

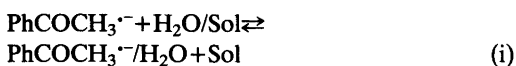
# The Association Reactions of Ion Radicals with Neutral Molecules.

## II. The One-to-One Complex Between Acetophenone Anion Radical and Water

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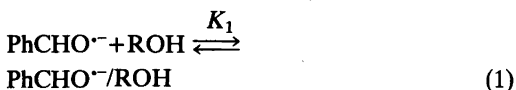
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Acetophenone anion radical forms a one-to-one complex with water in acetonitrile, in DMF and in mixtures of the two solvents. The reactions appear to be very nearly thermoneutral and are driven by positive entropies of reaction. The equilibrium constants for the association reactions were observed to be about 3 times as great in acetonitrile as in DMF and to decrease as the mol fraction of DMF was increased in the mixed solvent. It was only possible to make reliable measurements at water concentrations up to about 0.5 M. At higher  $[H_2O]$  a significant A.C. phase shift was observed, probably due to adsorption processes. The reason for the larger equilibrium constants in acetonitrile is most likely connected to the fact that water is less strongly bound to acetonitrile than to DMF. In either case the concentration of free water is very small and the equilibrium constants measured refer to reaction (i). It was concluded that hydrogen bonding



is the force holding the complexes together. No evidence was obtained for complexes involving more than one water molecule.

In the previous paper in this series, the thermodynamic parameters for the association reactions of benzaldehyde anion radical with alcohols (1) were discussed.<sup>1</sup> In all cases, where



R was methyl, ethyl, propyl, isopropyl, butyl or *tert*-butyl, only one-to-one complexes could be detected by phase selective second harmonic A.C. (SHAC) measurements. The reactions were found to be exothermic for the two smallest alcohols but approximately thermoneutral for the others. In the latter the reactions are made favourable by positive entropies of reaction.

The formation of one-to-one complexes between anion radicals and proton donors appears to be a widespread phenomenon. Such complexes have been detected by kinetic measurements during the hydrodimerization of diethyl fumarate anion radical in aqueous DMF<sup>2,3</sup> and during the dimerization of 9-cyanoanthracene anion radical in DMF in the presence of water.<sup>4</sup> In none of the cases recently examined<sup>1-4</sup> could any evidence indicating the formation of complexes containing one anion radical moiety and two proton donor molecules be found. It was recently proposed<sup>5</sup> that complexes of acetophenone anion radical with more than one molecule of water are involved in dimerization reactions. The basis for this proposal was that the standard potential for the reduction of acetophenone in acetonitrile was observed to shift by more than 90 mV per log unit of water concentration.<sup>6</sup>

The possibility that acetophenone anion radical forms 1 to 2 complexes with water while the others that have been investigated only form 1 to 1 complexes suggested further work on that system. In this paper results from an investigation of the effect of water on the reversible potential for the reduction of acetophenone in acetonitrile,

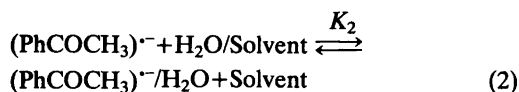
in acetonitrile-DMF mixtures and in DMF are discussed.

Considerable confusion exists in the literature regarding the effect of water on the kinetics of dimerization of anion radicals. For example, Lamy, Nadjo and Savéant<sup>7</sup> make the general proposal that the coupling of two anion radicals is easier when they are surrounded by more water molecules while Savéant and Tessier<sup>6</sup> state that the acceleration of the dimerization reaction is less pronounced as the water concentration increases owing to preferential solvation. In the latter case they go on to say that a water shell tends to build up around the anion radical which is therefore less and less sensitive to further additions. The source of this confusion is that the effect of water has been viewed to be due to a specific solvation effect in which the anion radicals are surrounded by several water molecules. One of the goals of this series of papers is to clear up some of the misunderstandings regarding the effect of water on the reactions of anion radicals in aprotic media.

