} & \quad \text{CN} \\
\text{O}_2\text{N} & \quad \text{3h}^- \\
\end{align*}
\]

3h: \(^1\)H NMR (\(d_6\)-DMSO, 200 MHz): \(\delta = 2.76 (s, 6 \text{ H}), 3.88 (d, J = 12.5 \text{ Hz}, 1 \text{ H}), 4.64 (d, J = 12.5 \text{ Hz}, 1 \text{ H}), 6.47 (d, J = 8.5 \text{ Hz}, 2 \text{ H}), 7.05 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.59–7.70 (m, 4 \text{ H}), 7.81 (d, J = 8.5 \text{ Hz}, 2 \text{ H}), 8.14 (d, J = 8.5 \text{ Hz}, 2 \text{ H}).

**Reaction of 1 with 2j**

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{OMe} \\
\text{O} & \quad \text{3j}^- \\
\end{align*}
\]

3j: \(^1\)H NMR (\(d_6\)-DMSO, 200 MHz): \(\delta = 3.58 (s, 3 \text{ H}), 4.63 (d, J = 12.6 \text{ Hz}, 1 \text{ H}), 5.82 (d, J = 12.6 \text{ Hz}, 1 \text{ H}), 6.59 (d, J = 8.5 \text{ Hz}, 2 \text{ H}), 7.12 (d, J = 8.9 \text{ Hz}, 2 \text{ H}), 7.36–7.71 (m, 6 \text{ H}), 7.89–7.95 (m, 6 \text{ H}).

**Reaction of 1 with 2l**

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{OMe} \\
\text{O} & \quad \text{3l}^- \\
\end{align*}
\]

3l: \(^1\)H NMR (\(d_6\)-DMSO, 400 MHz): \(\delta = 2.89 (s, 3 \text{ H}), 2.98 (s, 3 \text{ H}), 3.59 (s, 3 \text{ H}), 5.10 (d, J = 12.6 \text{ Hz}, 1 \text{ H}), 6.05 (d, J = 12.6 \text{ Hz}, 1 \text{ H}), 6.57 (d, J = 8.8 \text{ Hz}, 2 \text{ H}), 7.42 (d, J = 8.8 \text{ Hz}, 2 \text{ H}), 7.53 (d, J = 8.9 \text{ Hz}, 2 \text{ H}), 7.65 (d, J = 8.9 \text{ Hz}, 2 \text{ H}), 7.95 (d, J = 8.8 \text{ Hz}, 2 \text{ H}), 8.00 (d, J = 8.8 \text{ Hz}, 2 \text{ 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 KOt-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 $A_t = A_0 \exp(-k_{obs}t) + C$ 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 KOt-Bu the preparation of which was described above.

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

<table>
<thead>
<tr>
<th>[2a]₀ / mol L⁻¹</th>
<th>[C]₀ / mol L⁻¹</th>
<th>$k_{obs}$ / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.50 × 10⁻⁵</td>
<td>9.92 × 10⁻⁶</td>
<td>3.53 × 10⁻³</td>
</tr>
<tr>
<td>1.82 × 10⁻⁴</td>
<td>1.05 × 10⁻⁵</td>
<td>1.06 × 10⁻²</td>
</tr>
<tr>
<td>2.71 × 10⁻⁴</td>
<td>1.04 × 10⁻⁵</td>
<td>1.61 × 10⁻²</td>
</tr>
<tr>
<td>3.59 × 10⁻⁴</td>
<td>1.04 × 10⁻⁵</td>
<td>2.16 × 10⁻²</td>
</tr>
<tr>
<td>4.72 × 10⁻⁴</td>
<td>1.09 × 10⁻⁵</td>
<td>2.89 × 10⁻²</td>
</tr>
</tbody>
</table>

