dicted for N_2^+ is comparable to the ab initio result, −2949.78 eV, reported by Cade et al.[17]

Conclusion

The effective molecular pair correlation energies between valence electrons are found to change considerably upon ionization due to the nontransferable, correlation effects. The relative contribution to the ionization potential is higher for the electron pairs in the higher level orbitals. The total correlation contribution to the ionization potential for the investigated systems is found to be 11–14% of the experimental IP.

Rather good agreements have been observed, for some systems, between the calculated and experimental ionization potentials although SCF errors are not included.

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Free Energies and Free Energies of Activation for Ion Pairing and Hydrogen Bonding to an Anion Radical

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Abstract: The equilibria and rates were determined for two processes: (1) hydrogen bonding of *p*-cyanonitrobenzene radical anion by methanol in hexamethylphosphoramide (HMPA) and (2) ion pairing of this anion radical with K^+ in the same solvent. It was found that $\Delta G°$ for the formation of the ion paired species is smaller than that for the formation of the hydrogen bonded species. However, the formation of the hydrogen bond results in a larger perturbation of the electronic structure of the anion radical. This is probably due to the fact that the hydrogen bonding proton can approach the NO_2 group of the anion radical more closely than can the solvated cation. The rate of ion pair formation ($k_{\mathrm{If}} = 4.6 \times 10^8$ M^{-1} s^{-1}) is large and probably encounter controlled, while that of hydrogen bond formation to the anion radical is about 60 times slower ($k_{\mathrm{Hf}} = 7.5 \times 10^6$ M^{-1} s^{-1}). The free energy of activation necessary to break the hydrogen bond to the anion radical is 0.4 kcal/mol less than that necessary to break up the ion pair complex.

It is well recognized that two of the most important phenomena in the determination of solvation energies of anions are hydrogen bonding between solvent and anion and ion pairing. Consequently, there have been a large number of reports concerning the thermodynamic parameters controlling ion pair formation in a wide variety of solvent anion systems. Furthermore, these studies have been carried out using a wide variety of instrumental techniques.[1] Hydrogen bonding, on the other hand, is just as important in protic solvents in controlling the thermodynamic stability of anions, but there are few reports of thermodynamic parameters controlling hydrogen bonding to anions. This is true because of the experimental difficulties and complexities that arise from competing interactions such as ion pairing and solvent–solvent interactions. These problems are discussed in a recent report on the thermodynamic parameters controlling hydrogen bonding to the Cl^- ion in solution by Benoit and co-workers.[2] The enthalpies and free energies of hydrogen bond formation to the Cl^- ion reported by these workers must really represent reactions that are much more complex than that shown in eq 1. Since HR is a secondary solvent, there are interactions between HR and the solvent. Also, the counterion is possibly involved. This interesting work of Benoit and co-workers involves the use of NMR, calorimetry, vapor pressure measurements, and solubility measurements.

$$\mathrm{Cl^-(solution) + HR(solution)} \rightleftarrows \mathrm{Cl^- \cdots HR(solution)} \qquad (1)$$

Electron spin resonance (ESR) has also been recently used to obtain the free energies of the hydrogen bond exchange reaction (where the hydrogen bond is exchanged between the primary solvent and an anion radical) in hexamethylphosphoramide (HMPA) (see eq 2).[3] In HMPA ion pairing is not a complication.[4] Furthermore, the free energy and enthalpy of hydrogen bonding to the solvent can be determined via NMR measurements and subtracted out to yield the actual free energies of hydrogen bonding to the anion radical.[3,5,6]

$$\mathrm{X\cdot^- + HMPA \cdots HR \rightleftarrows X\cdot^- \cdots HR + HMPA} \qquad (2)$$

Even though there are many reports on the thermodynamic parameters controlling ion pairing and a few reports on these parameters for hydrogen bonding to anions,[7] the literature is devoid of reports on the kinetics of hydrogen bond formation to anions, and there is only one report to our knowledge on the rate constant for ion pair formation from the free ions.[8] It was our intention to measure the rate constants for formation and dissociation of a hydrogen bonded anion radical and compare them with the rate constants for the formation and dissociation of the ion pair. These two processes, ion pairing and hydrogen bonding, are very similar in that they both describe a 1:1 complex with the anion. In one case the complex is with an alkali metal cation and in the other it is with an acidic proton. This kinetic information is vital to the understanding of the fundamental processes involving anions in protic media.

