The Association Reactions of Ion Radicals with Neutral Molecules. VI. One-to-One and One-to-Two Complexes of Dianions with Hydroxyl Compounds

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Dianions of p-dinitrobenzene (p-DNB) and p-dibenzyloxybenzene (p-DBB) form both A\(^2^-\)/HOR and A\(^2^-\)/2HOR hydrogen-bonded complexes with water and methanol in DMF. Ranges of 0.1 M\(^-1\) to 1.3 M\(^-1\), 5 M\(^-1\) to 160 M\(^-1\), and 3 M\(^-1\) to 50 M\(^-1\) were observed at 273.2 K for \(K_1/\text{[DMF]}\), \(K_{III}/\text{[DMF]}\), and \(K_{IV}/\text{[DMF]}\), respectively. In general, for a particular hydrogen-bond donor/acceptor pair the relative values of \(K_1; K_{III}; K_{IV}\) are of the order of 1:(40–130):(10–40). The relatively small value of \(K_{III}/K_{IV} (\sim 3)\) is a consequence of the fact that the charges of the dianion are relatively distant and each can accommodate one H-bond. The fact that \(K_{IV}\) is invariably larger than \(K_{III}\) shows that partial neutralization of one charge by hydrogen-bonding makes A\(^2^-\)/HOR a weaker H-bond acceptor than A\(^2^-\).

\[
\begin{align*}
A^{--} + \text{ROH/DMF} & \rightleftharpoons A^{--}/\text{HOR} + \text{DMF} \quad (i) \\
A^{2-} + \text{ROH/DMF} & \rightleftharpoons A^{2-}/\text{HOR} + \text{DMF} \quad (ii) \\
A^{2-}/\text{HOR} + \text{ROH/DMF} & \rightleftharpoons A^{2-}/2\text{HOR} + \text{DMF} \quad (iii)
\end{align*}
\]

Anion radicals derived from aromatic compounds form 1:1 hydrogen-bonded complexes with hydroxyl compounds.\(^{1-5}\) The equilibria are readily studied by reversible electrode potential measurements. In aprotic solvents, such as acetonitrile or \(N,N\)-dimethylformamide (DMF), the equilibria are described by eqn. (1):

\[
A^{--} + \text{ROH/solvent} \rightleftharpoons K_A A^{--}/\text{HOR} + \text{solvent}
\]

(1)

in which ROH/solvent represents the hydroxyl compound hydrogen-bonded to the solvent.

Equilibrium constants, \(K/\text{[solvent]}\), ranging from about 0.3 to 50 M\(^-1\) (273–293 K) have been reported for these reactions.\(^{1-5}\) The relatively low values of \(K\) reflect the fact that the hydroxyl compounds are rather tightly hydrogen-bonded to the solvent.\(^{6-7}\)

In this paper we report equilibrium constants for hydrogen-bond formation between the dianions of some difunctional aromatic compounds and water and methanol in DMF, and compare these with those for the corresponding anion radicals. As anticipated, we find that the equilibrium constants for the reactions of the dianions are much larger than those for the corresponding anion radicals. Furthermore, while the anion radicals do not appear to show much tendency to complex with a second molecule of the hydrogen-bond donor, the dianions do.
Results and discussion

In order to study hydrogen-bonding of dianions of aromatic compounds by the effect of the equilibria on reversible potentials it is necessary that both the anion radicals and the dianions are stable under the conditions of the measurements. This places a severe limitation on the possible processes available for study. We selected two substrates which fulfil the necessary criteria, viz. p-dinitrobenzene (p-DNB) and p-dibenzoylbenzene (p-DBB). The consecutive reversible $e^-$ reductions, first to the anion radical and then to the dianion are illustrated in Fig. 1 for p-DNB in DMF.

Scheme 1.

Fig. 1. Cyclic voltammogram at a Pt electrode ($d = 0.6 \text{ mm}$) of 1.0 mM p-DNB in DMF (0.1 M Bu$_4$NBF$_4$, 0.01 M Me$_3$NI) at 0.1 V s$^{-1}$; $T = 273.2 \text{ K}$.