$y = 6.36 \times 10^¹ x - 0.001$

$R^2 = 0.999$

$k_2 = 6.36 \times 10^¹$ L mol⁻¹ s⁻¹

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

<table>
<thead>
<tr>
<th>[2b]₀ / mol L⁻¹</th>
<th>[C]₀ / mol L⁻¹</th>
<th>$k_{obs}$ / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.66 × 10⁻⁴</td>
<td>1.91 × 10⁻⁵</td>
<td>6.04 × 10⁻²</td>
</tr>
<tr>
<td>3.32 × 10⁻⁴</td>
<td>1.91 × 10⁻⁵</td>
<td>1.18 × 10⁻¹</td>
</tr>
<tr>
<td>4.98 × 10⁻⁴</td>
<td>1.91 × 10⁻⁵</td>
<td>1.76 × 10⁻¹</td>
</tr>
<tr>
<td>6.64 × 10⁻⁴</td>
<td>1.91 × 10⁻⁵</td>
<td>2.28 × 10⁻¹</td>
</tr>
<tr>
<td>8.30 × 10⁻⁴</td>
<td>1.91 × 10⁻⁵</td>
<td>2.86 × 10⁻¹</td>
</tr>
<tr>
<td>2.07 × 10⁻³</td>
<td>2.29 × 10⁻⁵</td>
<td>6.95 × 10⁻¹</td>
</tr>
</tbody>
</table>

$y = 3.32 \times 10^² x + 0.008$

$R^2 = 0.999$

$k_2 = 3.32 \times 10^²$ L mol⁻¹ s⁻¹
Reaction of 2c with 1 (J&M, 783 nm, 20 °C)

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

\[y = 5.29 \times 10^2 x + 0.052\]
\[R^2 = 0.999\]

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

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

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

\[y = 2.99 \times 10^4 x + 0.313\]
\[R^2 = 0.999\]

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

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

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

\[y = 1.46 \times 10^5 x + 5.41\]
\[R^2 = 0.999\]

\[k_2 = 1.46 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}\]
Reaction of 2f with 1 (stopped-flow, 700 nm, 20 °C)

<table>
<thead>
<tr>
<th>$[2f]_0$ / mol L$^{-1}$</th>
<th>$[C^-]_0$ / mol L$^{-1}$</th>
<th>$k_{obs}$ / s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.10 \times 10^{-4}$</td>
<td>$1.21 \times 10^{-5}$</td>
<td>$1.25 \times 10^{-1}$</td>
</tr>
<tr>
<td>$2.21 \times 10^{-4}$</td>
<td>$1.21 \times 10^{-5}$</td>
<td>$2.44 \times 10^{-1}$</td>
</tr>
<tr>
<td>$3.31 \times 10^{-4}$</td>
<td>$1.21 \times 10^{-5}$</td>
<td>$3.38 \times 10^{-1}$</td>
</tr>
<tr>
<td>$5.52 \times 10^{-4}$</td>
<td>$1.21 \times 10^{-5}$</td>
<td>$5.18 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>$[2g]_0$ / mol L$^{-1}$</th>
<th>$[C^-]_0$ / mol L$^{-1}$</th>
<th>$k_{obs}$ / s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.18 \times 10^{-4}$</td>
<td>$1.06 \times 10^{-5}$</td>
<td>$8.10 \times 10^{-1}$</td>
</tr>
<tr>
<td>$2.36 \times 10^{-4}$</td>
<td>$1.06 \times 10^{-5}$</td>
<td>1.69</td>
</tr>
<tr>
<td>$3.54 \times 10^{-4}$</td>
<td>$1.06 \times 10^{-5}$</td>
<td>2.54</td>
</tr>
<tr>
<td>$4.72 \times 10^{-4}$</td>
<td>$1.06 \times 10^{-5}$</td>
<td>3.20</td>
</tr>
<tr>
<td>$5.90 \times 10^{-4}$</td>
<td>$1.06 \times 10^{-5}$</td>
<td>4.19</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>$[2h]_0$ / mol L$^{-1}$</th>
<th>$[C^-]_0$ / mol L$^{-1}$</th>
<th>$k_{obs}$ / s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.47 \times 10^{-4}$</td>
<td>$4.86 \times 10^{-5}$</td>
<td>$6.00 \times 10^{-1}$</td>
</tr>
<tr>
<td>$3.01 \times 10^{-4}$</td>
<td>$4.86 \times 10^{-5}$</td>
<td>$9.52 \times 10^{-1}$</td>
</tr>
<tr>
<td>$4.54 \times 10^{-4}$</td>
<td>$4.86 \times 10^{-5}$</td>
<td>1.34</td>
</tr>
<tr>
<td>$5.31 \times 10^{-4}$</td>
<td>$4.86 \times 10^{-5}$</td>
<td>1.50</td>
</tr>
</tbody>
</table>

$k_2 = 2.39 \times 10^3$ L mol$^{-1}$ s$^{-1}$
Reaction of 2i with 1 (stopped-flow, 470 nm, 20 °C)

