The Association Reactions of Ion Radicals with Neutral Molecules.

I. Thermodynamic Parameters for the Association of
Benzenaldehyde Anion Radical with Alcohols in
N,N-Dimethylformamide

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Equilibrium constants for hydrogen bonding of benzenaldehyde anion radical to aliphatic alcohols in DMF were determined from reversible electrode potential measurements. Measurements were made by phase selective second harmonic A.C. voltammetry at temperatures ranging from 273 to 292 K. The thermodynamic parameters for hydrogen bonding equilibria were observed to depend upon the structure of the alcohol. The equilibrium constants at 273 K are related to the steric size of the alcohols, being largest for methanol (28.1 M⁻¹) and smallest for tert-butanol (6.8 M⁻¹). It was concluded that the data refer to equilibrium (i) and that equilibria involving the

\[
\text{PhCHO}^- + \text{ROH} \rightleftharpoons \text{PhCH}^- \cdots \text{HOR} + \text{Me}_2\text{NCHO} \tag{i}
\]

free alcohols do not play an important role. There is no evidence for the formation of complexes containing more than one molecule of alcohol.

The reactivity and the reaction pathways followed by ion radicals are strongly dependent upon the form in which the ion radical exists in solution. In aprotic solvents such as acetonitrile or N,N-dimethylformamide (DMF), the equilibrium constants for ion-pair formation between ion radicals and counter ions are generally small so that the ions can be considered to be essentially free species. On the other hand, when the ion pair is sufficiently more reactive than the free ion, reactions may pass through the thermodynamically unfavorable equilibrium anyway. For example, the dimerization of diethyl fumarate anion radical (DEF⁻) is greatly accelerated in the presence of alkali metal cations, ≈3 yet equilibrium (1) was not detected by reversible potential measurements during

\[
\text{DEF}^- + \text{M}^+ \overset{k_1}{\rightleftharpoons} \text{DEF}^-/\text{M}^+ \tag{1}
\]

\[
\text{DEF}^-/\text{M}^+ + \text{DEF}^- \overset{k_2}{\rightarrow} \text{dimer} \tag{2}
\]

the reduction of DEF in DMF. The rate acceleration was observed to be due to the fact that the specific rate constant for reaction (2) is of the order of 10⁶ times that for the dimerization of DEF⁻. In other cases, such as the reduction of quinones, aromatic nitro compounds, benzaldehydes, aromatic ketones and azo compounds, ion-pairing in aprotic solvents is readily detected by electrode potential measurements.

The association of ion radicals with neutral compounds has been investigated to a much lesser extent. Kinetic studies on the dimerization of DEF⁻ in DMF containing water indicate the existence of a 1/1 complex of the anion radical with water. The thermodynamics of this equilibrium (3) have been studied by

\[
\text{DEF}^- + \text{H}_2\text{O} \overset{K}{\rightleftharpoons} \text{DEF}^-/\text{H}_2\text{O} \tag{3}
\]
phase selective second harmonic A.C. voltammetry (SHAC). The reaction is exothermic with $\Delta H^\circ$ equal to $-6$ kcal/mol and is made less favorable by a large negative $\Delta S^\circ$, i.e. $-21$ cal/K mol. Other anion radicals also form 1/1 complexes with water. These have been detected during the dimerization of benzaldehyde anion radical in aqueous ethanol and during the dimerization of 9-cyanoanthracene anion radical in aqueous DMF. It has been suggested that the formation of 1/1 complexes of anion radicals with water is not general and that in some cases there is evidence, i.e. during the reduction of acetophenone in acetonitrile, for the formation of complexes containing more than one molecule of water. However, at low $[H_2O]$ in aprotic solvents it is likely that only the 1/1 complexes exist in significant concentrations. An early ESR study indicated that the equilibrium constant for the association of one molecule of water with the anion radical of benzoquinone is of the order of 10$^3$ greater than that for the association with a second water molecule.