Relationship between reversible electrode potentials and equilibrium constants for hydrogen-bonding. The formation of hydrogen-bonds to electrochemically formed dianions could follow several different pathways as outlined in Scheme 1.

In Scheme 1 and in the following, ROH represents the hydrogen-bonded species ROH/solvent, and the $K$'s (in M$^{-1}$) include the factor [solvent]$^{-1}$.

Previous papers in this series$^1$ have dealt with the determination of hydrogen-bonding equilibria constants ($K_a$) for equilibria (4), using reversible electrode potential measurements and employing eqn. (10) first used by Peover and Davies,$^8$ and in which:

$$\Delta E_2^{rev} = E_2^{rev} - E_2^o$$

$$K_a = \{\exp[\Delta E_2^{rev}/(RT/F)] - 1\}/[\text{ROH}] \quad (10)$$

A contribution to the reversible potentials ($E_2^{rev}$) deriving from equilibrium (7) would result in apparent equilibrium constants ($K_{app}$) which increase with increasing [ROH] as expressed in eqn. (11) (which obviously reduces to eqn. (10) when $K_a = 0$):

$$K_{app} = K_a + K_a K_a [\text{ROH}]$$

$$= \{\exp[\Delta E_2^{rev}/(RT/F)] - 1\}/[\text{ROH}] \quad (11)$$

The observation of constant values of $K_{app}$ over a range of [ROH] was taken as evidence that hydrogen-bonding to a second molecule of ROH does not contribute significantly to the reversible potentials for the formation of acetophenone anion radicals in aprotic solvents,$^2$ and the same observation has been made for p-DNB and p-DBB in this study. Consequently, a reaction pathway including reactions (7) and (9) can be ruled out.

Two pathways leading to hydrogen-bonded dianions remain: (a) The second electron transfer occurs only via A$^-$ [reaction (3)] and A$^2^-$ forms complexes with one or two molecules of ROH [reactions (5) and (8)]. (b) The second electron transfer takes place only via the hydrogen-bonded anion radical A$^-$/HOR [reactions (4) and (6)], and the hydrogen-bonded dianion
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\[ E_3^{rev} = E_3^o + RT/F \ln \left( 1 + K_4 [\text{ROH}] \frac{K_5 K_8[\text{ROH}]}{1 + K_4[\text{ROH}]} \right) \]

(12)

\[ E_6^{rev} = E_6^o + RT/F \ln \left( K_4 + K_4 K_5[\text{ROH}] + K_4 K_5 K_8[\text{ROH}]^2 \right) \]

(13)

may form a hydrogen-bond to an additional molecule of ROH via reaction (8). In case (a), the influence of equilibria (5) and (8) on the reversible potential, \( E_3^{rev} \), is given by eqn. (12), taking into account also the influence of equilibrium (4) on the concentration of \( A^- \). In case (b), the influence of equilibrium (4) and (8) on the reversible potential \( E_6^{rev} \) is given by eqn. (13), which takes into account the influence of equilibrium (5) on the concentration of \( \text{A}^-/\text{HOR} \). \( E_3^o \) can, like \( E_2^o \), be determined experimentally in the absence of ROH, whereas \( E_6^o \) cannot. However, \( E_3^o \) and \( E_6^o \) are related through eqn. (14), expressing that the reduction of \( \text{A}^-/\text{HOR} \) takes place at a more positive potential than reduction of \( \text{A}^- \), since the equilibrium constant for formation of a hydrogen-bond to the dianion, \( K_4 \), is expected to be larger than the equilibrium constant for hydrogen-bond formation to the anion radical, \( K_4 \). Substituting the expression for \( E_6^o \) in eqn. (14) in (13) makes the right-hand side of eqn. (13) equal to that of eqn. (12), i.e. \( E_6^{rev} = E_3^{rev} \). This shows that in the presence of ROH, the shift in reversible potential for the second electron transfer relative to \( E_3^o \) depends on \( K_4, K_5 \) and \( K_8 \) in the same way – namely as expressed in eqn. (12) – independently of the reaction pathway.

