formed in the rate-determining step. In keeping with the Curtin-Hammett principle, the distribution of product alcohols also is a function of the triazene tautomer distribution and basicity and the relative rates of the competing rate-determining steps. We must conclude from our results that the cationic species is most probably an alkanediazonium ion, rather than an alkyl carbonium ion.

Acknowledgment. We are grateful to Dr. Climaco J. Metral and John M. Roman for the mass spectrometry and John R. Klose for some of the NMR spectroscopy. This research was supported in part by grants (R.H.S.) from the National Science Foundation (Grant No. CHE-8521385); the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 17134-B4); and the William and Flora Hewlett Foundation Grant of Research Corporation. Partial support was also derived from the National Cancer Institute, DHHS, under contract No. NO1-74101 with Bionetics Research, Inc.

Registry No. DMT, 3585-32-8; DET, 63980-20-1; DPT, 118398-97-3; DBT, 118398-98-4; DIT, 84713-95-1; DTT, 79950-34-8; MET, 118398-99-5; MPT, 118399-00-1; MBT, 74649-51-7; MIT, 118399-01-2; MTT, 118399-02-3; MBzT, 74649-49-3; ethyl azide, 871-31-8; iodoethane, 75-03-6.

Structural and Energetic Analysis of Gas-Phase Hydrated Ammonium Ions with Relevance to the "Anomalous" Order in Amine Basicities

Russell S. Drago,* Thomas R. Cundari, and Donald C. Ferris

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received August 3, 1988

The underlying cause for the anomalous basicity of the methylamine series in aqueous solution is investigated. The proton affinity of the amines in the gas phase follows the order ($NMe_3 > NMe_2H > NMeH_2 > NH_3$) due in large part to the inductive effect of the methyl group. The aqueous-phase basicity order from protonation enthalpies is $NH_2Me > NH_3 > NHMe_2 > NMe_3$. An *E*, *C*, and *W* analysis of the gas-phase data for reaction of these amines with $(H_2O)_nH^+(g)$ was used to incorporate these acid–base interactions into the correlation. One of the key factors leading to the observed basicity order in aqueous solution is the increased fractional importance of the electrostatic interaction as *n* increases in the gas-phase $(H_2O)_nH^+$ species. The species with $n = 6$ undergoes an essential electrostatic interaction with the small covalent contribution giving an order that differs slightly in magnitude from the pure electrostatic order of the E_B numbers. The gas-phase proton affinities follow the trend of the amine C_B numbers though an appreciable electrostatic contribution occurs. In view of these differences, the gas-phase proton is concluded to be a poor model for predicting the chemistry of $H(H_2O)_n^+$ in aqueous solution. The *E*, *C*, and *W* analysis clearly shows that the addition of four and possibly up to as many as six water molecules to the ammonium ions leads to water clusters as opposed to water acting as a Lewis base toward the other NH protons of ammonia or methyl- or dimethylamine. Semiempirical intermediate neglect of differential overlap calculations were carried out in conjuction with the *E*, *C*, and *W* analysis. Both the *E*, *C*, and *W* and MO analyses conclude that hydrogen bonding of water (as a Lewis base) molecules up to $n = 6$ to the additional amine protons in ammonia, primary and secondary amines is disfavored in relation to binding this water to protons on oxygen forming a water chain in the gas-phase systems.

Introduction

The advent of ICR and related techniques for studying gas-phase ion equilibria has led to many interesting comparisons of gas phase to solution chemistry[1] with differences often attributed to solvation and no attempt made to discuss the fundamental interactions involved. The acceptance of such statements as "explanations" has served to cloud a basic understanding of the molecular interactions involving the solvent. In protonic solvents the term solvation is as difficult to define as is the chemical bond. In the extremes, the coordination (Lewis acid–base interactions) that hold clusters of solvent bound to the solute can be distinguished from a bulk dielectric effect (Born charging) that solvates these clusters. Variation in cluster size and the dynamics of these processes add to the complexity. We shall use the term nonspecific solvation for gross dielectric effects caused by the solvent and the term acid–base for specific, directional interactions involving localized sites that hold clusters of molecules together.

In this article, we explore solvation effects in aqueous protonation and gain further insight about the often analyzed "anomalous order" of amine basicities.[2] Gas phase data indicate that increased methyl substitution increases amine basicity toward H^+ as evidenced by more positive proton affinities.[1] This trend follows the inductive effect

Table I. Amine Proton Affinities and Aqueous Enthalpies of Protonation

base, B (*C*, *E*)	$-\Delta H$ $BH(g)^+$ or PA[a]	$-\Delta H$ $BH^+(aq)$[b]	$-\Delta H$ B(aq)[c]
NH_3 (3.32, 1.48)	204.0	12.5	8.5
NH_2Me (5.63, 1.50)	214.1	13.2	11.1
$NHMe_2$ (8.47, 1.33)	220.6	12.0	13.2
NMe_3 (11.20, 1.19)	225.1	8.8	13.2
H_2NEt (5.91, 1.51)	217.0	13.7	13.0
$HNEt_2$ (8.59, 1.11)	225.6	12.8	15.3
NEt_3 (10.83, 1.29)	232.3	10.3	16.7

[a] Equation 1, ref 5b. [b] $B(aq) + H^+(aq) \rightarrow BH^+(aq)$, ref 3. [c] $B(g) + H_2O(aq) \rightarrow BH_2O(aq)$, ref 5b.

(1) See for example: Aue, D. H.; Bowers, M. J. *Gas Phase Ion Chemistry*; Bowers, M. J., Ed.; Academic Press: New York, 1979 (and references therein).