<table>
<thead>
<tr>
<th>[2i]₀ / mol L⁻¹</th>
<th>[C⁻]₀ / mol L⁻¹</th>
<th>kₕobs / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.22 × 10⁻⁵</td>
<td>1.37 × 10⁻⁴</td>
<td>2.52</td>
</tr>
<tr>
<td>1.22 × 10⁻⁵</td>
<td>2.06 × 10⁻⁴</td>
<td>3.80</td>
</tr>
<tr>
<td>1.22 × 10⁻⁵</td>
<td>2.74 × 10⁻⁴</td>
<td>5.09</td>
</tr>
<tr>
<td>1.22 × 10⁻⁵</td>
<td>4.12 × 10⁻⁴</td>
<td>8.64</td>
</tr>
</tbody>
</table>

\[ k₂ = 2.24 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1} \]

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

<table>
<thead>
<tr>
<th>[2i]₀ / mol L⁻¹</th>
<th>[C⁻]₀ / mol L⁻¹</th>
<th>kₕobs / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.70 × 10⁻⁵</td>
<td>1.18 × 10⁻⁵</td>
<td>1.46</td>
</tr>
<tr>
<td>1.14 × 10⁻⁴</td>
<td>1.18 × 10⁻⁵</td>
<td>2.57</td>
</tr>
<tr>
<td>1.71 × 10⁻⁴</td>
<td>1.18 × 10⁻⁵</td>
<td>4.10</td>
</tr>
<tr>
<td>2.28 × 10⁻⁴</td>
<td>1.18 × 10⁻⁵</td>
<td>5.38</td>
</tr>
<tr>
<td>2.84 × 10⁻⁴</td>
<td>1.18 × 10⁻⁵</td>
<td>6.62</td>
</tr>
</tbody>
</table>

\[ k₂ = 2.33 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1} \]

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

<table>
<thead>
<tr>
<th>[2j]₀ / mol L⁻¹</th>
<th>[C⁻]₀ / mol L⁻¹</th>
<th>kₕobs / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.10 × 10⁻⁴</td>
<td>1.10 × 10⁻⁵</td>
<td>3.52 × 10¹</td>
</tr>
<tr>
<td>1.65 × 10⁻⁴</td>
<td>1.10 × 10⁻⁵</td>
<td>5.95 × 10¹</td>
</tr>
<tr>
<td>2.20 × 10⁻⁴</td>
<td>1.10 × 10⁻⁵</td>
<td>8.30 × 10¹</td>
</tr>
<tr>
<td>4.40 × 10⁻⁴</td>
<td>1.10 × 10⁻⁵</td>
<td>1.65 × 10²</td>
</tr>
<tr>
<td>5.50 × 10⁻⁴</td>
<td>1.10 × 10⁻⁵</td>
<td>1.89 × 10²</td>
</tr>
</tbody>
</table>

\[ k₂ = 3.54 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1} \]
Reaction of 2k with 1 (stopped-flow, 783 nm, 20 °C)

<table>
<thead>
<tr>
<th>[2k]₀ / mol L⁻¹</th>
<th>[C']₀ / mol L⁻¹</th>
<th>kₐ₁ / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84 × 10⁻⁴</td>
<td>1.89 × 10⁻⁵</td>
<td>3.46 × 10¹</td>
</tr>
<tr>
<td>3.77 × 10⁻⁴</td>
<td>1.89 × 10⁻⁵</td>
<td>6.88 × 10¹</td>
</tr>
<tr>
<td>5.80 × 10⁻⁴</td>
<td>1.89 × 10⁻⁵</td>
<td>1.05 × 10²</td>
</tr>
<tr>
<td>7.73 × 10⁻⁴</td>
<td>1.89 × 10⁻⁵</td>
<td>1.41 × 10²</td>
</tr>
<tr>
<td>9.66 × 10⁻⁴</td>
<td>1.89 × 10⁻⁵</td>
<td>1.76 × 10²</td>
</tr>
</tbody>
</table>

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

**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 benzylidenedemalononitrile 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).

\[
1 + 2h \underset{K}{\overset{K}{\rightleftharpoons}} 3
\]

\[ K = [3]_{\text{eq}} / ([1]_{\text{eq}}[2h]_{\text{eq}}) \]

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

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. $\varepsilon(1) = 97000$ L mol$^{-1}$cm$^{-1}$ (from ref. 5), $[1]_0 = 4.86 \times 10^{-5}$ mol L$^{-1}$

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

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

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (Ma 673/17) and the Fonds der Chemischen Industrie for support of this work.

References and Notes


10. See http://www.chem.wisc.edu/areas/reich/pkatable/.