Rearrangement of eqn. (12) to eqn. (15) using \( \Delta E_6^{rev} = E_6^{rev} - E_3^o \) shows that \( K_5 \) and \( K_8 \) can be determined from a plot of \( f(\Delta E_3^{rev}, [\text{ROH}]) \) against \([\text{ROH}]\).

The values of \( K_5 \) and \( K_8 \) may also be obtained from measurements of the changes in the difference in reversible potentials for the first and the second electron transfer:

\[ \Delta \Delta E^{rev} = (E_2^{rev} - E_3^{rev}) - (E_2^o - E_3^o) \]

\[ K_5 + K_8[\text{ROH}] = \exp[\Delta E_3^{rev}/(RT/F)] \frac{1}{(1 + K_4[\text{ROH}])} \]

(15)

\[ \Delta \Delta E^{rev} = RT/F \ln \left( (1 + K_4[\text{ROH}])^3/(1 + K_4 K_6[\text{ROH}] K_8 K_8[\text{ROH}]^2) \right) \]

(16)

\[ K_5 + K_8[\text{ROH}] = \exp[-\Delta \Delta E^{rev}/(RT/F)] \frac{1}{(1 + K_4[\text{ROH}])^2} \]

where \( E_2^o - E_3^o \) is the difference in reversible potentials in the absence of ROH. Combining eqns. (10) and (12) gives eqn. (16), similar to that presented earlier, but not used quantitatively, for the effect of \( \text{Li}^+ \) on the difference in reversible potentials for the first and second reduction of dinitrocompounds.\(^{11}\) Rearrangement of eqn. (16) gives eqn. (17), which can be used analogously to eqn. (15) for determination of \( K_5 \) and \( K_8 \).

**Electrode potential measurements.** The changes in peak potentials were assumed to reflect the changes in reversible potentials occurring upon changes in \([\text{ROH}]\). The peak potentials were measured at either a Pt (\( d = 0.6 \) mm), and Au (\( d \)

<table>
<thead>
<tr>
<th>[H₂O]/M</th>
<th>( \Delta E_3^{rev}/mV^b )</th>
<th>( \Delta \Delta E^{rev}/mV^c )</th>
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<tr>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.0056</td>
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</tr>
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<td>0.0278</td>
<td>13.9</td>
<td>–12.9</td>
</tr>
<tr>
<td>0.0333</td>
<td>16.8</td>
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<td>0.0399</td>
<td>19.2</td>
<td>–17.5</td>
</tr>
<tr>
<td>0.0444</td>
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<tr>
<td>0.0500</td>
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</tr>
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<td>0.0555</td>
<td>25.4</td>
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<tr>
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<td>–25.3</td>
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</tr>
<tr>
<td>0.0832</td>
<td>34.3</td>
<td>–32.4</td>
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\(^{a}\)In solvent containing \( \text{Bu}_4\text{NB}_{4} \) (0.1 M) and \( \text{Me}_4\text{NI} \) (0.01 M). \(^{b}\)\( E_3^o - (E_3^{rev})_{[\text{H}_2\text{O}]=0} = 0 \). \(^{c}\)\( (E_3^o - E_3^o) - (E_3^{rev} - E_3^{rev})_{[\text{H}_2\text{O}]=0} = 0 \).
Fig. 2. Plot of $f(\Delta E^o_p, [H_2O]) = \frac{\exp(\Delta E^o_p/(RT/F)(1+K([H_2O]) - 1)}{[H_2O]}$ vs. $[H_2O]$ for 1.0 mM p-dibenzoylbenezene in DMF (0.1 M Bu$_3$NBF$_4$, 0.01 M Me$_3$NI) at $T = 273.2$ K.

Fig. 3. Plot of $g(\Delta E^o_p, [H_2O]) = \frac{\exp(-\Delta E^o_p/(RT/F)(1+K([ROH])^2 - 1)}{[H_2O]}$ vs. $[H_2O]$ for 1.0 mM p-dibenzoylbenezene in DMF (0.1 M Bu$_3$NBF$_4$, 0.01 M Me$_3$NI) at $T = 273.2$ K.