(2) (a) Brown, H. C.; Bartholomay, H., Jr.; Taylor, M. D. *J. Am. Chem. Soc.* **1944**, *65*, 435. (b) Condon, F. E. *Ibid.* **1965**, *87*, 4481, 4485, 4494. (c) Pearson, R. G.; Vogelsong, D. C. *Ibid.* **1958**, *80*, 1038. (d) Trotman-Dickenson, A. F. *J. Chem. Soc.* **1949**, 1293. (e) Arnett, E. M.; Jones, F. M.; Taagepera, M.; Henderson, W. G.; Beauchamp, J. L.; Holtz, D.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 4724. (f) Jones, F. M.; Arnett, E. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 263.

(3) Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 1240.

0022-3263/89/1954-1042$01.50/0

$$:NR_3(g) + H^+(g) \rightarrow [HNR_3]^+(g) \qquad PA = -\Delta H\ BH(g)^+ \quad (1)$$

order of increased electron releasing ability of alkyl substituents compared to hydrogen. Taft has recently shown[4] that this inductive effect of alkyl substituents is adequately modeled by covalent type induced dipole interactions. In aqueous solution, the order[3] of amine basicities, as given by $-\Delta H\ BH^+(aq)$ for the protonation of the amines (see Table I), show a different trend: $CH_3NH_2 > NH_3 > (CH_3)_2NH \gg (CH_3)_3N$. Since this trend is not that expected on the basis of the inductive effect of the methyl group, it is referred to as an anomalous order, and the difference between the gas-phase and the aqueous-solution orders has been attributed to solvation. Clearly any interactions involving the primary coordination sphere of a cation are coordination. Thus, the coordination of a proton to a water molecule (forming H_3O^+) or to a water cluster (forming $H_2O)_nH^+$) is a specific Lewis acid–base interaction forming a new acid. Comparing a gas phase proton affinity to coordination of a base to H_3O^+ or $(H_2O)_nH^+$ involves comparing the coordination chemistry of different acids.

We have previously shown[6] that enthalpy data for the methylamines can be correlated with the E, C, W equation:

$$-\Delta H = E_A E_B + C_A C_B - W \quad (2)$$

The E (electrostatic) and C (covalent) approach[6] factors the enthalpy into terms related to covalent and electrostatic contributions. When the methylamines coordinate to an acid in which the covalent (C_AC_B) term dominates, the expected donor order is the inductive order. The order $CH_3NH_2 > NH_3 > Me_2NH > Me_3N$ is expected if the electrostatic (E_AE_B) term dominates and the acid–base interaction is mainly charge–dipole in nature (See Table I for the amine E_B and C_B parameters). Recent reports of data by Meot-Ner[5] enables us to take a more detailed look at the factors causing the anomalous order of amine basicity. Our approach involves attempting to understand the enthalpies of interaction of the amines with $(H_2O)_nH^+$(g). When these are understood, one can attempt to understand the solution data and, if so desired, any deviations of free energies from this order on the basis of entropy effects.[7c]

Calculations

The E and C analysis of acid–base interactions involves substituting experimental enthalpies and known[6] E_B and C_B parameters for bases (B) into eq 2, producing a series of equations. These simultaneous equations are solved for the E_A, C_A, and W values that best fit the enthalpies for each of the various acidic species (A) discussed in this article. The W parameter incorporates any energy terms for an acid or base reaction that is constant in all reactions the species undergoes.[6]

All molecular orbital calculations were of the intermediate neglect of differential overlap (INDO/1) type.[8a–c] Standard valence basis sets were used (C, O, N, 2s, 2p basis; H, 1s basis). Geometry optimizations were energy gradient driven. Convergence was assumed when the maximum component of the gradient was less than 1×10^{-3} hartrees. In all cases the energy convergence was on the order of 10^{-5} hartrees (6×10^{-3} kcal). Starting geometries were taken from a molecular mechanics minimization of the nonbonded atom repulsions. The initial bond angles were taken as standard (2 coordinatin, 180°; 3 coordination, 120°; 4 coordination, 109.5°). An INDO/1 energy minimization with the above-mentioned criterion was then performed. Finally, a single point INDO/1 calculation was run for the minimum energy geometry. All calculations were carried out on the University of Florida, Department of Chemistry, Quantum Theory Project VAX 11/780 with use of the ZINDO package.[8c] The ab initio calculation of the LUMO energies for $H^+(H_2O)_n$, $n = 1, 2$, were run with the HONDO-5 program with a 4-31G basis set[8d] on the calculated minimum energy geometries (vide infra).

Results and Discussion

Analysis of the Degree of Aquation on the Acidity of $H(H_2O)_n^+$. The bare proton does not exist in aqueous solution. In comparing solution basicity to gas-phase proton affinities different acids are involved: H^+ in the gas phase and $H(H_2O)_n^+$ in water. Donor orders are known[6] to reverse when different acids react (e.g., I_2 and C_6H_5OH lead to very different orders for the enthalpy of binding bases) because of differences in the magnitudes of the covalent and electrostatic contributions to the interaction. Data are now available to carry out an E and C analysis (see calculation section) of the enthalpies of various bases interacting with H^+, H_3O^+, $H_5O_2^+$, $H_7O_3^+$, HgO_4^+, $H_{11}O_5^+$, and $H_{13}O_6^+$. Quantitative C_A and E_A values for these acids will determine if the "anomalous order" of amine donor strengths observed in solution are expected from fundamental differences in the electrostatic and covalent nature of the gas-phase acid–base interactions. This analysis also provides fundamental information about the structure of the gas-phase clusters.