The proposed study would have to be carried out in a solvent where anions can be generated in the fully dissociated state, yet where ion pairs or hydrogen bonded anions could be formed by the addition of alkali metal salt or proton donor, respectively. HMPA fulfills these requirements. In order to utilize relaxation methods, the rate of formation and dissociation of the ion pair and hydrogen bond must be fast on the ESR time scale, and the ESR spectral parameters must be sensitive to both hydrogen bonding and ion pair formation. The nitrobenzene anion radical in HMPA yields dramatic line width alternation upon the addition of methanol (a proton donor).[9] The addition of potassium iodide to the anion radical solution yields ion pairs, which are observed simultaneously with the free ion.[10] Since the lifetime of the free ion and ion pair is long on the ESR time scale, kinetic data cannot be obtained for this system. It has been noted that the lifetime of the ion pair can be shortened by reducing the charge density on the site of ion pair formation.[8,11] This has been accomplished for the para-substituted nitrobenzene anion radicals by increasing the electron-withdrawing character of the para substituent.[5,12] *p*-Cyanonitrobenzene fits all of the requirements for the proposed study.

Before the kinetic study can be initiated, it is necessary to know the free energy for both the hydrogen bond exchange reaction (eq 3) and for the ion pair dissociation reaction (eq 4). These free energies can be determined by the use of time averaged ESR coupling constants,[13] and by the use of time averaged *g* values.[11]

$$\mathrm{NCPhNO_2{\cdot}^- + HMPA \cdots HOMe} \rightleftarrows \mathrm{NCPhNO_2{\cdot}^- \cdots HOMe + HMPA} \quad (3)$$

$$\mathrm{NCPhNO_2{\cdot}^-,K^+} \rightleftarrows \mathrm{K^+ + NCPhNO_2{\cdot}^-} \quad (4)$$

For the formation of any weak molecular complex (x′):

$$\mathrm{x + y} \rightleftarrows \mathrm{x'} \quad (5)$$

eq 6 can be utilized to obtain the equilibrium constant (K_{eq}) from the time averaged spectroscopic parameter of x (Γ). Equation 6 requires that this spectroscopic parameter for the uncomplexed species (Γ^0) be known, but it is not necessary to have an independent evaluation of the spectroscopic parameter for x′ (Γ').[13,14] As long as the concentration of y, which in our case will represent either K^+ or methanol, is large in comparison to that for x, K_{eq} can be determined from a plot of $1/(\Gamma - \Gamma^0)$ vs. $1/[\mathrm{y}]$. In this report the spectroscopic parameters to be inserted into eq 6 for Γ are the *g* value and coupling constant determined by ESR spectroscopy. Both of these parameters have to be known anyway for insertion into the Bloch equations in order to determine the rate constants for hydrogen bond formation (k_{Hf}) and dissociation (k_{Hd}) to the anion radical and the rate constants for ion pair formation (k_{If}) and dissociation (k_{Id}).

$$1/(\Gamma - \Gamma^0) = 1/\{K_{\mathrm{eq}}(\Gamma' - \Gamma^0)[\mathrm{y}]\} + 1/(\Gamma' - \Gamma^0) \quad (6)$$

The kinetic study is carried out by making use of the relaxation theory (in modified form) as applied to the two-site model, which has been derived in detail by Fraenkel.[15] His expression has been modified so that the kinetic parameters can be determined from the line heights, which change more rapidly with changes in the lifetime of the spin state than do the line widths. This modification has been previously described, and the resulting expression is:[8]

$$\tau = \delta^0\{1 - (h_{-1}/h_0)^{1/2}\}\sqrt{3}|\gamma_{\mathrm{e}}|/2 \times \{X_{-1}(h_{-1}/h_0)^{1/2} - X_0\} \quad (7)$$

where h_{-1} and h_0 are the heights of the low-field and central lines of the nitro group nitrogen triplet, γ_{e} is the gyromagnetic ratio for an electron, δ° is the line width in the absence of hydrogen bond or ion pair formation, and X_m is related to the probability of finding the anion radical in the free state (P_α) or complexed state (P_β) as shown in:

$$X_m = P_\alpha\{\omega_{\alpha,m} - \bar{\omega}_m\}^2 + P_\beta\{\omega_{\beta,m} - \bar{\omega}_m\}^2 \quad (8)$$

where $\omega_{\alpha,m}$, $\omega_{\beta,m}$, and $\bar{\omega}_m$ are the positions of the *m*th nitrogen line for the free ion, complexed ion, and time-averaged species, respectively. These values can be easily calculated from the *g* values and coupling constants. τ is related to the lifetimes τ_α and τ_β of the free state and the complexed state as given in eq 9.