Hydrogen bonding has been observed to be the attractive force in the 1/1 complexes between $p$-dinitrobenzene anion radical and some substituted phenylacetylenes. Ninyhydrin anion radical has also been observed to form a 1/1 hydrogen bonded complex with ethanol in hexamethylophosphoramide (HMPA). It is likely that the complexes between water or alcohols with anion radicals in general are of the hydrogen bonded type.

This paper is the first in a series which will describe the results of a systematic study of the association reactions of ion radicals with neutral compounds. The association of benzaldehyde anion radical with alcohols is discussed in this paper. The substrate was chosen because of the strong polarity of the carbonyl group which should accentuate the hydrogen bonding reactions of the anion radical so that the equilibrium constants are great enough to determine by electrode measurements. The alcohols offer the opportunity to make structural variations while keeping the nature of the functional group intact.

RESULTS AND DISCUSSION

The measurement technique. When a reversible charge transfer reaction (4) is coupled to equilibria involving the primary intermediate B (5), the reversible potential ($E_{rev}$) for (4) can be affected, depending on the magnitude of $K_s$. The effect of reaction (5)

$$A + e^- \rightleftharpoons B$$  (4)

$$B + X \rightleftharpoons B/X$$  (5)

$$\Delta E_{rev} = RT/F \ln(1 + K_s[X])$$  (6)

on $E_{rev}$ is given by eqn. (6). The determination of $E_{rev}$ as a function of $[X]$ allows for the determination of $K_s$. The potential measurements are frequently complicated by other rapid irreversible reactions of intermediate B. When this is the case, the most effective method to determine $E_{rev}$ is by the use of phase sensitive second harmonic A.C. voltammetry (SHAC). The reactions are often second order in B and their effect on the electrode potential can be minimized by employing low substrate concentrations. In related measurements we have observed precision in $E_{rev}$ measurements of the order of $\pm 0.1$ mV using SHAC.

Reversible potential measurements. Reversible potentials for reactions (7) + (8) were carried out by SHAC on solutions of

$$\text{PhCHO} + e^- \rightleftharpoons \text{PhCHO}^-$$  (7)

$$\text{PhCHO}^- + \text{ROH} \rightleftharpoons \text{PhCHO}^{2-} + \text{ROH}$$  (8)

benzaldehyde in $N,N$-dimethylformamide in the presence of a number of aliphatic alcohols (ROH). Under the conditions of the measurements $\text{PhCHO}^{2-}$ undergoes a rapid second order dimerization. In order to insure that the potentials measured by SHAC are the reversible values very low substrate concentrations (0.1 mM) were employed. It was also shown that the measured $E_{rev}$ were both frequency (100 and 300 Hz) and phase (quadrature and in phase components) independent. For each equilibrium constant measurement, ($E_{rev}$)$_0$ (the reversible potential in the absence of alcohol) had to be determined. This was accomplished by measurements carried out immediately after passing the solvent—electrolyte solution through a column containing neutral alumina into a pre-dried

Table 1. Reversible potential changes and equilibrium constants for the association of benzaldehyde anion radical with methanol in DMF.\textsuperscript{a}