The Proton. The enthalpies for the interaction of donors with H^+ are larger than those for which the approximations, that were used to theoretically justify the E and C equation, hold.[6d,7a] Thus, we attempted the E, C, and W approach to fitting the proton affinities, assuming that W will incorporate a constant contribution from the acid for the series of bases. W can be viewed as displacing a fixed, unspecified base from the acid leading to enthalpies small enough for the E and C approximations to hold. Now, the C_A and E_A values for the cations will incorporate not only the electrostatic and covalent binding contributions but variations that occur[7] in t that are not accommodated by a constant W. An excellent fit of a large amount of gas-phase ion data results by using reported[6] E_B and C_B values from the weaker interactions of the

(4) Taft, R. W. *Prog. Phys. Org. Chem.* **1987**, *16*, 120.

(5) (a) Meot-Ner, M. *J. Am. Chem. Soc.* **1984**, *106*, 1257, 1265. (b) Meot-Ner, M. *Molecular Structure and Energetics*; **1987**, *4*, 71. (c) Meot-Ner, M.; Speller, C. V. *J. Phys. Chem.* **1986**, *90*, 6616.

(6) (a) Drago, R. S.; Wong, N.; Bilgrien, C.; Vogel, G. C. *Inorg. Chem.* **1987**, *26*, 9 contains the most recent set of parameters. (b) Drago, R. S. *Coord. Chem. Revs.* **1980**, *33*, 251. (c) Drago, R. S.; Meek, D. W.; Longhi, R.; Joesten, M. D. *Inorg. Chem.* **1963**, *2*, 1056. (d) Marks, A. P.; Drago, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 3324. (e) Kroeger, M. K.; Drago, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 3250.

(7) (a) An ect analysis of the large enthalpies of gas-phase cation–anion, and cation–molecule interactions was carried out and reported.[7b] The term t is added (for larger enthalpies) to accommodate the energy contribution to the interaction associated with the electron transfer from the base to the acid.[9] These latter parameters (e, c, t) are poorly defined because the data base is too small, and as a result the ability of the model to predict enthalpies is low for new systems not included in the parameterization. The ect parameters for neutral bases can be transformed into E_B and C_B via a 3×2 transformation matrix.[7d] (b) Drago, R. S.; Ferris, D. manuscript in preparation. (c) Doan, P. E.; Drago, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 2772. (d) Doan, P. E. Ph.D. Thesis, University of Illinois, 1987.

(8) (a) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026. (b) Pople, J. A.; Beveridge, J. A. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970. (c) The ZINDO package was written by M. C. Zerner of the University of Florida. (d) Dupuis, M.; King, H. F.; Rys, J. *QCPE* **1981**, *13*, 401.

(9) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 546.

Table II

B	PA exp	PA calcd	$-\Delta H(H_3O^+)$ exp[a]	$-\Delta H(H_3O^+)$ calcd[b]	$-\Delta H$-$[(H_2O)_2H^+]$ exp[c]	$-\Delta H$-$[(H_2O)_2H^+]$ calcd[d]	$-\Delta H$-$[(H_2O)_3H^+]$ exp[c]	$-\Delta H$-$[(H_2O)_3H^+]$ calcd[d]	$-\Delta H$-$[(H_2O)_4H^+]$ exp[c]	$-\Delta H$-$[(H_2O)_4H^+]$ calcd[d]	$-\Delta H$-$[(H_2O)_5H^+]$ exp[c]	$-\Delta H$-$[(H_2O)_5H^+]$ calcd[d]	$-\Delta H$-$[(H_2O)_6H^+]$ exp[c]	$-\Delta H$-$[(H_2O)_6H^+]$ calcd[d]
NH_3	204.0	206.6	60.0	60.0	46.0	45.1	37.3	38.2	32.0	32.5	27.9	27.8	23.9	23.8
CH_3NH_2	214.1	214.2	66.5	65.5	48.6	49.2	41.5	41.4	34.7	35.0	30.1	30.2	25.7	25.8
$(CH_3)_2NH$	220.6	219.9	68.4	69.4	51.4	51.1	42.4	42.3	35.8	35.0	29.7	29.7	25.1	25.1
$(CH_3)_3N$	225.1	225.9	73.9	73.6	53.5	53.3	43.3	43.6	35.0	35.6		29.6		24.7
CH_3CN	189.2	190.1	48.4	46.9	32.9	32.4	28.0	26.9	21.1	20.6	16.0	16.0	13.1	13.1
$(CH_3)_2CO$	196.1	195.3	49.3	50.9	33.0	35.9	28.6	29.9	23.2	23.5	18.8	18.8		15.6
dioxane	198.8	196.5	50.9	51.9		37.0		30.8		24.5		19.9		16.6
$(C_2H_5)_2O$	200.2	198.7	53.1	53.5		38.2		31.8		25.4		20.6		17.2
THF	198.8	201.6	56.9	55.6		39.6		32.8		26.1		21.2		17.6
$C_2H_5NH_2$	217.0	215.2	66.2	66.3	49.5	49.8	43.0	41.9	35.9	35.5		30.6		26.1
$(CH_3)_2O$	192.1	198.2	54.8	53.2	37.0	37.9	31.7	31.6	24.8	25.2		20.5		17.1
Py	220.8	213.9	62.4	65	43.1	47.7	36.0	39.7	30.7	32.7		27.6		23.3
DMA	216.8	201.2	51.2	55.7	36.5	41.1	30.4	34.7	26.9	28.8		24.3		20.7
Et_3N	232.9	226.5	75.2	74.2		54.4		44.7		36.8		31.0		26.1
4pic	225.7	216.1	64.3	66.6		48.9		40.6		33.5		28.2		23.8
4CN·py	209.4	202.3	51.8	56.2	35.1	40.5	29.4	33.7	24.9	27.2		24.1		23.4

