A Method for Estimating the Enthalpy of Hydrogen Bonding of a Proton Donor with an Anion Radical Acceptor

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Abstract: Methylacetylene, acting as a hydrogen bonding donor, has been added to the *p*-dinitrobenzene anion radical in hexamethylphosphoramide (HMPA). An equilibrium has been observed between hydrogen bonded HMPA plus the free anion radical and the free HMPA and hydrogen bonded anion radical. The thermodynamic parameters controlling this hydrogen bond exchange reaction were determined. The enthalpy (ΔH_t°) was found to be 0.76 kcal/mol. Further, the enthalpy of hydrogen bonding between the acidic proton of methyl acetylene and HMPA was determined using standard nmr techniques, and this enthalpy ($\Delta H_s^\circ = -2.69$ kcal/mol) was added to the enthalpy for the hydrogen bond exchange reaction to yield the first estimate of the hydrogen bonding energy to an anion radical. This enthalpy (ΔH_a°) was found to be -1.74 kcal/mol. The total heat of solution of methylacetylene in HMPA was determined by gas solubilities, and this value was compared with the enthalpies of hydrogen bonding.

Several spectroscopic techniques have been used to investigate the nature of hydrogen bonding, such as infrared and Raman spectroscopy, electronic absorption and fluorescence spectroscopy, and nuclear magnetic resonance (nmr).[1] A wide variety of proton donors and acceptors have been studied, but, to our knowledge, the hydrogen bonding energy between a proton donor and an anion radical acceptor has never been reported.

Recently it has been shown that additions of small amounts of proton donor to the system nitrobenzene (PhNO$_2$)–HMPA–Li affords an increase in the nitrogen coupling constant of the free ion.[2] This increase in the nitrogen splitting is due to hydrogen bonding of the proton donor to the nitro group of the anion radical. Further, the concentration of the hydrogen bonded ion was found to be controlled by a hydrogen bond exchange reaction between the solvent, hexamethylphosphoramide (HMPA), and the anion radical (eq 1).
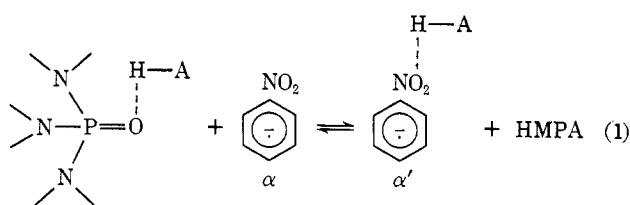

Since the equilibrium is fast on the esr time scale, the equilibrium constant and thus the thermodynamic parameters for reaction 1 could be obtained by the use of time averaging equations. The expression for the equilibrium constant in measurable esr parameters is given by

$$K_{eq} = (\bar{A}_N - A_N{}^\circ)[\text{HMPA}]/(A_{N'} - \bar{A}_N)[\text{HMPA}'] \quad (2)$$

$\bar{A}_N$ represents the time averaged coupling constant, $A_{N'}$ is the coupling constant for the fully hydrogen bonded anion radical, $A_N{}^\circ$ represents the coupling constant of the free ion, and [HMPA'] is the concentration of the hydrogen bonded HMPA and was

assumed to be equal to the concentration of the added proton donor.[2]

One of the most useful techniques for the determination of hydrogen bonding energies between proton donors and neutral proton acceptors is nmr.[3] The chemical shift of a proton participating in hydrogen bonding is displaced downfield due to a modification of its electronic environment. As is the case with the esr study,[4] the hydrogen bond exchange (eq 3) is fast

$$A\text{-}H + B \rightleftharpoons A\text{-}H\cdots B \quad (3)$$
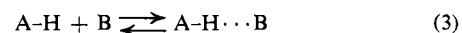
on the nmr time scale and again time averaging equations can be utilized. After the determination of the chemical shift for the monomer proton donor (ν^0) and the chemical shift for the hydrogen bonded proton in the complex (ν'), the equilibrium constant can be determined in terms of the weighted average chemical shift (ν). The equilibrium constant for reaction 3 is given by[1]

$$1/(\nu - \nu^0) = 1/(K_{eq}\{\nu' - \nu^0\}C_B{}^0) + 1/(\nu' - \nu^0) \quad (4)$$

where $C_B{}^0$ represents the initial concentration of hydrogen bond acceptor. K_{eq} can be calculated from the slope of a plot of $1/(\nu - \nu^0)$ *vs.* $1/C_B{}^0$. The intercept is $1/\Delta$ where $\Delta = (\nu' - \nu^0)$.