<table>
<thead>
<tr>
<th>T/K</th>
<th>[CH\textsubscript{3}OH]/M</th>
<th>$\Delta E_{rev}$/mV</th>
<th>$K^b/M^{-1}$</th>
<th>$(K/M^{-2})^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>289.9</td>
<td>0.164</td>
<td>28.3</td>
<td>12.8</td>
<td>78.3</td>
</tr>
<tr>
<td>289.9</td>
<td>0.325</td>
<td>45.4</td>
<td>15.9</td>
<td>48.9</td>
</tr>
<tr>
<td>289.9</td>
<td>0.485</td>
<td>56.3</td>
<td>17.6</td>
<td>36.3</td>
</tr>
<tr>
<td>289.9</td>
<td>0.642</td>
<td>62.6</td>
<td>17.6</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.0 (2.2)</td>
<td></td>
</tr>
<tr>
<td>282.7</td>
<td>0.164</td>
<td>34.2</td>
<td>18.8</td>
<td>114.6</td>
</tr>
<tr>
<td>282.7</td>
<td>0.325</td>
<td>49.5</td>
<td>20.4</td>
<td>62.7</td>
</tr>
<tr>
<td>282.7</td>
<td>0.485</td>
<td>60.2</td>
<td>22.4</td>
<td>46.2</td>
</tr>
<tr>
<td>282.7</td>
<td>0.642</td>
<td>67.5</td>
<td>23.4</td>
<td>36.4</td>
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<td></td>
<td></td>
<td></td>
<td>21.3 (2.1)</td>
<td></td>
</tr>
<tr>
<td>273.1</td>
<td>0.164</td>
<td>38.2</td>
<td>25.3</td>
<td>232.9</td>
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<td>273.1</td>
<td>0.325</td>
<td>53.8</td>
<td>27.7</td>
<td>85.2</td>
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<tr>
<td>273.1</td>
<td>0.485</td>
<td>63.2</td>
<td>28.8</td>
<td>59.4</td>
</tr>
<tr>
<td>273.1</td>
<td>0.642</td>
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<td>30.5</td>
<td>47.5</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>28.1 (2.2)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measurements by SHAC in DMF containing Bu\textsubscript{4}NBF\textsubscript{4} (0.1 M). \textsuperscript{b} Calculated assuming the formation of 1/1 complexes of anion radical with the alcohols. \textsuperscript{c} Calculated assuming that two molecules of alcohol complex with one anion radical.

Table 2. Reversible potential changes and equilibrium constants for the association of benzaldehyde anion radical with ethanol in DMF.\textsuperscript{a}

<table>
<thead>
<tr>
<th>T/K</th>
<th>[ethanol]/M</th>
<th>$\Delta E_{rev}$/mV</th>
<th>$K^b/M^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>291.6</td>
<td>0.0856</td>
<td>14.8</td>
<td>9.3</td>
</tr>
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<td>291.6</td>
<td>0.171</td>
<td>23.6</td>
<td>9.1</td>
</tr>
<tr>
<td>291.6</td>
<td>0.257</td>
<td>30.5</td>
<td>9.2</td>
</tr>
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<td>0.343</td>
<td>37.6</td>
<td>10.1</td>
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<td></td>
<td></td>
<td>9.4 (0.5)</td>
</tr>
<tr>
<td>283.0</td>
<td>0.0856</td>
<td>18.6</td>
<td>13.4</td>
</tr>
<tr>
<td>283.0</td>
<td>0.171</td>
<td>29.4</td>
<td>13.7</td>
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<tr>
<td>283.0</td>
<td>0.257</td>
<td>37.5</td>
<td>14.2</td>
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<td>0.343</td>
<td>43.4</td>
<td>14.4</td>
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<td></td>
<td></td>
<td></td>
<td>13.9 (0.5)</td>
</tr>
<tr>
<td>273.0</td>
<td>0.0856</td>
<td>21.1</td>
<td>17.0</td>
</tr>
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<td>0.171</td>
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<td>18.1</td>
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<td>0.343</td>
<td>49.0</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.6 (1.5)</td>
</tr>
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\textsuperscript{a} Measurements by SHAC in DMF containing Bu\textsubscript{4}NBF\textsubscript{4} (0.1 M).