## RESULTS AND DISCUSSION

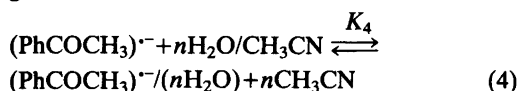
Reversible electrode potentials for the reduction of acetophenone in acetonitrile in the presence of water over a range of concentrations were determined at 293.3 and 273.2 K. The potentials were obtained using the quadrature component of the SHAC current. One of the primary advantages of SHAC for such measurements is that very low substrate concentrations can be used. In this work the concentration of acetophenone was 0.1 mM but even much lower concentrations can be used. The use of low substrate concentrations is of particular importance when the primary intermediate undergoes second order reactions following charge transfer. The reactions of acetophenone anion radical in acetonitrile under the conditions of the measurements were slow enough so that there was no difficulty in obtaining the reversible potentials at an applied a.c. frequency of 300 Hz. The shifts in the reversible potential ( $\Delta E_{\text{rev}}$ ) along with the equilibrium constants for reaction (2) at the various  $[\text{H}_2\text{O}]$  are listed in Table 1.

The equilibrium constants for reaction (2) were calculated using eqn. (3) which is based on that used by Peover and Davies



$$K_2 = [\exp(\Delta E_{\text{rev}}/(RT/F)) - 1]/[\text{H}_2\text{O}/\text{Solvent}] \quad (3)$$

for the analysis of ion-pair equilibria of anion radicals.<sup>8</sup> The equilibrium constants calculated were independent of  $[\text{H}_2\text{O}]$  and were equal to 21.1(0.6) and 20.2(0.3) $\text{M}^{-1}$  at 292.2 and 273.2 K, respectively. The fact that no trend in  $K_2$  with  $[\text{H}_2\text{O}]$  was observed indicates that eqn. (2) describes the equilibrium for the formation of acetophenone anion radical/water complexes. Any contribution from reaction 4), where  $n$  is greater than 1,



would cause the apparent value of  $K_2$  to increase with increasing  $[\text{H}_2\text{O}]$ . The corresponding equation for calculating  $K_4$  differs from eqn. (3) in that  $[\text{H}_2\text{O}]$  must be raised to the  $n$ th power. Thus, there is no evidence for the formation of complexes of acetophenone anion radical containing more than one water molecule in acetonitrile containing water up to about 0.5 M. Furthermore, it was not possible to measure the reversible potential ( $E_{\text{rev}}$ ) with higher water concentrations. Under the latter conditions the A.C. response was distorted by a substantial phase shift with the quadrature component shifting to negative and the in phase component

Table 1. Reversible potential shifts and equilibrium constants for the association of acetophenone anion radical and water in acetonitrile.<sup>a</sup>

| $T/\text{K}$ | $[\text{H}_2\text{O}]/\text{M}$ | $\Delta E_{\text{rev}}^b/\text{mV}$ | $K/\text{M}$ |
|--------------|---------------------------------|-------------------------------------|--------------|
| 273.2        | 0.0278                          | 10.6                                | 20.5         |
| 273.2        | 0.0556                          | 17.5                                | 19.9         |
| 273.2        | 0.112                           | 27.6                                | 20.1         |
| 293.3        | 0.0694                          | 22.1                                | 20.2         |
| 293.3        | 0.139                           | 35.0                                | 21.6         |
| 293.3        | 0.278                           | 48.4                                | 20.9         |
| 293.3        | 0.556                           | 64.7                                | 21.5         |

<sup>a</sup> In solvent containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M). <sup>b</sup> Measurements by phase selective second harmonic a.c. voltammetry at 300 Hz with a d.c. sweep rate of 40.0 mV/s.