[a] Calculated from

$$BH^+(g) + H_2O(g) \rightarrow BH_3O^+(g) \quad \text{(i)}$$

$$+ [B(g) + H^+(g) \rightarrow BH^+(g)] \quad \text{(ii)}$$

$$+ [H_3O^+(g) \rightarrow H^+(g) + H_2O(g)] \quad \text{(iii)}$$

$$B(g) + H_3O^+(g) \rightarrow BH_3O^+(g) \quad \text{(iv)}$$

Reported data[5] are used for step i, calculated proton affinities are used for step ii, and 166.5 kcal mol^{-1} is used[5] for step iii. [b] According to our report on the theoretical justification for the E and C equation, these enthalpies are on the large side for an E and C analysis. Accordingly, we have used E, C, and W ($-\Delta H + W = E_AE_B + C_AC_B$) in an attempt to let W pick up a constant amount of stabilization from the transfer term, enabling E_A and C_A to adjust for any differences. Any constant errors in the data, e.g., the value of the proton affinity of water, can also be accommodated by W. These values are calculated from reported E_B and C_B values and values of $E_A = 14.76$, $C_A = 2.27$, and $W = -30.6$ for $H_3O^+(g)$. [c] These and enthalpies for more extensively hydrated species $(H_2O)_nH^+$ are calculated from reported data[5] by

$$BH(H_2O)_{n-1}^+(g) + H_2O(g) \rightarrow BH(H_2O)_n^+(g) \quad \text{(v)}$$

$$+ [B(g) + H(H_2O)^+_{n-1}(g) \rightarrow BH(H_2O)_{n-1}^+(g)] \quad \text{(vi)}$$

$$+ [(H_2O)nH^+(g) \rightarrow H(H_2O)_{n-1}^+(g) + H_2O(g)] \quad \text{(vii)}$$

$$B(g) + (H_2O)_nH^+(g) \rightarrow BH(H_2O)_n^+(g) \quad \text{(viii)}$$

To prevent the propagation of error that would arise from using the experimental data for the previous $H(H_2O)_{n-1}^+$ analysis, the calculated values in Table II are used for step vi. [d] H^+: $E = 17.87$, $C = 3.90$, $W = -169.9$. H_3O^+; $E = 14.76$, $C = 2.27$, $W = -30.6$. $H_5O_2^+$; $E = 16.15$, $C = 1.65$, $W = -15.7$. $H_7O_3^+$; $E = 15.34$, $C = 1.24$, $W = -11.4$. $H_9O_4^+$; $E = 16.78$, $C = 1.02$, $W = -4.1$. $H_{11}O_5^+$; $E = 17.47$, $C = 0.86$, $W = 0.9$. $H_{13}O_6^+$; $E = 16.07$, $C = 0.71$, $W = 2.3$.

reported E, C, and W data base. By use of reported values of E_B and C_B, the linear least-squares fit of the proton affinity data for the first 10 donors in Table II gives the three parameters, $E_A = 17.87$, $C_A = 3.08$, and $W = -169.9$ for H^+. The C/E ratio is 0.18. We attempted to expand the bases in the correlation to include data reported on substituted pyridines, triethylamine, and dimethyl ether. A reasonable fit was obtained ($E = 17.75$, $C = 3.50$, $W = -169.0$), but the deviations of the calculated and experimental values of the amines increased. Thus, we selected the intial set of parameters and included proton affinities calculated with these parameters for the last four bases[10] in Table II. Except for *N,N*-dimethylacetamide,[10] the PA values calculated with these E, C, and W parameters are well within the experimental error of the proton affinity determination as evidenced by the discrepancy in values reported by different investigators.

Hydronium Ion. The next problem involves an analysis of the gas-phase data for the reaction:

$$B(g) + H_3O^+(g) \rightarrow BH_3O^+(g) \quad (3)$$

The enthalpies for eq 3 can be calculated from reported gas-phase hydration energies of protonated bases and proton affinities (footnote *a*, Table II). The enthalpies for the first 10 bases in Table II undergoing the reaction in eq 3 give an excellent fit to the E, C, and W equation as indicated by agreement of the experimental enthalpies with those calculated with $E_A = 14.76$, $C_A = 2.27$, and $W = -30.60$ for the gas-phase hydronium ion. Note that the C/E ratio for the H^+ and H_3O^+ (0.18 vs 0.15) both indicate significant covalent contribution but a greater fractional importance of electrostatic bonding in the latter. Reversals in the donor order of the methylamines do not occur when comparing $H^+(g)$ and $H_3O^+(g)$. The lower E_A and C_A values for H_3O^+ indicate this species is a weaker acid than the H^+, and the lower W value for H_3O^+ is consistent with less electron transfer from a base into H_3O^+ than into H^+. The acidity of the proton has been greatly reduced by coordination of one water by decreasing the amount of electron transfer when the hydronium ion reacts with a base. The weaker acidity and greater fractional importance of the electrostatic term is consistent with a higher energy LUMO for H_3O^+ than for H^+ (−2.92 vs −13.6 eV).