$$\tau = \tau_\alpha\tau_\beta/(\tau_\alpha + \tau_\beta) \quad (9)$$

Results and Discussion

Hydrogen Bonding. Knowing the value for the equilibrium constant ($K_{\mathrm{H}} = [\mathrm{HMPA}][\mathrm{NCPhNO_2{\cdot}^- \cdots HOMe}]/[\mathrm{HMPA \cdots HOMe}][\mathrm{NCPhNO_2{\cdot}^-}]$) k_{Hf} can be determined from eq 10, which is deduced from eq 7 and 9. The equilibrium constant and the positions of the $m = 0$ and $m = -1$ lines can be determined from the time averaged *g* values and coupling constants. It should be noted here that eq 10 has been derived only in terms of the $m = -1$ and $m = 0$ lines, because the $m = +1$ lines are broadened and shortened by the *g*-tensor anisotropy effects.

$$k_{\mathrm{Hf}} = \frac{2\{X_{-1}(h_{-1}/h_0)^{1/2} - X_0\}}{(\delta^0\{1 - (h_{-1}/h_0)^{1/2}\}\sqrt{3}|\gamma_{\mathrm{e}}|\{[\mathrm{HMPA \cdots HOMe}] + [\mathrm{HMPA}]/K_{\mathrm{H}}\})} \quad (10)$$

The equilibrium constant for the reaction given in eq 3 has been determined by the use of time averaged coupling constants.[5] However, the use of time averaged *g* values for the determination of hydrogen bond formation has not been reported. Thus, the application of *g* values to eq 6 is threefold in purpose: (1) to demonstrate that *g* values can be used for the measurement of hydrogen bonding equilibrium constants, (2) to obtain accurate $\Delta\bar{g}$ values for use in eq 10, and (3) to verify the value for K_{H} previously reported.

Successive additions of methanol to the free anion radical of *p*-cyanonitrobenzene in HMPA ($A_{\mathrm{N}} = 4.90$ G) result in an increase in the observed coupling constant and a decrease in the observed *g* value due to the formation of the hydrogen bonded anion radical. As previously reported, the hydrogen bonding takes place exclusively with the $\mathrm{NO_2}$ group.

Utilizing the free anion radical as a standard, the difference in the observed *g* value for a sample containing MeOH and that of the standard is $\Delta\bar{g}$. Substituting 0, $\Delta\bar{g}$, and $\Delta g'$ (the difference in *g* value between the hydrogen bonded and free anion radical) for Γ^0, Γ, and Γ', respectively, in eq 6 yields:

$$1/\Delta\bar{g} = 1/K_{\mathrm{H}}\Delta g'[\mathrm{HMPA \cdots HOMe}] + 1/\Delta g' \quad (11)$$

Since the total concentration of MeOH is much larger than that for the anion radical, a plot of $1/\Delta\bar{g}$ vs. $1/[\mathrm{MeOH}]$ is linear and has a slope of $1/\Delta g' K_{\mathrm{H}}$ and an intercept of $1/\Delta g'$ (Figure 1). At 25 °C K_{H} was found to be 0.48 ± 0.09 in excellent agreement with the previously reported value of 0.44.[5]

Utilizing the coupling constants and *g* values determined for each concentration of added MeOH, 0.44 for K_{H}, and the line height fluctuations (Figure 2), the observed rate constant

Table I. ESR Parameters and Observed Rate Constant for Hydrogen Bond Formation to the Anion Radical (Only Representative Data Shown)

[MeOH], M	$\bar{A}_N$, G	$10^5\Delta g$	h_{-1}/h_0	$10^9\tau$, s	$10^{-7}k_{Hf,obsd}$, M^{-1} s^{-1}
0	4.90	0	1.00		
0.20	5.00	0.54	0.76	3.70	2.03
0.29	5.05	0.76	0.56	2.50	3.05
0.53	5.16	1.40	0.54	1.42	5.29
0.62	5.20	1.64	0.51	1.35	5.53
1.16	5.42	3.03	0.50	0.76	9.65
1.32	5.54	3.45	0.48	0.67	10.9
2.31	5.85	5.88	0.47	0.37	18.7
∞	11.0	32.3			