Here we wish to report a technique to determine the hydrogen bonding energy of a proton donor to an anion radical acceptor utilizing both esr and nmr spectroscopy. This technique consists of a thermochemical cycle and utilizes the fact that the enthalpy of the hydrogen bond exchange reaction between an anion radical and HMPA consists of four predominant terms: the enthalpy of hydrogen bonding to the HMPA (ΔH_s°), the enthalpy of hydrogen bonding to the anion radical (ΔH_a°), and the enthalpy of solution of both the products and reactants.

Experimental Section

The esr spectrometer system, the method of reduction of the

(1) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding," Van Nostrand-Reinhold, New York, N. Y., 1971, pp 47 and 91.
(2) G. R. Stevenson and H. Hidalgo, *J. Phys. Chem.*, **77**, 1027 (1973).

(3) J. A. Pople, W. G. Schneider, and H. I. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 15.
(4) G. R. Stevenson, L. Echegoyen, and L. Lizardi, *J. Phys. Chem.*, **76**, 1439 (1972).
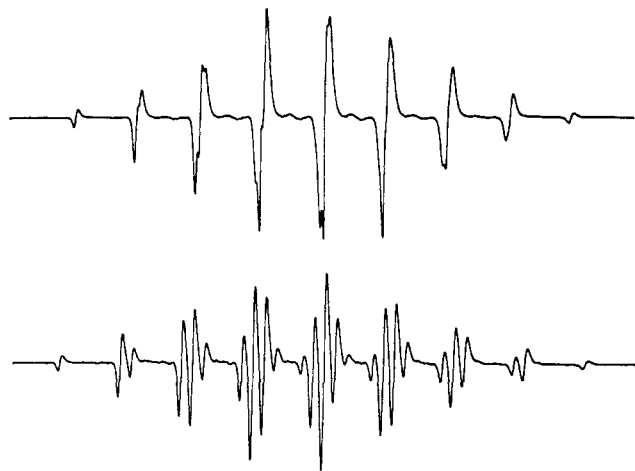
Figure 1. Esr spectra of the system DNB–HMPA–Na at 25°: (upper) containing 0.27 M methylacetylene; (lower) containing 3.81 M methylacetylene.

neutral molecule to form the anion radical, and the method of purification of the HMPA have been previously described.[4]

The nmr spectra were recorded on a Varian T-60 nmr spectrometer. The temperature was controlled with a Varian variable temperature controller to within ±2°.

Quantitative additions of methylacetylene to the p-dinitrobenzene anion radical solutions in HMPA were carried out with the use of a toepler pump connected with a gas buret. Methylacetylene was allowed to enter the calibrated gas buret under high vacuum (10^{-6} Torr). The number of moles of methylacetylene was then calculated using the ideal gas equation of state. The initial pressures in the gas buret were between 10 and 400 Torr. This methylacetylene was then allowed to pass into the bulb containing the anion radical solution. Quantitative additions were carried out by cooling the reaction bulb with liquid nitrogen.

Methylacetylene was quantitatively added to the HMPA–CCl₄ solutions for nmr analysis in an identical manner, except that an nmr tube replaced the esr tube. All of the esr and nmr samples were prepared and sealed under high vacuum.