Fig. 4. Plot of $f(\Delta E^o_p, [MeOH]) = \frac{\exp(\Delta E^o_p/(RT/F)(1+K([MeOH]) - 1)}{[MeOH]}$ vs. $[MeOH]$ for 1.0 mM p-dibenzoylbenezene in DMF (0.1 M Bu$_3$NBF$_4$, 0.01 M Me$_3$NI) at $T = 273.2$ K.
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Fig. 5. Plot of \( g(\Delta \Delta E\,^c, [\text{MeOH}]) = \{\exp[-\Delta \Delta E\,^c/(RT/F)](1+K([\text{MeOH}])^2-1)/[\text{MeOH}] \} \) vs. [MeOH] for 1.0 mM \( p \)-dibenzoylbenzene in DMF (0.1 M Bu,NBF_4, 0.01 M Me,NI) at \( T = 273.2 \) K.

= 0.8 mm) or an Hg-plated Pt (\( d = 0.8 \) mm) electrode, using derivative linear sweep voltammetry. With a voltage sweep rate equal to 0.10 V s\(^{-1}\) and substrate concentrations equal to 1.0 mM, the peak potentials can be measured with a precision of about ±0.1 mV.\(^9\) Measurements were first made on solutions of the substrate prepared from dry solvent and supporting electrolyte passed through a column of neutral alumina (Woelm neutral W200) under nitrogen immediately before use. The hydroxylic compounds were then added and measurements were made after each new addition. A complete set of data for one particular experiment, viz. the reduction of \( p \)-DBB in the presence of water, is summarized in Table 1. Data for the reduction of both \( p \)-DNB and \( p \)-DBB are illustrated in Figs. 2–9.

Equilibrium constants for hydrogen-bonding. Equilibrium constants were obtained from plots of the data according to both eqns. (15) and (17),

Fig. 6. As in Fig. 2. Substrate: 1.0 mM \( p \)-dinitrobenzene.
Fig. 7. As in Fig. 3. Substrate: 1.0 mM p-dinitrobenzene.

Fig. 8. As in Fig. 4. Substrate: 1.0 mM p-dinitrobenzene.

Fig. 9. As in Fig. 5. Substrate: 1.0 mM p-dinitrobenzene.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>$K_\text{s}/\text{M}^{-1}$</th>
<th>Measurement</th>
<th>Fig.</th>
<th>ROH</th>
<th>$K_\text{s}/\text{M}^{-1}$</th>
<th>$K_\text{a}/\text{M}^{-1}$</th>
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<tbody>
<tr>
<td>p-DBB</td>
<td>0.84, 0.50$^c$</td>
<td>$\Delta E_\text{p}$</td>
<td>2</td>
<td>HOH</td>
<td>25</td>
<td>8.4</td>
</tr>
<tr>
<td>p-DBB</td>
<td></td>
<td>$\Delta E_\text{p}$</td>
<td>3</td>
<td>HOH</td>
<td>23</td>
<td>8.6</td>
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<tr>
<td>p-DBB</td>
<td>1.25</td>
<td>$\Delta E_\text{p}$</td>
<td>4</td>
<td>MeOH</td>
<td>160</td>
<td>49</td>
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<tr>
<td>p-DBB</td>
<td></td>
<td>$\Delta E_\text{p}$</td>
<td>5</td>
<td>MeOH</td>
<td>161</td>
<td>44</td>
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<tr>
<td>p-DNB</td>
<td>0.35, 0.11$^c$</td>
<td>$\Delta E_\text{p}$</td>
<td>6</td>
<td>HOH</td>
<td>4.7</td>
<td>4.4</td>
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<td>p-DNB</td>
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<td>$\Delta E_\text{p}$</td>
<td>9</td>
<td>MeOH</td>
<td>19</td>
<td>4.6</td>
</tr>
</tbody>
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$^a$Measurements in DMF/ Bu$_4$NBF$_4$ (0.1 M)/Me$_2$N(0.1 M) by derivative linear sweep voltammetry at 100 mV s$^{-1}$. All measurements were made at 0°C. $^b$Equilibrium constant for hydrogen-bonding reactions of the anion radicals reported in Ref. 5. $^c$Values observed in this work.