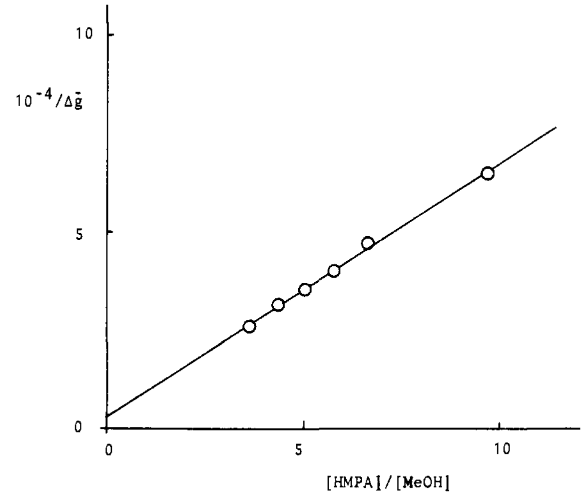


Figure 1. Plot of $1/\Delta\bar{g}$ vs. the reciprocal of the methanol concentration in moles/liter times the HMPA concentration.

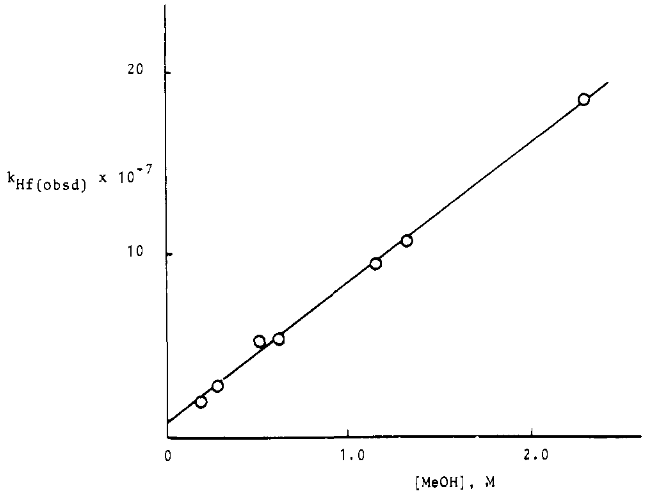


Figure 3. Plot of $k_{Hf,obsd}$ vs. the concentration of MeOH added to the anion radical solution.

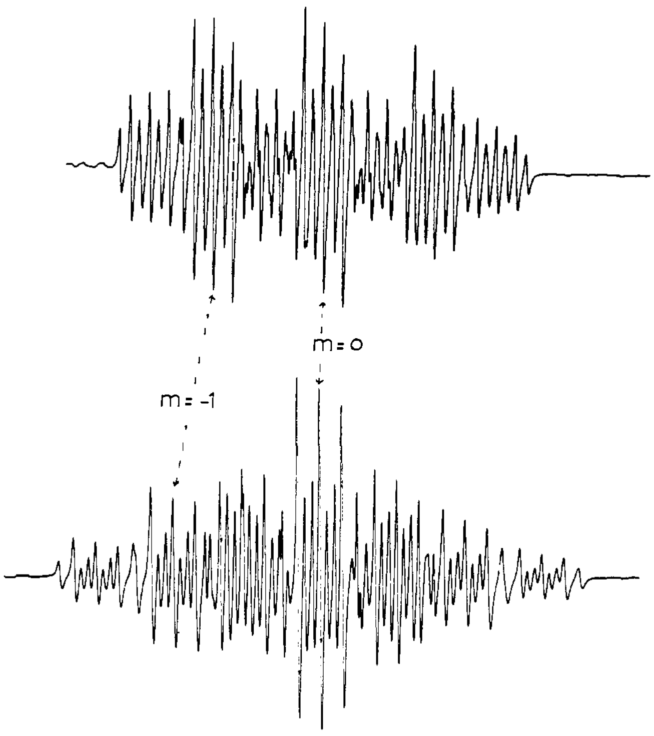


Figure 2. ESR spectra of the *p*-cyanonitrobenzene anion radical in HMPA: (top) without added proton donor; (bottom) with 1.32 M MeOH added. δ^0 taken from the top spectrum is 0.09 G. Note that h_0/h_{-1} is about 1 in the upper spectra but is much greater than 1 in the lower spectra.