Table 3. Reversible potential changes and equilibrium constants for the association of benzaldehyde anion radical with 1-propanol in DMF.\textsuperscript{a}

<table>
<thead>
<tr>
<th>T/K</th>
<th>[1-propanol]/M</th>
<th>$\Delta E_{rev}$/mV</th>
<th>$K^b/M^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>290.6</td>
<td>0.0881</td>
<td>17.7</td>
<td>11.7</td>
</tr>
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<td>290.6</td>
<td>0.175</td>
<td>29.2</td>
<td>12.6</td>
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<td>290.6</td>
<td>0.261</td>
<td>37.9</td>
<td>13.6</td>
</tr>
<tr>
<td>290.6</td>
<td>0.346</td>
<td>44.8</td>
<td>14.4</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>13.2 (1.2)</td>
</tr>
<tr>
<td>283.9</td>
<td>0.0881</td>
<td>17.8</td>
<td>12.2</td>
</tr>
<tr>
<td>283.9</td>
<td>0.175</td>
<td>28.4</td>
<td>12.5</td>
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<tr>
<td>283.9</td>
<td>0.261</td>
<td>36.9</td>
<td>13.5</td>
</tr>
<tr>
<td>283.9</td>
<td>0.346</td>
<td>44.1</td>
<td>14.7</td>
</tr>
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<td></td>
<td></td>
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<td>13.2 (1.1)</td>
</tr>
<tr>
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<td>0.0881</td>
<td>17.2</td>
<td>12.2</td>
</tr>
<tr>
<td>272.7</td>
<td>0.175</td>
<td>27.1</td>
<td>12.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measurements by SHAC in DMF containing Bu\textsubscript{4}NBF\textsubscript{4} (0.1 M).

Table 4. Reversible potential changes and equilibrium constants for the association of benzaldehyde anion radical with 2-propanol in DMF.\textsuperscript{a}

<table>
<thead>
<tr>
<th>T/K</th>
<th>[2-propanol]/M</th>
<th>$\Delta E_{rev}$/mV</th>
<th>$K^b/M^{-1}$</th>
</tr>
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<tr>
<td>290.6</td>
<td>0.0861</td>
<td>13.1</td>
<td>8.0</td>
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<td>290.6</td>
<td>0.171</td>
<td>21.8</td>
<td>8.1</td>
</tr>
<tr>
<td>290.6</td>
<td>0.255</td>
<td>28.6</td>
<td>8.4</td>
</tr>
<tr>
<td>290.6</td>
<td>0.378</td>
<td>34.2</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.1 (0.3)</td>
</tr>
<tr>
<td>281.1</td>
<td>0.0861</td>
<td>11.6</td>
<td>7.1</td>
</tr>
<tr>
<td>281.1</td>
<td>0.171</td>
<td>18.8</td>
<td>6.9</td>
</tr>
<tr>
<td>281.1</td>
<td>0.255</td>
<td>24.7</td>
<td>7.0</td>
</tr>
<tr>
<td>281.1</td>
<td>0.378</td>
<td>29.4</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.8 (0.4)</td>
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<tr>
<td>273.1</td>
<td>0.0861</td>
<td>12.9</td>
<td>8.6</td>
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<tr>
<td>273.1</td>
<td>0.171</td>
<td>20.3</td>
<td>8.1</td>
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<tr>
<td>273.1</td>
<td>0.255</td>
<td>28.8</td>
<td>9.5</td>
</tr>
<tr>
<td>273.1</td>
<td>0.378</td>
<td>33.5</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.7 (0.6)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measurements by SHAC in DMF containing Bu\textsubscript{4}NBF\textsubscript{4} (0.1 M).

Table 5. Reversible potential changes and equilibrium constants for the association of benzaldehyde anion radical with 1-butanol in DMF.

<table>
<thead>
<tr>
<th>T/K</th>
<th>[1-butanol]/M</th>
<th>ΔE&lt;sub&gt;rev&lt;/sub&gt;/mV</th>
<th>K/M&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
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<tr>
<td>290.6</td>
<td>0.072</td>
<td>14.4</td>
<td>10.8</td>
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<td>290.6</td>
<td>0.143</td>
<td>24.4</td>
<td>11.5</td>
</tr>
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<td>290.6</td>
<td>0.213</td>
<td>32.3</td>
<td>12.4</td>
</tr>
<tr>
<td>290.6</td>
<td>0.283</td>
<td>38.5</td>
<td>12.9 (0.9)</td>
</tr>
<tr>
<td>282.5</td>
<td>0.072</td>
<td>17.6</td>
<td>14.7</td>
</tr>
<tr>
<td>282.5</td>
<td>0.143</td>
<td>27.0</td>
<td>14.2</td>
</tr>
<tr>
<td>273.3</td>
<td>0.072</td>
<td>14.3</td>
<td>11.6</td>
</tr>
<tr>
<td>273.3</td>
<td>0.143</td>
<td>23.4</td>
<td>11.9</td>
</tr>
</tbody>
</table>