The determination of the gas solubilities and Henrys' constants for the methylacetylene, acetylene, and dimethylacetylene was carried out by allowing the gas to pass from the gas buret into the vacuum line manifold and make contact with the rapidly stirred HMPA. The gas was allowed to come to equilibrium with the stirred solution for a period of 2 hr. The stopcock to the apparatus containing the HMPA was then shut, and the remaining gas was toepled back into the gas buret. The amount of gas that had dissolved in the HMPA was simply taken as the difference between the initial and final quantities of gas. The temperature of the HMPA solutions was controlled to ±1° by the use of a constant temperature jacket, and the pressure in the manifold was measured using a standard mercury manometer. The fact that HMPA has a very low vapor pressure (0.07 Torr at 30°)[5] and that the proton donors are quite soluble in this solvent allows the use of the simple apparatus described above to obtain gas solubilities of high accuracy.

The methylacetylene was purchased from Gas Products, the acetylene from General Gases of Puerto Rico, and the CCl₄ spectro quality from Matheson Coleman and Bell. The gases were purified by low-temperature distillation and degassed in a freeze–pump–thaw cycle under high vacuum. The gases were stored in gas storage bulbs before use.

Results and Discussion

Esr. Alkali metal reduction of p-dinitrobenzene (DNB) in HMPA results in a solution that yields a nine-line spectrum upon esr analysis. The nine lines result from two equivalent nitrogens and four protons which are magnetically equivalent to the nitrogens.[6] This radical has been shown to be the free DNB anion

(5) H. Normant, *Angew. Chem., Int. Ed. Engl.*, **6**, 1046 (1967).
(6) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, **77**, 2339 (1973).

radical.[6] Under very high resolution conditions, however, some splitting of the central lines can be observed indicating that the nitrogen splitting is slightly larger than that for the four protons ($A_{N^0} = 1.155$ and $A_{H^0} = 1.099$ G). Both A_{N^0} and A_{H^0} are thermally independent just as the nitrogen splitting for the nitrobenzene free ion is.[4] For the esr spectrum of DNB·⁻ the splitting observed in the second line represents the difference in A_N and A_H (δ).

As is the case for the PhNO₂ anion radical in HMPA the addition of proton donors increases the nitrogen coupling constant, due to the formation of hydrogen bonds with th NO₂ groups (Figure 1). The reaction leading to the formation of the hydrogen bonded anion radical is given by

$$\text{DNB} \cdot^- + \text{HMPA} \cdots \text{HA} \rightleftharpoons \text{DNB} \cdot^- \cdots \text{HA} + \text{HMPA} \quad (5)$$
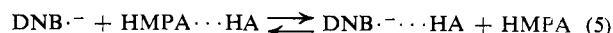
This increase in the nitrogen splitting in the DNB anion radical is accompanied by a decrease in A_H; thus δ increases rapidly with increasing concentration of proton donor (methylacetylene). Since the two nitrogens remain equivalent after the addition of the proton donor to the HMPA anion radical solution, there must exist a fast intramolecular hydrogen bond shift between the two nitro groups.

Taking the value of δ as a weighted average between the hydrogen bonded anion radical and the free ion, an expression can be developed for the determination of the equilibrium constant for the hydrogen bond exchange reaction (eq 5). The development of this expression for K_{eq} in terms of δ, δ', and δ^0 is exactly the same as for the case for the PhNO₂ anion radical except that δ replaces A_N. The resulting expression is given by

$$K_{eq} = (\delta - \delta^0)[\text{HMPA}]/(\delta' - \delta)[\text{HMPA} \cdots \text{HA}] \quad (6)$$

where δ^0 and δ' represent the difference in A_N and A_H for the free ion and the hydrogen bonded ion, respectively. δ' (0.536 G) was determined from an extrapolation of a plot of δ vs. the concentration of the proton donor to 100% proton donor. Since HMPA is the solvent and the concentration of proton donor is small, the concentration of HMPA was taken to be the concentration of pure HMPA. For all cases the observed δ is much closer to δ^0 than to δ' (Table I). This indicates that the concentration of HMPA···HA is much larger than that of the hydrogen bonded ion (DNB·⁻···HA). This is the expected result since HMPA is a much better hydrogen bond acceptor than are nitrobenzenes.[7,8]

Using the technique described above, the equilibrium constants were determined for the DNB–HMPA–metal systems with added methylacetylene. The equilibrium constants determined in this manner gave quantitative agreement for methylacetylene concentrations varying from 1.0 to 2.5 M. The exact anion radical concentrations were not determined, but all were between 10^{-5} and 10^{-3} M. The equilibrium constants from a representative set of data along with K_{eq} taken form the average of six determinations at room temperature are given in Table I.