**Table 2.** Reversible potential shifts and equilibrium constants for the association of acetophenone anion radical and water in *N,N*-dimethylformamide.<sup>a</sup>

| R <sub>2</sub> O | [R <sub>2</sub> O]/M | ΔE <sub>rev</sub> <sup>b</sup> /mV | K/M | K <sub>H</sub> /K <sub>D</sub> |
|------------------|----------------------|------------------------------------|-----|--------------------------------|
| H <sub>2</sub> O | 0.0694               | 6.9                                | 4.6 | 1.15                           |
| D <sub>2</sub> O | 0.0694               | 6.1                                | 4.0 |                                |
| H <sub>2</sub> O | 0.139                | 13.3                               | 5.0 | 1.20                           |
| D <sub>2</sub> O | 0.139                | 11.5                               | 4.2 |                                |
| H <sub>2</sub> O | 0.208                | 17.8                               | 5.0 | 1.14                           |
| D <sub>2</sub> O | 0.208                | 16.4                               | 4.4 |                                |
| H <sub>2</sub> O | 0.276                | 22.3                               | 5.2 | 1.13                           |
| D <sub>2</sub> O | 0.276                | 20.7                               | 4.6 |                                |

<sup>a</sup> In solvent containing Et<sub>4</sub>NBF<sub>4</sub> (0.1 M) at 18.7 °C.

<sup>b</sup> Measurements by phase selective second harmonic *a.c.* voltammetry at 300 Hz with a *d.c.* sweep rate of 40.0 mV/s.

shifting to more positive potentials. This was not investigated further but is most likely due to adsorption of products on the electrode.

Since the observed values of *K*<sub>2</sub> were nearly identical, *i.e.* within experimental error, at 292.2 and 273.1 K, it appears that reaction (2) is very nearly thermoneutral. Thus, the formation of the complex is driven by a positive Δ*S*<sup>o</sup>. The values calculated from the equilibrium constants were

**Table 3.** Reversible potential shifts and equilibrium constants for the association of acetophenone anion radical with water in acetonitrile–DMF mixtures.

| Mol fraction DMF <sup>a</sup> | [H <sub>2</sub> O]/M | ΔE <sub>rev</sub> <sup>b</sup> /mV | K/M <sup>-1</sup> |
|-------------------------------|----------------------|------------------------------------|-------------------|
| 0.19                          | 0.139                | 25.4                               | 12.6              |
| 0.19                          | 0.208                | 33.4                               | 13.4              |
| 0.19                          | 0.276                | 39.3                               | 13.5              |
| 0.19                          | 0.414                | 47.4                               | 13.5              |
| 0.41                          | 0.0694               | 10.6                               | 7.6               |
| 0.41                          | 0.139                | 18.8                               | 8.0               |
| 0.41                          | 0.208                | 25.1                               | 8.2               |
| 0.41                          | 0.276                | 30.6                               | 8.6               |
| 0.67                          | 0.0694               | 8.1                                | 5.5               |
| 0.67                          | 0.139                | 14.6                               | 5.7               |
| 0.67                          | 0.208                | 20.5                               | 6.0               |
| 0.67                          | 0.276                | 25.2                               | 6.3               |

<sup>a</sup> In acetonitrile–DMF mixtures containing Et<sub>4</sub>NBF<sub>4</sub> (0.1 M) at 291.9 K. <sup>b</sup> Measurements by phase selective second harmonic *a.c.* voltammetry at 300 Hz with a *d.c.* sweep rate of 40.0 mV/s.

**Table 4.** Equilibrium constants for the association of acetophenone anion radical with water.

| Mol fraction DMF <sup>a</sup> | Electrolyte                      | T/K   | K/M <sup>-1</sup> |
|-------------------------------|----------------------------------|-------|-------------------|
| 0                             | Bu <sub>4</sub> NBF <sub>4</sub> | 293.3 | 21.6(0.6)         |
| 0                             | Bu <sub>4</sub> NBF <sub>4</sub> | 273.2 | 20.2(0.3)         |
| 0                             | Et <sub>4</sub> NBF <sub>4</sub> | 292.2 | 16.6(0.2)         |
| 0.19                          | Et <sub>4</sub> NBF <sub>4</sub> | 291.9 | 13.3(0.4)         |
| 0.41                          | Et <sub>4</sub> NBF <sub>4</sub> | 291.9 | 8.1(0.4)          |
| 0.67                          | Et <sub>4</sub> NBF <sub>4</sub> | 291.9 | 5.9(0.3)          |
| 1.00                          | Et <sub>4</sub> NBF <sub>4</sub> | 291.9 | 5.0(0.3)          |

<sup>a</sup> In acetonitrile–DMF mixtures containing electrolyte (0.1 M).