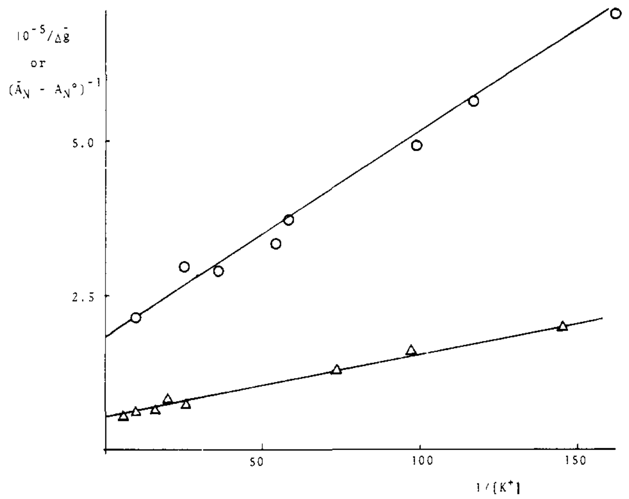


Figure 4. Plots of $1/(\bar{A}_N - A_N^0)$ (○) and $10^{-5}/\Delta\bar{g}$ (△) vs. the reciprocal of the potassium ion concentration. Both plots yield the same value for the ion pair dissociation constant, 0.018.

$k_{Hf,obsd}$ was calculated according to eq 10, Table I. It is immediately noted from Table I that the observed rate constant increases with increasing concentration of added MeOH. Change in the observed rate constant with concentration is expected, since there is some methanol-methanol self-association at the higher concentrations and the viscosity of the solution increases with increasing concentration of methanol. An extrapolation of $k_{Hf,obsd}$ to zero [MeOH] yields k_{Hf}, Figure 3. The value obtained from this extrapolation for k_{Hf} is $(7.5 \pm 1.4) \times 10^6$ M^{-1} s^{-1} and that for k_{Hd} is $(1.70 \pm 0.32) \times 10^7$ M^{-1} s^{-1}.

Ion Pairing. In a manner completely analogous to the case for ion pairing, eq 7 must now be rewritten to yield k_{Id}:

Table II. ESR Parameters and Observed Rate Constant for Ion Pair Formation to the Anion Radical (Only Representative Data Are Shown)

[KI], M	$\bar{A}_N$, G	$10^6\Delta\bar{g}$	$h_{-1}h_0$	$10^8\tau$, s	$10^{-8}k_{\mathrm{If,obsd}}$, M^{-1} s^{-1}
0	4.90	0	1.00		
0.0045	5.00	3.62	0.24	15.55	2.86
0.0082	5.04	5.68	0.089	26.52	1.44
0.0102	5.10	6.12	0.035	50.66	0.70
0.0172	5.17	8.93	0.022	66.22	0.43
0.0185	5.20	9.25	0.022	52.91	0.52
0.0395	3.58	12.10			
0.102	5.36	16.36			
∞	5.45	18.50			

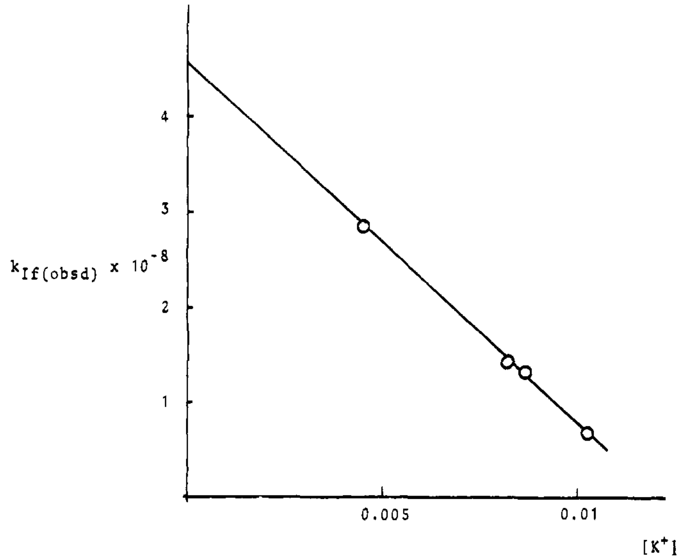


Figure 5. Plot of $k_{\mathrm{If,obsd}}$ vs. the concentration of added KI in the anion radical solution.