*Measurements by SHAC in DMF containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M).*

lated using eqn. (6) and assuming reaction (8) are tabulated in Tables 1 to 6 where ROH is methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and tert-butanol, respectively. Eqn. (8), as will be discussed later, is an oversimplification in that all alcohols used are hydrogen bonded to the solvent. This method of determining equilibrium constants, like other related spectroscopic methods, requires that the stoichiometric coefficient of ROH in eqn. (8) [or X in the general equation (5)] be known or assumed. On the other hand, if measurements are made at several concentrations the consistency of the equilibrium constants obtained gives a measure of how well the data fit eqn. (6). In some cases, there appears to be a slight upward trend in the K values while in others no trends are apparent. The last column in Table 1 gives equilibrium constants which assume that two molecules of methanol complex with benzaldehyde anion radical. Very large downward trends as [MeOH] increases are observed in these K values. The stoichiometric coefficient for methanol which gives the most consistent equilibrium constants was found to be 1.1. In fact, in all of the cases where an upward trend is observed in K, more consistent equilibrium constants were obtained by assuming stoichiometric coefficients of 1.1 for the alcohols.

Since trends in the calculated equilibrium constants are only observed in some of the cases and when they are the deviations are not great, it appears safe to assume that equilibria (8) describes the interactions between PhCHO<sup>−</sup> and aliphatic alcohols in DMF. Making this assumption resulted in K values with standard deviations of less than ±10 % in all cases other than when ROH was methanol. It is possible that the small deviations are due to equilibria involving more than one molecule of alcohol. If this is the case, these equilibria are of minor importance as compared to the primary equilibria.

Table 6. Reversible potential changes and equilibrium constants for the association of benzaldehyde anion radical with tert-butanol in DMF.

<table>
<thead>
<tr>
<th>T/K</th>
<th>[r-butanol]/M</th>
<th>ΔE&lt;sub&gt;rev&lt;/sub&gt;/mV</th>
<th>K/M&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>291.0</td>
<td>0.0694</td>
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<td>5.7</td>
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<td>291.0</td>
<td>0.138</td>
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<td>5.3</td>
</tr>
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<td>0.205</td>
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<td>0.272</td>
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<td>7.8</td>
<td>5.5</td>
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<td>0.204</td>
<td>19.8</td>
<td>6.1</td>
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<td></td>
<td>5.8 (0.3)</td>
</tr>
<tr>
<td>273.1</td>
<td>0.0694</td>
<td>9.7</td>
<td>7.4</td>
</tr>
<tr>
<td>273.1</td>
<td>0.138</td>
<td>15.9</td>
<td>7.0</td>
</tr>
<tr>
<td>273.1</td>
<td>0.204</td>
<td>19.1</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.8 (0.7)</td>
</tr>
</tbody>
</table>

*Measurements by SHAC in DMF containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M).*

\[
\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]

with \( \Delta H^o \) equal to -5.3 and -5.7 kcal/mol, respectively. There were only small effects of temperature on K for the other alcohols and the plots were not linear.

There are a number of features of the data which warrant discussion. The equilibrium constants are related to the steric size of the alcohols, decreasing in magnitude from methanol to tert-butanol. With the primary alcohols, 1-propanol and 1-butanol, K was very nearly the same while
Table 7. Thermodynamic parameters for the hydrogen bonding of alcohols to DMF and to benzaldehyde anion radical.