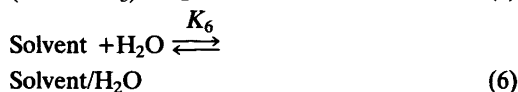
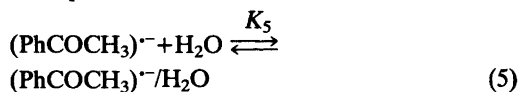
6.1 and 6.0 cal/K mol and are surely identical within experimental error.

Reversible potential shifts and equilibrium constants for the association of acetophenone anion radical with water in DMF are summarized in Table 2. Measurements were made in the presence of both H<sub>2</sub>O and D<sub>2</sub>O. The calculated values of *K*<sub>2</sub> were independent of water concentration and found to be equal to 5.0(0.3) and 4.3(0.3), respectively, which corresponds to *K*<sub>H</sub>/*K*<sub>D</sub> equal to 1.16(0.03).

Measurements made in solvent mixtures of CH<sub>3</sub>CN and DMF are summarized in Table 3. The calculated *K*<sub>2</sub> were again observed to be independent of [H<sub>2</sub>O] which confirms the applicability of eqn. (3). The value of *K*<sub>2</sub> was observed to decrease progressively as the mol fraction of DMF in the solvent mixture was increased.

Equilibrium constants, *K*<sub>2</sub> obtained under all conditions used in this study are summarized in Table 4. A plot of ln *K*<sub>2</sub> vs. mol fraction of DMF (*n*) is shown in Fig. 1. The straight line corresponds to the linear regression correlation with a correlation coefficient of 0.94. The curved line corresponds to a second order polynomial equation and appears to fit the data somewhat better.

Under the same measurement conditions, *K*<sub>2</sub> appears to be about 3 times as great in CH<sub>3</sub>CN as in DMF. It seems most likely that *K*<sub>5</sub> depends less upon the solvent and that the



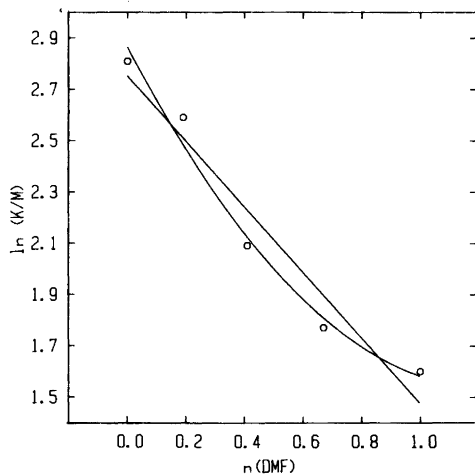
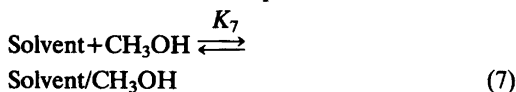


Fig. 1. The effect on the equilibrium constant for association of acetophenone anion radical with water of increasing the mol fraction of DMF in acetonitrile at 292 K.

difference in  $K_2$  observed is due to the differences in  $K_6$ , *i.e.* water is bound more tightly to DMF than to  $\text{CH}_3\text{CN}$ . Data are not available for equilibrium (6) when the solvent is  $\text{CH}_3\text{CN}$  but are available for the association of methanol with both solvents. Equilibrium data are summarized in Table 5 for reaction (7). All of the parameters,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  are more negative when the solvent in DMF. The equilibrium



constant at 273 K was observed to be 4.8 times greater for DMF than when  $\text{CH}_3\text{CN}$  was the

Table 5. Thermodynamic parameters for the association of methanol with acetonitrile and DMF.

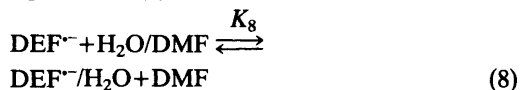
| Parameter  | Aceto-<br>nitrile <sup>a</sup> | DMF <sup>b</sup> |
|--|--------------------------------|------------------|
| $-\Delta G_{273}^\circ/\text{kcal mol}^{-1}$       | 0.45                           | 1.3              |
| $-\Delta H^\circ/\text{kcal mol}^{-1}$             | 0.93                           | 3.8              |
| $-\Delta S^\circ/\text{cal K}^{-1}\text{mol}^{-1}$ | 1.8                            | 9.1              |
| $K_{273}/\text{M}^{-1}$                            | 2.3                            | 11               |

<sup>a</sup> From correlation of the data reported in Ref. 9.