$$K_{\mathrm{Id}} = [K^+][\mathrm{NCPhNO_2\cdot^-}]/[\mathrm{NCPhNO_2\cdot^-},K^+] = \tau_\alpha/\tau_\beta = k_{\mathrm{Id}}/k_{\mathrm{If}} \quad (12)$$

and thus

$$k_{\mathrm{Id}} = \tau^{-1}(K_{\mathrm{Id}} + [K^+])^{-1} \quad (13)$$

Successive additions of KI, which is fully dissociated in HMPA,[16] leads to a decrease in the observed g value and an increase in the observed A_N due to the rapid formation and dissociation of the ion pair, eq 4. Rewriting eq 6 in terms of A_N and g values yields:

$$1/(\bar{A}_N - A_N^0) = K_{\mathrm{Id}}/(A_N' - A_N^0)[K^+] + 1/(A_N' - A_N^0) \quad (14)$$

and

$$1/\Delta\bar{g} = K_{\mathrm{Id}}/\Delta g'[K^+] + 1/\Delta g' \quad (15)$$

(see Figure 4). Plots of $1/\Delta\bar{g}$ vs. $1/[K^+]$ and $1/(\bar{A} - A_N^0)$ vs. $1/[K^+]$ are linear and yield exactly the same value for K_{Id} (0.018 ± 0.002). Representative data are shown in Table II. The dramatic line width alternation observed upon the addition of K^+ has already been noted.[13b]

From Figure 5 it is clear that the observed rate constant for ion pair formation to the anion radical is decreasing with increasing concentration of added salt. This is opposite to the effect obtained upon MeOH addition. However, it is the expected result, since addition of KI increases the viscosity of the solution.[14a] Extrapolation of the data to a zero concentration of added salt eliminates the error due to an increased viscosity with salt addition and due to possible association of the K^+ and I^- ions. The extrapolated values for k_{ID} and k_{If} are $(8.21 \pm 0.46) \times 10^6$ s^{-1} and $(4.56 \pm 0.06) \times 10^8$ M^{-1} s^{-1}.

Since δ^0 is not affected by either the hydrogen bond or ion pair formation dissociation process, the viscosity of the media

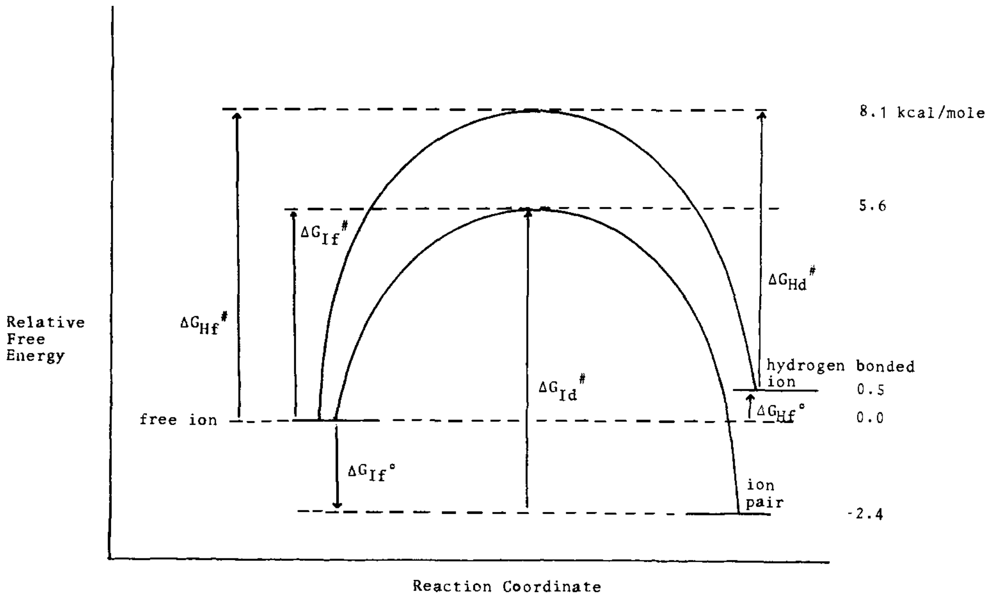
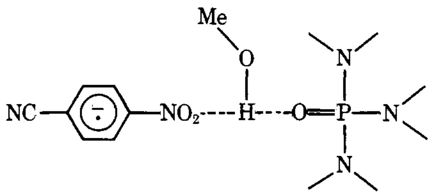


Figure 6. Free-energy diagram for the ion pairing and hydrogen bonding of the *p*-cyanonitrobenzene anion radical.

probably has only a slight effect upon $T_{2,0}$ while having a large effect upon the observed rate constants for ion pair and hydrogen bond formation. However, the extrapolated rate constants are valid even if $T_{2,0}$ is more severely affected by viscosity changes due to salt or MeOH addition. This is true, since the data are extrapolated to zero salt concentration where $T_{2,0}$ is responsible for the entire line width (δ^0).