$(H_2O)_2H^+$. The next system to consider is the acid $(H_2O)_2H^+$. For nonprotonic bases the resulting adducts, $BH(H_2O)_2^+$, can exist as two isomers (Figure 1 parts a and b) while for protonic bases, all three isomers shown in Figure 1 are possible. The E, C, W analysis requires that all adducts in the fit have the same geometry or that the energies of the different isomers differ in magnitude only

(10) We note a larger than expected deviation for DMA but this could result from the fact that the E and C values are for the carbonyl oxygen and the proton may coordinate to the nitrogen.

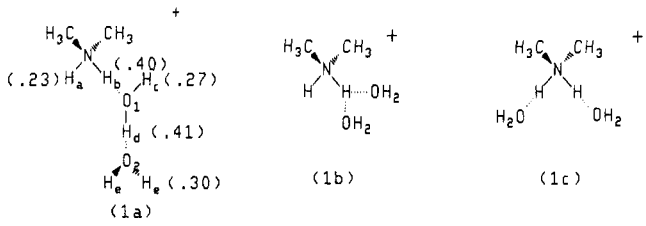

Figure 1. Various isomers for $BH(H_2O)_2^+$. Charges are indicated for the minimum energy doubly hydrated dimethylammonium ion.

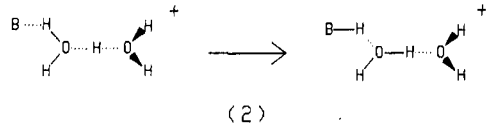

Figure 2. Schematic diagram showing transfer of the proton from an internal to terminal position conversion of polar covalent to hydrogen bonds in the base adduct of $H(H_2O)_2^+$.

to the extent of the experimental error in the data. The fit of the nonprotonic bases was excellent, indicating a common geometry (1a or 1b). We shall subsequently indicate a preference for the structure in 1a and assume this to be the structure for now to simplify the discussion. The resulting E, C, W parameters obtained for the linear $BH(H_2O)_2^+$ structure also predict the enthalpies of the protonic bases [NH_3, CH_3NH_2, $(CH_3)_2NH$, $C_2H_5NH_2$] very well. If these bases formed more stable ions with the structure shown in 1c, their experimental enthalpies would be more negative than those calculated with eq 2, using E_A, C_A, W parameters for the adduct structure in 1a formed by the nonprotonic bases. This result enables us to eliminate structure in 1c as a possibility and to obtain an excellent fit to eq 2 of the 11 enthalpies of protonic and nonprotonic bases binding to $(H_2O)_2H^+$ with the parameters $E_A = 16.15$, $C_A = 1.65$, and $W = -15.7$ (see Table II).

As expected, there is a decrease in the magnitude of the enthalpy of adduct formation when $(H_2O)_2H^+$ is compared to H_3O^+. Lower E and C values are consistent with a weaker acid caused by the inductive effect of a second coordinated water and the distribution of the positive charge over more hydrogens. The C_A/E_A ratio for this acid (0.10) is reduced significantly compared to H^+ and H_3O^+, indicating that electrostatic interactions make a larger fractional contribution to the bonding. The 6% difference in the $(CH_3)_3N$ and $(CH_3)_2NH$ enthalpies toward H_3O^+ is reduced to 4% toward $(H_2O)_2H^+$ because of the larger fractional contribution of the E_AE_B term to the total enthalpy. These differences again are consistent with a higher energy LUMO in $(H_2O)_2H^+$ than in H_3O^+ (−0.68 vs −2.92 eV).

In order to form a linear chain adduct from $(H_2O)H(H_2O)^+$, a water molecule can be dissociated from the proton coordination sphere and hydrogen bonded to the protons of the other coordinated water. The same geometry could also be achieved by coordination to a terminal hydrogen and changing hydrogen bonds to polar covalent water molecules as shown in Figure 2. The constant energy contribution from this step to all the $(H_2O)_2H^+$ enthalpies would be included in W. Any contribution from the reorganization that is related to the donor strength of B would be incorporated into the E_A and C_A values as a factor influencing the acidity of $(H_2O)_2H^+$.

The tentative selection of the isomer in 1a is based on INDO/1 calculations of the dimethylammonium ion, which show this isomer to be 19.5 kcal mol^{-1} more stable than that in 1b.[11] For $(H_2O)_2H^+$ INDO/1 produces the same

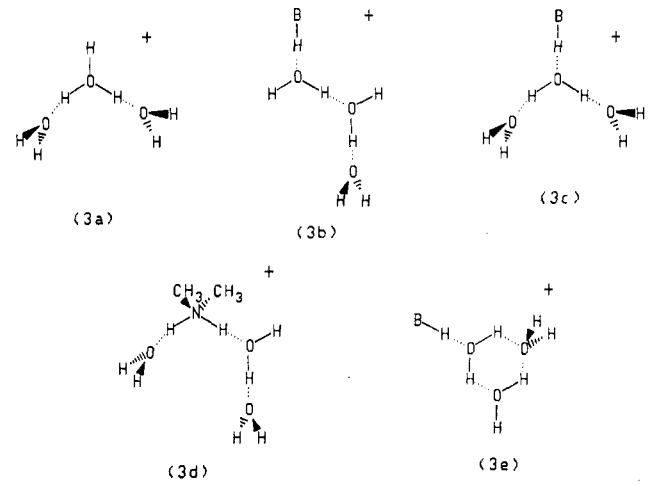

Figure 3. (a) Structure of minimum energy triply hydrated proton. (b,c) Two possible modes of coordination in the base adduct. (d) Coordination of the third water to the amine proton. (e) Low energy cyclic intermediate.

global minimum energy allene type structure as that found experimentally[12a] and calculated by Newton and Ehrenson.[12b]