The possibility exists that the experimental value for δ' is not exactly equal to δ[complex]. This would result

(7) T. Olsen, *Acta Chem. Scand.*, **24**, 3081 (1970).
(8) W. F. Baitinger, P. v. R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron*, 1635 (1964).

Table I. Hydrogen Bond Exchange Parameters for the System DNB–HMPA–Metal with Added Methylacetylene

	$-15°$	$0°$	$20°$	$44°$	$50°$
$\delta(2.33\ M)(Na^+)^a$	0.097	0.104	0.105		0.112
$\delta(3.42\ M)(K^+)$	0.119	0.123	0.127	0.135	
$K_{eq}(K^+)$	0.259	0.280	0.296	0.339	
$K_{eq}(Na^+)$	0.241	0.280	0.289		0.335
		$\Delta H_t°(K^+) = 0.72^b$			
		$\Delta H_t°(Na^+) = 0.78\ kcal/mol^b$			
		$K_{eq}(25°) = 0.31 \pm 0.04$			

[a] The numbers in parentheses represent the concentration of the methylacetylene and the counterion, respectively. [b] The average $\Delta H_t°$ for all systems is 0.76 ± 0.06 kcal/mol.

in an almost constant error in K_{eq} but would not result in a major error in the enthalpy. In Table II K_{eq} and

Table II. K_{eq} and $\Delta H_t°$ for the System DNB–HMPA–Na$^+$ with a Methylacetylene Concentration of 2.33 M

K_{eq}	T, °C	K_{eq}	T, °C
0.155	-15	0.187	20
0.183	0	0.217	50
	$\Delta H_t° = 0.78$ kcal/mol		

$\Delta H_t°$ are calculated using a value of 0.75 G for δ' instead of the experimental 0.536 G.

It is clear from Tables I and II that K_{eq} is a sensitive function of the choice of δ', but the enthalpy for the hydrogen bond exchange reaction does not vary even with a 50% error in δ'.

Deranleau[9] has recently pointed out that equilibrium constants for weak complexes are most reliable when they are based upon spectral data that extend as much as possible into the region where the saturation factor (s) is between 0.2 and 0.8. For the esr experiment described here

$$s = [DNB \cdot^-]/[DNB \cdot^- \cdots HA] =$$
$$(\delta - \delta^0)/(\delta' - \delta^0) \quad (7)$$

Calculated from eq 7 our saturation factor (s) varied from 0.2 to 0.3.

For all of the systems studied linear plots of ln K_{eq} vs. $1/RT$ were obtained (Figure 2). The positive enthalpies (Table I) indicate that HMPA is a better hydrogen bond acceptor than is the anion radical of DNB. Further, the enthalpies for the hydrogen bond exchange reaction (eq 5) are essentially independent of the counterion (either K$^+$ or Na$^+$). This indicates that the counterion is not directly involved in the hydrogen bond exchange reaction. This is suprising, since the counterion was found to be directly involved in the hydrogen bond exchange reaction for the system PhNO$_2$–HMPA–metal with added methanol or ammonia.[10]

Nmr. Upon nmr analysis, methylacetylene (in HMPA) yields a quartet due to the acetylenic proton and a doublet due to the methyl protons. The chemical shift of the quartet is concentration dependent, while that for the doublet is independent of the concentration. This allows the use of the methyl proton