Conclusions

The kinetic and thermodynamic data are summarized in Figure 6. It is clear that $\Delta G°$ for the formation of the ion paired anion is more negative than it is for the formation of the hydrogen bonded species. This is in part due to the stronger Coulombic interaction between the anion and cation than between the anion and the partial positive charge on the acidic proton of methanol, although the facts that the ion pair formation involves solvent reorientation and that the hydrogen bond formation requires the rupture of the hydrogen bond to HMPA must also be important. The rate of ion pair formation is probably diffusion controlled,[8,12a] and has a barrier that is relatively small ($\Delta G_{\mathrm{If}}^{\ddagger} = 5.6$ kcal/mol). Hydrogen bond formation to the anion radical, on the other hand, goes through a more energetic activated complex such as that depicted below.



It is, of course, easier to break the hydrogen bond to the anion ($\Delta G_{\mathrm{Hd}}^{\ddagger} = 7.6$ kcal/mol) than the ion pair ($\Delta G_{\mathrm{Id}}^{\ddagger} = 8.0$ kcal/mol). But strangely, the formation of the hydrogen bond has a greater effect upon the electron distribution in the anion radical than does the formation of the ion pair, as evidenced by the fact that both $\Delta g'$ and A' for the hydrogen bonded species (3.2×10^{-4} and 11.0 G, respectively) are larger than those values for the ion paired species (1.85×10^{-5} and 5.45 G, respectively). This may be explained by recalling that the potassium cation involved in ion pairing is still highly solvated by the HMPA.[17] The bulky cation plus its solvation sheath cannot approach the anion as closely as can the hydrogen bonding proton.

The rate of ion pair formation is diffusion controlled and is the same for all para-substituted nitrobenzene anion radicals, but the rates of hydrogen bond and ion pair dissociation are both apparently decreased by increasing the charge density on the NO_2 group.[11,13] The ion pairing reaction is affected more severely, at least with respect to the free energies, as evidenced by the larger ρ value obtained from a plot of log K vs. the σ value of the para substituent.[12,13c] From this, one might expect for para-substituted nitrobenzene anion radicals, where the substituent is not strongly electron withdrawing, that hydrogen bond formation would be faster than ion pair formation (diffusion-controlled hydrogen bond exchange is expected to be faster than ion pair formation, since the coordination number for K^+ in HMPA is 4[18]). For the anion radical of nitrobenzene this is the case. For this system k_{If} cannot be measured, because the rate of ion pair formation and dissociation is slow on the ESR time scale (ion pair and free ion are observed simultaneously).[10] The rates of hydrogen bond formation and dissociation, on the other hand, are fast on the ESR time scale for $PhNO_2\cdot^-$.[9] This effect cannot be attributed to smaller changes in the spectral parameters upon hydrogen bond formation, since for $PhNO_2\cdot^-$ $A_N' - A_N^0 = 5.5$ G for hydrogen bonding and 1.3 G for ion pairing. Although the relative rates of ion pair and hydrogen bond dissociation are reversed in going from $PhNO_2\cdot^-$ to $NCPhNO_2\cdot^-$, the relative effects of the formation of these two weak complexes on the electronic structures of the anion radicals remain about the same.

Finally it should be noted that at higher line widths there is considerable overlap of the ESR lines, which invalidates the use of line heights in the Bloch equations. This, however, does not affect our values for k_{Hf}, k_{Hd}, k_{If}, and k_{Id} since these were obtained by extrapolation of the observed rate constants to infinite dilution in complexing agent where the overlap is negligible. Line overlap and methanol–methanol self-association affect the slope of Figure 3, while viscosity change, association of K^+ with I^-, and overlap affect the slope of Figure 5. It is not clear as to the relative importance of each of these factors, but the extrapolation circumvents the problem.

Experimental Section

The ESR spectrometer system, the formation of the free anion radical by sodium reduction, and the techniques for the addition of salt and proton donor have been previously described.[8,9]

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