<sup>b</sup> Data from Ref. 10.

solvent. The same relative values of  $K_6$  are not necessarily expected but the trend should be in the same direction. Thus, it seems plausible that the factor of 3 difference in  $K_2$  on changing the solvent from DMF to  $\text{CH}_3\text{CN}$  is indeed due to the differences in  $K_6$ .

It is of interest to compare the value of  $K_H/K_D$  (1.16) for equilibrium (2) with that estimated for equilibrium (8),



where  $\text{DEF}^{\cdot-}$  is the anion radical of diethyl fumarate. The value found by kinetic measurements was  $1.11(0.03)^2$  which is within experimental error of that found here for equilibrium (2). This suggests that the two equilibria, as well as the others involving anion radicals with proton donors in aprotic solvents, involve the same type of binding forces. It is well known that complexes of proton donors with aprotic solvents are held together by hydrogen bonding.<sup>11</sup> Hydrogen bonding has been suggested to be involved in the formation of anion radical/proton donor complexes by Stevenson and co-workers.<sup>12</sup>

With the data now available as a background we can examine more closely the views of Savéant and co-workers<sup>5-7</sup> regarding the effect of water on the kinetics of anion radical dimerizations in aprotic solvents. Contrary to their view, the effect on the kinetics is due to the formation of 1:1 hydrogen bonded complexes. There is no evidence for the formation of complexes containing more than one molecule of water. The proposals concerning the anion radicals being surrounded by several molecules of water neglect the fact that water does not exist in the free state in the solvents but rather is bound tightly by hydrogen bonding to the solvent. It is clear that several water molecules do not gather in a shell<sup>6</sup> around the anion radicals.

The reason that 1:1 complexes are preferred over those containing two or more molecules of water is also clear. Considerable energy is necessary to break the water-solvent hydrogen bond. After having accepted one H bond, the anion radical is much less able to provide this energy. In this respect it has been known for a long time that the equilibrium constant for the association of benzoquinone anion radical with one molecule of water is of the order of  $10^3$  greater than that for

the association with a second molecule of water.<sup>13</sup> These results were apparently overlooked in the more recent discussions.<sup>5-7</sup>

## EXPERIMENTAL

Reversible potential measurements by SHAC have been described in detail in an earlier paper.<sup>14</sup> The instruments and data handling procedures were similar to those described earlier.<sup>15</sup> Acetophenone was reagent grade and used without further purification. No electroactive impurities could be detected by the voltammetric measurements.

## REFERENCES

1. Parker, V. D. *Acta Chem. Scand. B* 38 (1984) 125.
2. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 147.
3. Parker, V. D. *Acta Chem. Scand. B* 37 (1983) 393.
4. Parker, V. D. *Acta Chem. Scand. B* 37 (1983) 163.
5. Amatore, C., Pinson, J. and Savéant, J. M. *J. Electroanal. Chem.* 137 (1982) 143.
6. Savéant, J. M. and Tessier, D. *J. Electroanal. Chem.* 61 (1975) 251.
7. Lamy, E., Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem.* 50 (1974) 141.
8. Peover, M. E. and Davies, J. D. *J. Electroanal. Chem.* 6 (1963) 46.
9. Lowenstein, A. and Margalit, Y. *J. Phys. Chem.* 69 (1965) 4152.
10. Becker, E. D. *Spectrochim. Acta* 17 (1963) 46.
11. Joesten, M. D. and Schaad, L. J. *Hydrogen Bonding*, Dekker, New York 1974.
12. Stevenson, G. R. and Pourian, M. *J. Phys. Chem.* 86 (1982) 1871.
13. Stone, E. W. and Maki, A. H. *J. Am. Chem. Soc.* 87 (1965) 454.
14. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 559.
15. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 97.

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