<table>
<thead>
<tr>
<th>ROH</th>
<th>$-(\Delta H^0)_{10}/$ kcal/mol</th>
<th>$-(\Delta S^0)_{10}/$ cal/mol</th>
<th>$-(\Delta G^0)_{273}/$ kcal/mol</th>
<th>$(K_8)_{273}/$ M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>3.8</td>
<td>9.1</td>
<td>3.1</td>
<td>300</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.9</td>
<td>10.5</td>
<td>2.6</td>
<td>120</td>
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<tr>
<td>t-Butanol$^c$</td>
<td>3.9</td>
<td>11.0</td>
<td>1.9</td>
<td>33</td>
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</table>

$^a$ Parameters for equilibrium (10) from Ref. 35. $^b$ Parameters for equilibria (8) at 273 K. $^c$ Assumes $\Delta H^o$ of 0 for the data in Table 6.

the value in the presence of 2-propanol was significantly smaller. This suggests that as the congestion around the hydroxyl group gets greater, $K$ becomes smaller. Another interesting feature of the data is that the two equilibria with measurable $\Delta H^0$ are made less favorable by significantly large negative values of $\Delta S^0$.

A more detailed description of the equilibria. The alcohols used in this study are strongly hydrogen-bonded to the solvent, DMF. Thermodynamic data have been reported for equilibria (10) where

\[
R-O-H + HCON(CH_3)_2 \rightleftharpoons K_{10}^{10} \text{ROH} - H + HCON(CH_3)_2
\]

\[
R-O-H \ldots O = C - N(CH_3)_2 \quad (10)
\]

\[\text{H}\]

ROH is methanol, ethanol and tert-butanol.$^{35}$ The values reported for $\Delta H^0$ and $\Delta S^0$ for equilibria (10) measured in CCl$_4$ are summarized in Table 7. Since there is very little dependence of the parameters on the structure of the alcohol, it is most likely that values for the other alcohols used in this study would fall within the ranges of values in Table 7. These data indicate that in all cases equilibria (10) will lie far to the right when the solvent is DMF and very little alcohol will exist in the free form. Thus, the equilibria that are reflected in the reversible potential changes are (11). In order to estimate the thermodynamic parameters for

\[
\text{PhCHO}^- + \text{ROH}/\text{DMF} \rightleftharpoons K_{11}^{11} \text{PhCHO}^-/\text{ROH} + \text{DMF}
\]

equilibria (8), in which ROH is not hydrogen bonded to the solvent, it is necessary to add the parameters for (10) and (11). The last two columns in Table 7 contain estimates of $\Delta G^0$ and $K_8$ at 273 K. These estimates are enlightening. The equilibrium constants for hydrogen bonding to PhCHO$^-$ with free alcohol [eqn. (8)] are only from 5 to 10 times as great as those for hydrogen bonding with the ROH/DMF complex [eqn. (11)]. Thus, equilibria (8) are of minor importance in the discussion of the behaviour of PhCHO$^-$ in DMF containing alcohols since the ratio [ROH/DMF]/[ROH] is in all cases of the order of $10^2$. In order for equilibrium (8) to become significant in comparison to (11), it would be necessary to have mol ratios, $n_{\text{ROH}}/n_{\text{DMF}}$, greater than unity, i.e. [ROH]$>_{13}$ M.

Conclusions. This work, as well as other recent studies,$^{22,23}$ shows that anion radicals form hydrogen bonded complexes with proton donors. The formation of these 1/1 complexes are made somewhat less favorable in solvents such as DMF since the proton donors also undergo hydrogen bonding with the solvent. There is no evidence at this time for complexes of anion radicals with more than one molecule of the proton donor.

EXPERIMENTAL

Reversible potential measurements by SHAC have been described in detail in a previous paper.$^{27}$ The instrumentation and data handling procedures were similar to those described earlier.$^{36}$ Reagent grade alcohols were used without further purification.

REFERENCES


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