(9) D. A. Deranleau, *J. Amer. Chem. Soc.*, **91**, 4044 (1969).
(10) L. Echegoyen, H. Hidalgo, and G. R. Stevenson, *J. Phys. Chem.*, **77**, 2649 (1973).
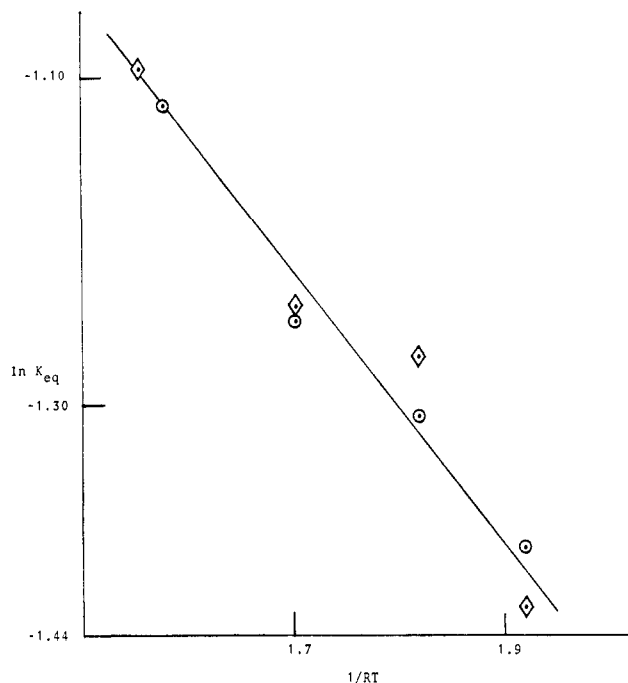
Figure 2. Plot of ln K_{eq} for the hydrogen bond exchange reaction vs. $10^3/RT$ for the systems DNB–HMPA–M$^+$: (○) is for potassium, (◇) is for sodium.

resonance as an internal standard. All of the chemical shifts reported are relative to this standard. By extrapolating a plot of the chemical shift of the quartet vs. the methylacetylene concentration to infinite dilution in pure CCl$_4$, a value of ν^0 (the chemical shift of the acidic proton for the monomeric methylacetylene) was found to be -9.61 Hz. The fact that the chemical shift of the quartet is dependent upon the HMPA concentration in CCl$_4$ is evidence for the formation of a hydrogen bonded complex between methylacetylene and the HMPA as shown by

$$CH_3C\equiv CH + HMPA \rightleftharpoons CH_3C\equiv CH \cdots HMPA \quad (8)$$
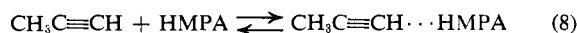
Since the formation and dissociation of the hydrogen bonds are fast on the nmr time scale, the observed chemical shift for the acidic proton of methylacetylene is a weighted average between the monomeric species and the hydrogen bonded species. If the 1:1 association described in eq 8 is correct then K_{eq} is given by

$$K_{eq} = [CH_3C\equiv CH \cdots HMPA]/$$
$$[CH_3C\equiv CH][HMPA] \quad (9)$$

and this equilibrium constant can be determined by the use of eq 4 providing that the initial concentration of HMPA (represented by C_B^0 in eq 4) is large in comparison to the initial concentration of methylacetylene. The samples used in this experiment contained methylacetylene concentrations varying from infinite dilution to 0.5 M, and the HMPA concentrations varied from 1.2 to 5.7 M in CCl$_4$. The ratio of the initial HMPA to methylacetylene concentration varied from 12 to infinity. Thus, the condition that C_B^0 must be much larger than the intial proton donor concentration is met.