MO investigations into the hydration of various ammonium ions produce conflicting results.[13-18] An investigation by Deakyne,[18] using the 6-31G* basis set, predicts only a 4 kcal mol^{-1} range for the various $NH_4(H_2O)_n^+$ isomers with coordination to the NH protons favored by 1–2 kcal mol^{-1}. The calculations by both Deakyne and Ikuta consistently place a higher positive charge on the oxygen protons in accord with simple electronegativity arguments. In an electrostatic interaction, water will coordinate to the most highly charged proton as evidenced by stronger O–H–O hydrogen bond than N–H–O.[19] Given the highly electrostatic nature of hydrogen bonding and the small energy differences, the MO results are inconclusive. Deakyne states that further calculational improvements (electron correlation, inclusion of zero-point energies, use of larger basis sets, etc.) will favor O–H bound water over N–H. At any rate, the established ability of the E, C, W model to correlate enthalpies leads us to eliminate 1c as a possible structure. Our tentative preference for 1a over 1b in no way influences our basic con-

(11) The calculations were carried out to probe the potential energy surface for the interaction of dimethylamine with $(H_2O)_2H^+$. The reported geometry was used for dimethylamine and the theoretically determined minimum energy geometry was used for $(H_2O)_2H^+$. The two species were placed at a relatively large separation (approximately 2 Å between the N and the central hydrogen in $H_5O_2^+$) and brought together to produce the structure in Figure 1c. Calculations were performed for a series of geometries leading to the structure in Figures 1a and 1b. All $3N - 6$ degrees of freedom were allowed to vary in every calculation.

(12) (a) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978. (b) Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971. $r(O-H_{central}) = 1.22$ Å, $r(O-H_{terminal}) = 0.97$ Å, angle$(O-H_{central}-O) = 171°$.

(13) Interactions similar to this, in general, and this ion in particular, have been researched before. Though considerable error is expected in the absolute value of the energy for any of these species, the differences in energies of isomers is much better. The larger energy differences found in this study lend credence to the global minimum calculated. The species $[NH_3Me\cdot(H_2O)_2]^+$ has been studied by Ikuta[15] in an ab initio MO analysis of the hydration of ammonium ions. In his optimization only the bond lengths of N–H and O–H ionic hydrogen bonds (five degrees of freedom) were optimized in contrast to the present work in which all degrees of freedom ($3N - 6 = 36$) were allowed to vary.

(14) Ikuta, S. *Chem. Phys. Lett.* **1983**, *85*, 604.

(15) Bukrstein, K. Y.; Isaev, A. N. *Theor. Chim. Acta* **1984**, *64*, 397.

(16) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898.

(17) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3898.

(18) Deakyne, C. A. *J. Phys. Chem.* **1986**, *90*, 6625.

(19) Coulson, C. A. *Valence*; Clarendon: Oxford, 1952; p 301.

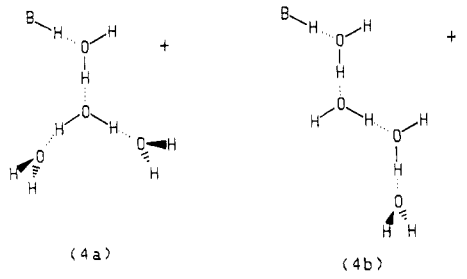

Figure 4. (a) Coordination of the base to $H^9O_4^+$. (b) The minimum energy $H_9O_4^+$–base adduct.

clusions. It is interesting that INDO/1 predicts the structure in Figure 1c to be 10.7 kcal mol^{-1} higher energy than Figure 1a for the dimethylammonium ion and also higher in energy for comparable ammonium ion structures in keeping with the ECW model and electronegativity considerations.

$H_7O_3^+$. The trend continues for the acid $H_7O_3^+$. The decreases in E, C, and W to E_A = 15.3, C_A = 1.24, and W = −11.4 reflect the inductive properties of the additional water and further delocalization of the positive charge. The excellent fit of the data for bases with and without protonic hydrogens to the E and C equation (see Table II) indicates that clustering of water is still preferred over coordination to the free NH protons of ammonium and methyl- and dimethylammonium ions. The C/E ratio further decreases for this acid, and the trimethylamine and dimethylamine enthalpies only differ by 3%.

MO calculations on the tris(aquo) species gave the linear chain (see Figure 3a) minimum energy structure for $H_7O_3^+$, calculated by Newton and Ehrenson.[12b] Possible structures for the base adducts are shown in Figure 3 with that in 3b being lowest energy when $(CH_3)_2NH$ is the base. The structure in 3d, in which the NH proton behaves as an acid center, is less stable than 3b or 3c by more than 8 kcal mol^{-1}. This global minimum corresponds to coordination of the third water molecule to the terminal proton of the minimum energy structure of the $B(H_2O)_2H^+$ ion and is consistent with attaching water to the most positively charged terminal hydrogen (as derived from a Mulliken Population Analysis) of the doubly hydrated isomer (see Figure 1a). The isomer in 3d is eliminated on the basis of the E, C, W fit and predicted to be unstable by INDO/1 on the basis of charge and energy and also on the basis of electronegativity considerations.[20]

$H_9O_4^+$ and Higher Hydrated Homologues. Addition of four waters to the proton continues the trend to decreasing acidity, and the excellent fit of protonic and nonprotonic bases again (see Table II) suggests that the fourth water also coordinates to the water cluster rather than hydrogen bond to the free NH protons. Values of E_A = 16.78, C_A = 1.02, and W = −4.1 are obtained for $H_9O_4^+$. The basicities of all three alkylamines are now comparable due to compensatory covalent and electrostatic contributions. With the formation of the four water and higher species, the number of possible isomers that exist for the water cluster increase substantially, and, if their energy differences are slight, different geometries could