using the measured values of $\Delta E_{\text{p}}$ and $\Delta E_{\text{p}}$ for $\Delta E_{\text{p}}$ and $\Delta E_{\text{p}}$, respectively. Values of $K_\text{s}$ for ROH = H$_2$O were obtained from independent measurements of $E_\text{p}$ in the concentration range 0–0.5 M and application of eqn. (10); for ROH = MeOH they were taken from previous work.$^3$ The quantities on the right-hand sides of eqns. (15) and (17), $f(\Delta E_{\text{p}},[\text{ROH}])$ and $g(\Delta E_{\text{p}}, [\text{ROH}])$, respectively, were plotted as the ordinate vs. [ROH] as the abscissa. The intercepts of the plots gave $K_\text{s}$ while the slopes of the linear regression lines gave values of $K_\text{s}/K_\text{s}$. The data were plotted according to eqn. (15) in Figs. 2, 4, 6 and 8, and according to eqn. (17) in Figs. 3, 5, 7 and 9. In general, the correlation for data sets obtained measuring $\Delta E_{\text{p}}$ is slightly better than for those obtained measuring $\Delta E_{\text{p}}$. This could be related to the fact that small instabilities in the reference electrode are compensated for by the recording of potential differences, $E_{\text{p}} - E_\text{p}$, in the former type of measurements. The apparent curvature in the $\Delta E_{\text{p}}$-data for the complexation of MeOH with the p-DNB dianion (Fig. 9) was considered insignificant, as no such trend was found for the corresponding $\Delta E_{\text{p}}$-measurements (Fig. 8). The equilibrium constants resulting from the linear regression analyses are tabulated in Table 2.

In all cases the values for $K_\text{s}$ determined by the two types of measurements are in excellent agreement, while the values obtained for $K_\text{s}$ are more uncertain as could be expected due to their smaller magnitude.

### Hydrogen-bonding equilibria of dianions

Three of the four hydrogen-bond donor/acceptor pairs exhibit $K_\text{s}/K_\text{s}$ values of 3–5. The exception, i.e. p-DNB$^2^- +$ H$_2$O, shows an equilibrium constant ratio of about 1.5. The reason for this exception is not clear, but as evident from Figs. 4 and 5 this is the data set for which the poorest correlation was found.

The charge in both dianions can be considered to be strongly localized on the oxygen atoms of the functional groups. Thus, the equilibria can be approximated by eqns. (18) and (19), where Z represents the functional group (either NO$_2$ or PhCO). The charges in the corresponding anion radicals are considerably more dispersed since both functional groups are equally involved. It seems likely that hydrogen-bonding localizes the charge to a certain degree, so that the equilibria can be approximated by eqn. (20). A comparison of eqn. (19) with eqn. (20), and of the corresponding equilibrium constants, $K_\text{s}$ and $K_\text{s}$, is revealing. Even when one of the charges in the mono-hydrogen-bonded dianion is essentially localized by the existing H-bond, hydrogen-bonding to the other site is still considerably more favorable than H-bonding to the anion radical, i.e. $K_\text{s}/K_\text{s}$ falls in the range of about 10 to 40.

$$
\text{Z} = \text{Z} + \text{ROH} \rightleftharpoons \text{ROH} = \text{Z} + \text{Z} \quad (18)
$$

$$
\text{ROH} = \text{Z} + \text{Z} + \text{ROH} \rightleftharpoons \text{ROH} = \text{Z} + \text{Z} \quad (19)
$$

$$
\left[ \text{Z} = \text{Z} \right] = \text{Z} + \text{Z} \quad (20)
$$
Experimental

The cells, electrodes and instruments employed were as previously described. The potential measurements were made by derivative linear sweep voltammetry (DLSV), and the peak potentials were determined from linear regression of a few points around the apparent zero-crossings. All measurements were carried out at 0.1 V s\(^{-1}\) and \(T = 273.2\) K.

\(p\)-Dinitrobenzene and \(p\)-dibenzoylbenzene were of reagent grade and were purified by conventional methods before use.

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References


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