A plot of $1/(\nu - \nu^0)$ vs. $1/C_B^0$ should yield a straight line with a slope of $1/\Delta K_{eq}$ and an intercept of $1/\Delta$. Treated in this manner our data did yield linear plots (Figure 3). At room temperature this plot yields an
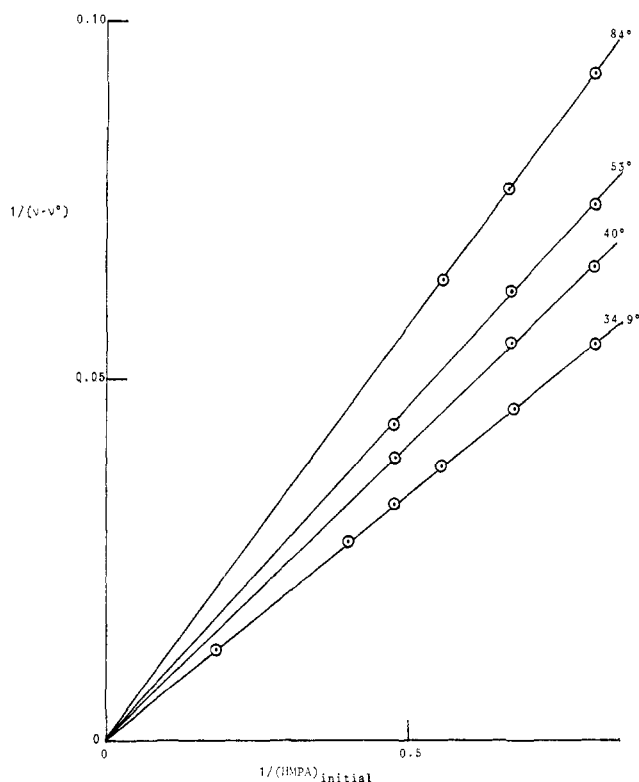
Figure 3. Plot of $1/(\nu - \nu^0)$ $vs.$ $1/[\text{HMPA}]$ for solutions of HMPA and methylacetylene in CCl_4.

intercept and slope of 1.22×10^{-3} and 6.69×10^{-2}, respectively. This leads to a value for Δ of 822 Hz and a value for K_{eq} of 1.82×10^{-2} (Table III).

Table III. Nmr Parameter for the Hydrogen Bonding between HMPA and Methylacetylene in CCl_4 at 34.9°

| C_B^0, M	ν	C_B^0, M	ν
1.24	8.60	2.10	20.89
1.50	12.05	2.50	26.36
1.80	16.30	5.75	67.90

The intercept in Figure 3 is very close to 0,0 and thus the reciprocal of this intercept (Δ) is extremely sensitive to small changes in this intercept. This leaves us with a very uncertain value for Δ and thus K_{eq}. All of this shows that "weak" hydrogen bonding complexes as defined by small equilibrium constants necessarily contain large errors in Δ and K_{eq} as previously pointed out by Wiley and Miller.[11] Also the saturation factor (s) in this experiment varied from 0.01 to 0.09 as defined by

$$s = (\nu - \nu^0)/\Delta = \frac{[\text{CH}_3\text{CCH}\cdots\text{HMPA}]}{[\text{CH}_3\text{CCH}]_{\text{initial}}}$$

This further indicates the possibility of large error in K_{eq}.

Several workers have shown that the value for Δ is weakly temperature dependent,[11-13] but this temperature dependence can be ignored for systems where

(11) G. R. Wiley and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 3287 (1972).
(12) F. Takahashi and N. C. Li, *J. Phys. Chem.*, **69**, 2950 (1965).
(13) C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962).
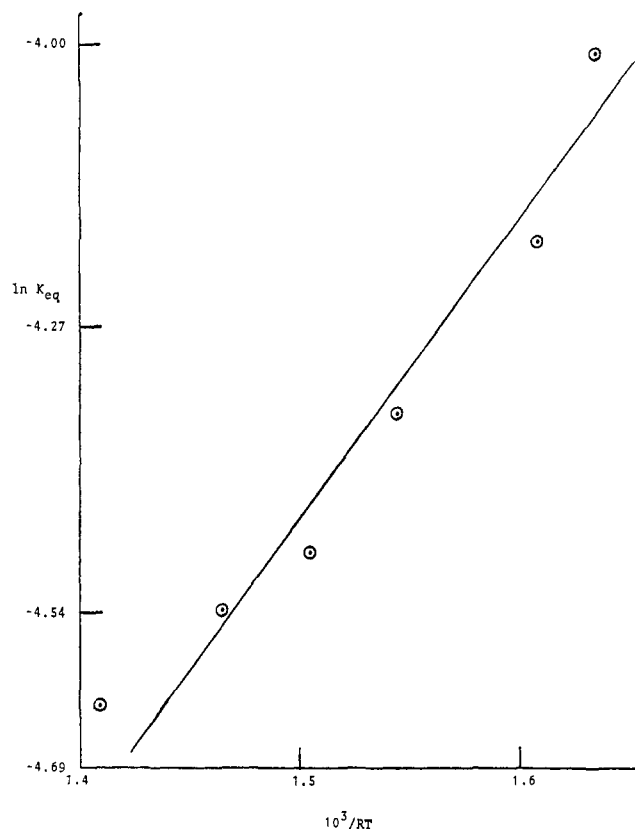
Figure 4. Plot of $\ln K_{eq}$ for the formation of hydrogen bonded complex between methylacetylene and HMPA in CCl_4 $vs.$ $10^3/RT$.

