

The Association Reactions of Ion Radicals with Neutral Molecules. IV. Substituent Effects on Hydrogen Bonding Equilibria between Benzaldehyde Anion Radicals and Hydroxylic Compounds

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Equilibria (i) were studied by determining reversible electrode potentials as a function of [ROH], where R was either H or CH₃.



The equilibrium constants (K_1) were observed to vary with the para-substituent (X) from 1.2 M⁻¹ (X=CN) to 9.6 M⁻¹ (X=N(CH₃)₂) for the reaction with water at 273.2 K. In general K_1 were observed to be about 5 times as great when R=CH₃. The equilibria lie further to the right for electron donating substituents but no linear relationship with Hammett substituent constants could be found. Enthalpies and entropies are reported for equilibria (i).

Previous papers in this series have dealt with the hydrogen bonding equilibria between anion radicals (A^{·-}) of benzaldehyde,¹ acetophenone,² and *p*-methylbenzylidenemalononitrile³ with hydroxylic compounds [eqn. (1)] in either acetonitrile or *N,N*-dimethylformamide (DMF) as solvent.



Water and alcohols are strongly hydrogen bonded to these solvents and at low concentrations significant quantities of the free hydroxylic compounds do not exist. Equilibria (1) appear to be general for anion radicals with the equilibrium constants being strongly dependent upon the nature of the anion radical. The K_1 for anion radicals of benzaldehyde and acetophenone in which the negative charge is localized to a large extent on the carbonyl oxygen are significantly larger than that for the anion radical of *p*-methylbenzylidenemalononitrile in which the charge is more delocalized. Equilibria (1) cannot be detected by reversible potential measurements for anion radicals such as that of 9-cyanoanthracene in which the charge is extensively delocalized.⁴

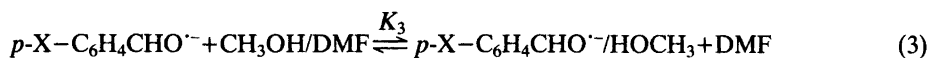
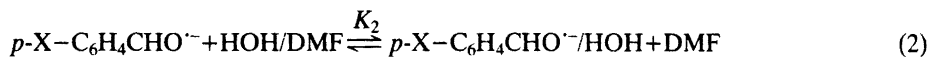
In view of the previous work¹⁻⁴ we anticipated that any structural change in a series of anion radicals which brings about a more highly localized anionic charge center would

Table 1. Thermodynamic parameters for the association of benzaldehyde anion radicals with water.^a

p-X ^b	K ₂ ^c /M ⁻¹	-ΔH°/(kcal/mol)	ΔS°/(cal/K mol)
H	5.8	0.64	1.1
CH ₃	7.0	0.79	1.0
CH(CH ₃) ₂	7.3	1.60	-1.9
CN	1.2	1.10	-3.7
N(CH ₃) ₂	9.6	0.65	2.1
OCH ₃	8.1	1.41	1.0

^a From reversible potential measurements at temperatures ranging from from 243 to 303 K in DMF containing Bu₄NBF₄ (0.1 M) using phase selective second harmonic *a.c.* voltammetry. Residual water concentrations, determined as described in the text, were found to range from about 5 to 10 mM. ^b The para substituent of the benzaldehyde. ^c At 273.2 K.

enhance the value of K₁. In order to test the validity of this hypothesis and to attempt to find quantitative relationships between structure and the extent of reaction (1) we have examined the effect of para-substituents on equilibria (2) and (3).



RESULTS AND DISCUSSION

Determination of Equilibrium Constants. The reversible electrode potentials (E^{rev}) were determined by phase selective second harmonic *a.c.* voltammetry as in the previous papers.^{1,2} Measurements were first made on solutions without the intentional addition of water and then repeated at 4 different [H₂O] or [CH₃OH]. Equilibrium constants were then calculated from (4) or

$$K_2 = \{\exp[\Delta E^{\text{rev}}/(RT/F)] - 1\} / [\text{H}_2\text{O}] \quad (4)$$

the corresponding equation involving [CH₃OH]. In the first iteration, ΔE^{rev} was taken as the difference in E^{rev} for the solution to which water was added and that without added

Table 2. Thermodynamic parameters for the association of benzaldehyde anion radicals with methanol.^a

p-X	K ₃ ^b /M ⁻¹	K _H /K _D ^b	-ΔH°/(kcal/mol)	ΔS°/(cal/K mol)
H	27.1	1.43	4.5	-10.0
CH ₃	29.7	1.19	1.1	2.9
CH(CH ₃) ₂	28.2	1.06	0.5	4.8
CN	1.9	1.36	-2.1	8.9
N(CH ₃) ₂	50.9	1.23	1.0	4.3
OCH ₃	38.1	1.43	3.0	-3.8

^a As in Table 1. ^b At 273.2 K.

water. These ΔE^{rev} are always minimum values because the true water concentration is not known and consists of that added plus that present in the solvent-electrolyte at the start of the experiment. In order to estimate the true $[\text{H}_2\text{O}]$, each ΔE^{rev} was incremented by δE and K_2 was calculated again at each $[\text{H}_2\text{O}]$. The value of δE was then adjusted until the standard deviation in K_2 was a minimum.

$$[\text{H}_2\text{O}] = \{\exp[\Delta E^{\text{rev}} + \delta E]/(RT/F) - 1\}/K \quad (5)$$

This value of δE was then used in eqn. (5) to give estimates of the true $[\text{H}_2\text{O}]$. In (5) K is the average value obtained when the standard deviation was a minimum. The iteration procedure was repeated 10 times. The values of K_2 were generally constant after the first few iterations.