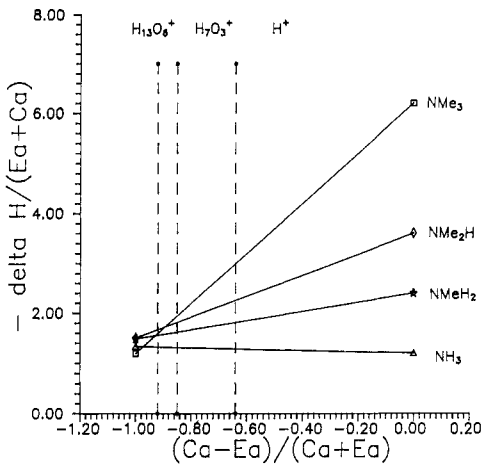

Figure 5. E and C plot for the amines illustrating different orders of donor strength as the E and C values of the acid change on the horizontal axis. (□, $(CH_3)_3N$; (◇), $(CH_3)_2NH$; (☆), CH_3NH_2; (△), NH_3.

be accommodated by E, C, W. The chain structure, Figure 4d, would require dissociating a water and reattaching it to another water when base coordinates to $(H_2O)_4H^+$. This would make a positive contribution to the W term, adding to the negative electron transfer contribution and giving a smaller negative value for W.

A 4-31G ab-initio calculation[12b] on $H_4O_9^+$ places the Eigen structure[21] (Figure 4a minus the base, B) at an energy 4.7 kcal mol^{-1} below the "linear" structure. Our calculations showed a similar energy for the two isomers. The various isomers that were considered for coordinating our base to $H_9O_4^+$ are illustrated in Figure 4. The most stable isomer by 5 kcal mol^{-1} is the linear structure shown in 4d.[22] As the chain length increases, the inductive effect of the donor decreases and the energetic differences between the linear form and those with branching further down the chain diminishes. However, adding one of the waters to the NH proton again produces an isomer that is 10 kcal mol^{-1} less stable than the minimum energy chain. It is likely that coordination of the amine proton to water does not take place until many more water molecules are present. Various isomers were also investigated for ammonia as the Lewis base coordinating to $H_9O_4^+$. Once again the linear isomer is calculated to be most stable. Placing four waters onto the four ammonium protons led to an isomer 25 kcal mol^{-1} less stable than the linear chain.

The good agreement of our calculated structure with the experimental finding is gratifying in view of literature reports of the inadequacy of NDO and related methods for hydrogen-bonding systems.[15,16,17] Ab initio calculations give the conclusion that $NH_4{\cdot}4H_2O^+$ has all four waters attached to NH protons.[16,18]

The data set for $H_{11}O_5^+$ is small and produces a set of tentative values of E = 17.5, C = 0.86, W = 0.9. Now the number of waters has increased to the point where the enthalpy of acid–base interaction is low, and W becomes positive from dominance by the endothermic rearrangements that occur to form chains when base coordinates to $(H_2O)_nH^+$ cluster species with $n > 5$.

Finally, with $H_{13}O_6^+$, we obtain tentative values of E_A = 16.1, C_A = 0.71 and W = 2.3. The interaction is now

(20) In $(H_2O)_3H^+$ the central proton has the highest positive charge. Coordination of a base to the central proton (Figure 3c) puts electron density on the oxygen of the B–H–O system in a three-center description of this interaction. The nonbonding MO is composed mostly of O and N, decreasing the basicity of the proton attached to this oxygen. The bound water molecule transfers to the more acidic proton at the end of the water chain (Figure 3b). The cyclic structure shown in Figure 3e is calculated to be 1.3 kcal mol^{-1} less stable than the straight chain Figure 3b. This small difference indicates that this ring structure is an energetically feasible structure for the trisaquo species.

(21) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(22) The formation of the linear form from the cluster is aided by the weakening of hydrogen bonds to waters that would lead to branching from the presence of 3-center, 4-electron H–O–H interactions. These lower the positive charge on the neighboring hydrogens, thus weakening their ability to hydrogen bond to the coordinated water.

essentially electrostatic. Use of these values to calculate the enthalpy of interaction of $(H_2O)_6H^+$ with $(CH_3)_3N$ produces an enthalpy of 24.7 kcal mol^{-1}, giving the order of amine basicity in parentheses [CH_3NH_2 > $(CH_3)_2NH$ > $(CH_3)_3N$ > NH_3]. The donor order for this acid is scrambled from the inductive order due to decreased contributions from covalent bonding. Thus, $(H_2O)_6H^+$ is a quite different acid than the proton, and an order other than the inductive order of the gas-phase proton can result from significant electrostatic contributions in the acid–base interaction in the gas phase and need not be attributed to solvation. For those used to thinking in terms of linear pK_B plots, the double scale, *E*, *C*, *W* equation requires a change in concept. The plot of eq 2 reported by Cramer and Bopp and shown in Figure 5 illustrates how donor orders can change as the nature of the covalent and electrostatic properties of the acid is varied. The vertical axis is a normalized enthalpy, and the bottom axis characterizes the acid in terms of its fractional covalent and electrostatic bonding properties. On the different sides of an intersection for two bases the donor order reverses. The dashed lines indicate the relative donor orders (normalized enthalpies) for the amines toward acids with varying fractions of covalent and electrostatic contributions.