"weak" hydrogen bonding exists or where there are large errors in K_{eq}.[11,14,15] Our apparent large error in K_{eq} is not particularly disappointing since only the value of ΔH_s° is of interest for obtaining the ultimate hydrogen bonding enthalpy to the anion radical. However, our data must be considered as inherently imprecise, and there must be substantial uncertainties in K_{eq} and ΔH°.

The enthalpy of hydrogen bonding to the HMPA was taken from the slope of a plot of $\ln K_{eq}$ $vs.$ $1/RT$ (Figure 4). Δ was considered to be independent of temperature. This same assumption has been made in many previous reports.[14-17] Δ is known to gradually decrease with increasing temperature;[11] however, this decrease amounts to less than 5% over a 40° temperature range. The dependence upon temperature for Δ is probably responsible for a curvature noted in Figure 4. The enthalpy taken from Figure 4 is $\Delta H_s^\circ = -2.69 \pm 0.20$ kcal/mol.

Gas Solubilities. Since HMPA is a strong hydrogen bond acceptor, gases that are good proton donors readily dissolve in this solvent. To check the technique described in the Experimental Section we determined the enthalpy of solution of acetylene in HMPA. The number has previously been determined and found to be -6.57 kcal/mol.[18] We obtained a value of

(14) Y. H. Shaw and N. C. Li, *Can. J. Chem.*, **48**, 2090 (1970).
(15) S. Nishimura, C. H. Ke, and N. C. Li, *J. Phys. Chem.*, **72**, 1297 (1968).
(16) T. J. V. Findlay, J. S. Keniry, A. D. Kidman, and V. A. Pickles, *Trans. Faraday Soc.*, **63**, 846 (1967).
(17) R. Mathur, E. D. Becker, R. B. Bradley, and N. C. Li, *J. Phys. Chem.*, **67**, 2190 (1963).
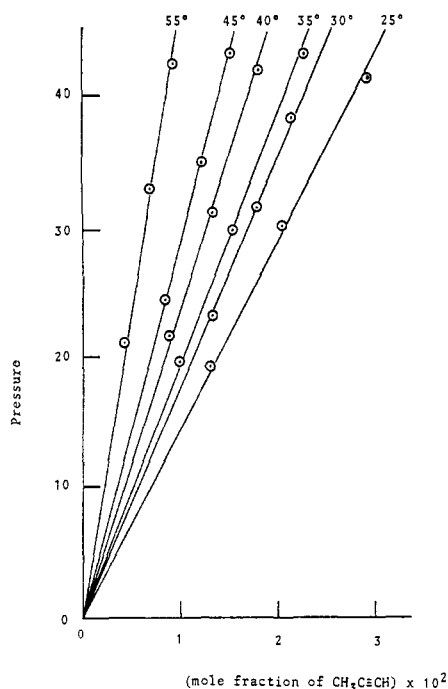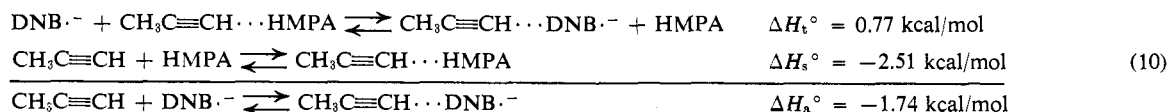(18) G. Schay, Gy. Székely, Gy. Rácz, and G. Traply, *Period. Polytech. Eng.*, **2**, 1 (1958).