A similar procedure was used to calculate K_3 . This was necessary to account for the anion radicals hydrogen bonded to water. The corrections in these cases were small due to the low residual $[\text{H}_2\text{O}]$ and to the fact that K_3 was observed in all instances to be considerably larger than K_2 .

Thermodynamic Data for the Hydrogen Bonding Equilibria. The data for reaction (2) are summarized in Table 1. The equilibrium constants measured at 273.2 K show that hydrogen bonding is enhanced by electron donating groups. We have noted one exception to this, *i.e.* K_2 was observed to be equal to 27.4 at 273.2 K when $X=p\text{-NO}_2$. This data is not included in the table because it is likely that the nitro group is involved in the H-bonding in this case and therefore does not belong in this series. In all cases ΔH° was observed to be small and negative indicating that reaction (2) is slightly exothermic. Likewise, ΔS° is small in all cases, but is positive in some cases and negative in others.

The data for reaction (3) are gathered in Table 2. In most cases, K_3 is of the order of 5 times the corresponding K_2 . Once again, electron donating groups enhance the degree of H-bonding. The second column gives values of the equilibrium deuterium isotope effects obtained by measurements using both CH_3OH and CH_3OD . The values range from 1.06 to 1.43 and do not appear to be related to the magnitudes of K_3 . Negative values of ΔH° were

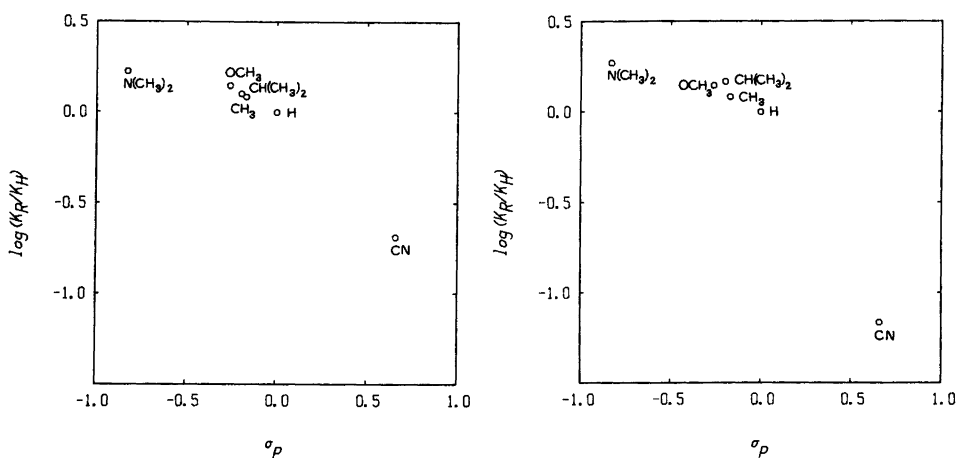


Fig. 1. Hammett plots for the hydrogen bonding equilibria of benzaldehyde anion radicals with (a) water and (b) methanol.

observed in all cases other than when $X=CN$. Both negative and positive values of ΔS° were observed.

The equilibrium constants were used to construct the Hammett plots in Fig. 1. In both cases, for the reactions of the anion radicals with water (a) and methanol (b), the plots show a dependence of $\log(K_R/K_H)$ on σ_p but it is clear that there is not a linear free energy relationship for the data in either case.

CONCLUSIONS

The anion radicals of *p*-substituted benzaldehydes form hydrogen bonded complexes with water and methanol in DMF. The extent of the formation of the complexes is, as anticipated, dependent upon the electron donating ability of the substituents. However, there do not appear to be any quantitative relationships between substituent constants and equilibrium constants for the reactions. In general, the equilibrium constants appear to be about 5 times greater when the proton donor is methanol as compared to water. No indication of the formation of complexes containing more than one molecule of hydroxylic compound was found.

EXPERIMENTAL

The reversible potential measurements by phase selective second harmonic *a.c.* voltammetry have been described in detail in a previous paper.⁵ The benzaldehydes were reagent grade and purified by conventional methods before use. The instrumentation was similar to that described previously.⁶

REFERENCES

1. Parker, V.D. *Acta Chem. Scand. B* 38 (1984) 125.
2. Parker, V.D. *Acta Chem. Scand. B* 38 (1984) 189.
3. Eliason, R. and Parker, V.D. *Acta Chem. Scand. B* 38 (1984) 741.
4. Hammerich, O. and Parker, V.D. *Acta Chem. Scand. B* 37 (1983) 379.
5. Svaan, M. and Parker, V.D. *Acta Chem. Scand. B* 35 (1981) 559.
6. Ahlberg, E. and Parker, V.D. *Acta Chem. Scand. B* 34 (1980) 97.

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