The Aqueous Proton. The next issue to be addressed involves the aqueous data. Fitting all the available enthalpy data[3] with *E*, *C*, and *W* produces poor results. Even restricting the data set to just the aliphatic amines in aqueous solution produces a poor fit. If the *E*, *C*, and *W* data fit is limited to ammonia and the methylamines, large deviations exist in the calculated and experimental values. The protonic amine bases and the tertiary amines are incompatible in that enthalpies that are too large are predicted for the latter. It is gratifying that the *E*, *C*, *W* fit did not work on this system. This is the expected result if hydrogen bonding (water as the Lewis base) to the NH protons of the protonic bases occurs and is larger in the ammonium ions than in the free amines.

Extrapolating the gas-phase trend to larger clusters would lead to a positive *W* and a smaller *C*/*E* ratio. A ratio of 0.04 or less for the large clusters in aqueous solution would produce the trend found in water: CH_3NH_2 > NH_3 > $(CH_3)_2NH$ > $(CH_3)_3N$.

Thus, a quantitative understanding of the deviation of the aqueous solution data for methylamines from the order of gas-phase proton affinities involves two effects. First, the proton in the gas phase is a very different acid than $(H_2O)_nH^+$, giving rise to different amine donor orders because of a decreased fractional contribution from covalent effects in the acid–base interaction for the latter. A value of $n > 6$ in solution leads to an acid that is essentially electrostatic, and this produces the anomalous order. Second, though water does not hydrogen bond to the NH hydrogens of $R_2HN\ H(H_2O)_n^+$ (with R = CH_3 or H) in the gas phase, these protons bind water (with water functioning as a Lewis base) to the extent of ~2 kcal mol^{-1} more strongly in the ammonium ion than they do in the corresponding free amine in aqueous solution. Hydrogen bonding to the NH proton and possible variations in the extent of nonspecific solvation lead to a set of enthalpy data for aqueous protonation that do not fit *E*, *C*, *W*.

Conclusions

We have shown that gas-phase ion data for the interaction of the proton and various species of the general formula $H(H_2O)_n^+$ with a series of bases can be fit to the *E*, *C*, *W* equation. As expected from qualitative molecular orbital considerations of donor–acceptor energy match, the acids become weaker and the interaction has a larger percentage electrostatic and less covalent character as *n* increases from zero to six. The influence that changes in the relative importance of electrostatic and covalent binding can have on donor orders is illustrated by the plot of the *E* and *C* equation reported by Cramer and Bopp[23] (Figure 5). The aqueous proton would be represented by a dashed line to the left of $H_{13}O_6^+$ in Figure 5, giving the order CH_3NH_2 > NH_3 > $(CH_3)_2NH$ > $(CH_3)_3N$.

The *E*, *C*, *W* fit also provides structural information about the adducts of various protonic bases with $H(H_2O)_n^+$ in the gas phase. In all instances of n = 0–6, coordination of water to the NH protons of the protonic bases is not occurring.

The discrepancy between the results of the INDO/1 calculation and SCF reports is not understood at present. Since hydrogen bonding is essentially electrostatic and since both SCF and our calculations indicate that the protons on the oxygen of H_3N–H–OH_2 are more positively charged than those on nitrogen (as simple electronegativity considerations predict), the SCF result is in contrast to chemical intuition and emphasizes the difficulties in calculating small energy differences. This shortcoming is appreciated by the authors of the SCF report.[19] They state that "fully optimizing the geometries using larger basis sets including higher orders of electron correlation..." would favor the O-bound isomers. In all of our INDO results, we are gratified that both charge and energy conclusions give the same result and are consistent with the experimental data.

A final example of the potential confusion that arises by simply attributing differences in gas-phase and solution data to solvation is the relative acidity of toluene and methanol.[24] The proton affinity of CH_3O^- is larger than that of $C_6H_5CH_2^-$ (380.0 vs 378.1 kcal mol^{-1}), making toluene a stronger acid than methanol in the gas phase with respect to proton dissociation. However, the gas-phase reaction of these conjugate bases toward H_3O^+ involves different reactions:

$$CH_3O(g)^- + H_3O(g)^+ \rightleftharpoons CH_3O\text{–}H\text{–}OH_2(g) \quad (4)$$

$$C_6H_5CH_2(g)^- + H_3O(g)^+ \rightleftharpoons C_6H_5CH_3(g) + H_2O(g) \quad (5)$$

Here, the weak acidity of toluene results in complete displacement of water. In aqueous solution toward H_{aq}, $C_6H_5CH_2^-$ is a strong base displacing water from the coordination sphere of the proton. Methoxide reacts to form methanol, which remains hydrogen bonded to a water cluster. Thus, eq 4 and 5 are better gas-phase models than the proton affinities for the solution chemistry. The strong conjugate basicity of $C_6H_5CH_2^-$ and the poor acidity of the methyl protons of toluene in the gas phase and in solution causes its reaction with $H(H_2O)_n^+$ to be a displacement reaction in the gas phase and in solution while the reaction of CH_3O^- is adduct formation. Again the gas-phase proton becomes an incomplete model for the condensed phase reactions, and when the enthalpies of the gas phase reactions in eq 4 and 5 are compared to the solution chemistry, the methanol–toluene acidity anomaly disappears.

Acknowledgment. We acknowledge support of this research by the National Science Foundation Grant 86-18766 and helpful discussions with P. E. Doan of Bowdoin College.

(23) See Cramer, R. E.; Bopp, T. T. *J. Chem. Ed.* **1977**, *54*, 612 for a generalization of changing donor or acid orders.
(24) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986.