Figure 5. Henry's plot for methylacetylene–HMPA systems.

Figure 6. Plot of ln of Henry's constant $vs.$ $10^3/RT$ for the methylacetylene–HMPA system.

−6.59 ± 0.1, which is in excellent agreement with the previously reported value.

The solubility of methylacetylene was found to be directly proportional to the pressure, yielding a Henry's constant of 1946.7 at 35° (Figure 5). A plot of ln Henry's constant $vs.$ $1/RT$ is perfectly linear (Figure 6) and yields an enthalpy of solution of −5.82 ± 0.22 kcal/mol.

Conclusion

From the gas solubility study and the nmr experiment it is clear that the enthalpy of solution of methylacetylene in HMPA is considerably larger than the enthalpy of hydrogen bonding between the HMPA and methylacetylene. This means that the HMPA is involved in solvation of the methyl group of the methylacetylene. If it is assumed that the interaction be-

A source of error in this calculation results from the fact that due to solubility and nmr interference considerations CCl_4 and not hexane had to be used as the solvent for the nmr experiment. It has previously been pointed out that CCl_4 is not necessarily an "inert" solvent for the proton donor.[19] Due to this problem $\Delta H_a°$ really represents the enthalpy of hydrogen bonding to the anion radical minus the enthalpy of hydrogen bonding between methylacetylene and CCl_4. It is safe to assume that the enthalpy of hydrogen bonding to the anion radical is large compared to that for the CCl_4; however, this problem still introduces error in $\Delta H_a°$. The error in $\Delta H_a°$ is due to the combined errors in $\Delta H_t°$ and $\Delta H_s°$, which have been discussed above, and the error due to possible interaction between the solvent (CCl_4) and the proton donor. The estimated total error in $\Delta H_a°$ is a summation of these errors. Considering the error due to the CCl_4 to be about 0.2 kcal/mol using the tables of data given in ref 1, the total error in $\Delta H_a°$ is estimated to be 0.46 kcal/mol.

The authors are aware of the relatively large error in the final enthalpy due to the numerous assumptions that have been made. However, this report represents the only technique for estimating the enthalpy involved in hydrogen bonding for anion radical systems.

DNB·⁻ + CH₃C≡CH···HMPA ⇌ CH₃C≡CH···DNB·⁻ + HMPA $\Delta H_t°$ = 0.77 kcal/mol

CH₃C≡CH + HMPA ⇌ CH₃C≡CH···HMPA $\Delta H_s°$ = −2.51 kcal/mol   (10)

CH₃C≡CH + DNB·⁻ ⇌ CH₃C≡CH···DNB·⁻ $\Delta H_a°$ = −1.74 kcal/mol

tween HMPA and the methyl protons is independent of the proton acceptor, $\Delta H_a°$ (the actual enthalpy of hydrogen bonding to the anion radical) can now be calculated. The calculation is carried out using the simple thermochemical cycle shown in eq 10.
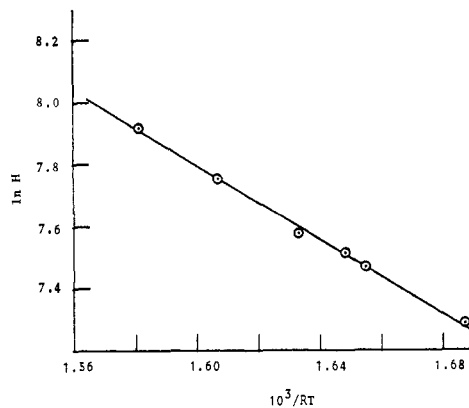
(19) D. H. McDaniel and W. G. Evans, *Inorg. Chem.*, **5**, 2180 (1966).