unlikely that D_n will change, i.e., experience some oscillation at higher n. Unfortunately measurements of $\Delta G^\circ_{n-1,n}$ for high n are difficult because condensation of the solvent vapor occurs at the walls of the reaction chamber. This happens at the point where the vapor pressure of the gas phase cluster $M^+(S)_n$ becomes larger than the vapor pressure of the solvent S (with a flat surface). A new experimental approach is being presently tried in our laboratory which promises to overcome the above difficulty. Controlled adiabatic expansion is used to cool the gas below its dew point, while the walls of the flow system are kept at temperatures above the dew point. If these measurements prove successful, they might provide information not only on the single ion solvation energies but also on the question of the accommodation of a cluster consisting of an ion and several solvent molecules S into a cavity of the (liquid) solvent. Evidently if eq 7 becomes valid already for relatively low n, solvation of the clusters $X^-(S)_n$ and $M^+(S)_n$ (with this n) into the liquid solvent S must release the same amount of energy. This would mean that the solvent structure at the interface of the cavity will be able to change equally well for the accommodation of the positive and negative cluster. If this can occur at low n it would mean that there is considerable structural flexibility in the clusters and the solvent.

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(27) NOTE ADDED IN PROOF. Because of an inadvertent mistake, the adjustment factor by which the net atomic charges of acetonitrile[13] must be multiplied is not 1.91 as given in the text but 1.68. The corrected changes for acetonitrile (see Figure 9) are N −0.311, C 0.035, C(methyl) 0.104 and H 0.057. A recalculation shows that the equilibrium distance between the positive ion and acetonitrile increases by ~0.01 Å and the negative ion and acetonitrile by ~0.02 Å (see Table II). The total binding energies decrease by less than 4%. Since these changes are very small, the conclusions given in the discussion remain unchanged.

Binding Energies and Stabilities of Potassium Ion Complexes from Studies of the Gas Phase Ion Equilibria[1] $K^+ + M = K^+M$

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Abstract: The ΔG, ΔH, and ΔS values for the gas phase reactions $K^+ + M = K^+M$ were determined from the temperature dependence of the corresponding equilibria observed with a mass spectrometer equipped with a special high pressure ion source and a potassium ion thermionic emitter. The compounds M were the nitrogen and oxygen bases: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, *n*-propylamine, pyridine, aniline, H_2O, $(CH_3)_2O$, and $(C_2H_5)_2O$. Recent theoretical SCF-MO calculations of K^+OH_2 have shown that the bond is largely of electrostatic nature. Classical electrostatic calculations were performed in the present work for K^+M where $M = OH_2$, NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$. The results were found in good agreement with the experimental determinations. A comparison between the stability of the complexes K^+M and the Bronsted basicities (proton affinities of M) is made. The difference between the stabilities of the K^+ complexes with nitrogen and oxygen bases is very much smaller than the difference between the proton affinities. This is shown to be a consequence of the electrostatic character of the K^+M bonding. The increases of stability with methyl substitution in the ammonia methylamines series is very much smaller for K^+M complexes than for the corresponding H^+M. A brief comparison with the boron complexes $(CH_3)_3BM$, observed in the gas phase, is also made.

A program of studies based on ion-molecule equilibria in the gas phase was initiated in the present laboratory several years ago.[2,3] An important part of this research were studies of alkali ion-solvent molecule equilibria. Data for the alkali ions interacting with water molecules in the equilibria ($n-1$, n) for $n = 1$ to $n = 6$ or 7 were published earlier.[4]

$$M^+(OH_2)_{n-1} + OH_2 = M^+(OH_2)_n \qquad (n-1, n)$$

Recently a similar study involving the aprotic solvent acetonitrile[5] was also completed. The $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ obtained from van't Hoff plots of the equilibrium constants $K_{n-1,n}$ have been of value in giving the strength of the interaction with the first molecule (vis $\Delta H^\circ_{0,1}$ and $\Delta S^\circ_{0,1}$) and the changes of these interactions on successive additions of further molecules. The determination of such successive ion equilibria is generally straightforward, but nevertheless time consuming.

The present work concentrates only on the first (0, 1) equilibrium, and uses only the potassium ion:

$$K^+ + M = K^+M \qquad (0, 1)$$

This permits the examination of the interactions with a wide range of molecules M, The important group of nitrogen and oxygen bases, i.e., ammonia, alkylamines, aniline, pyridine, and the dialkyl ethers, was selected for the present study. In a subsequent publication the work is expanded to cover bifunctional molecules like diamines (i.e., ethylenediamine), diethers, and polyethers. The selection of potassium as the cation was made largely for convenience. The interactions of M with Na^+ and Li^+ are considerably stronger. This means that the (0, 1) equilibria must be measured at higher temperatures where many of the molecules M are themselves thermally unstable. The potassium ion is a middle size classical ion of noble gas structure and the energetics of the complex formation should be of considerable interest. Formally the (0, 1) reaction can be considered as a Lewis acid-base interaction in which the Lewis acid (K^+) reacts with the Lewis base M. In solution potassium ion complexes with M have often been treated as a Lewis acid base reaction and the potassium ion has been classified in Lewis acidity orders. Since these classifications are affected by the nature of the solvent, it appears of some interest to examine the nature of the intrinsic interactions in the absence of solvent.

Experimental Section

The measurements were done in an alkali ion source capable of operating at neutral gas pressures up to 4 Torr. The ion source used is similar to that described earlier[6] but incorporating a few modifications,[5,7] made to increase the leak tightness of the source and the temperature homogeneity of the gas in the equilibration chamber.

The principle of the experimental method is as follows. Potassium ions are produced by thermionic emission from a heated platinum filament coated with potassium alumosilicate melt. Weak electric fields drift the ions through the gas into a thermostated equilibration chamber which is free of electrical fields. The ion-molecule reactions reach equilibrium in this chamber. A probe of the gas plus ions bleeds continuously through a small slit out of the chamber into an evacuated space where the gas is pumped out and the ions accelerated, magnetically mass analyzed, and detected. The relative intensities of the detected ions K^+ and K^+M are taken equal to the relative equilibrium concentrations $[K^+]$ and $[K^+M]$ in the equilibrium chamber.

Some specific problems were encountered in the present study. Pyrolysis of the neutral base was observed to occur for the alkylamines. For example, when working with primary amines $R\text{-}CH_2\text{-}NH_2$, in addition to ions of mass corresponding to $K^+(RCH_2\text{-}NH_2)$ also ions of mass two and four units lower were observed. These ions must result from thermal decomposition of the amines. Thermal decomposition of primary amines is known[8,9] to proceed in two steps:

$$R\text{-}CH_2\text{-}NH_2 \rightarrow RCH{=}NH + H_2 \qquad (1)$$

$$RCH{=}NH \rightarrow RC{\equiv}N + H_2 \qquad (2)$$

In the present experiments with ethylamine an ion of mass four units lower than $K^+(C_2H_5NH_2)$ was observed to be very prominent. It was assumed that this is $K^+(CH_3CN)$ formed from acetonitrile produced by reactions 1 and 2. The $K_{0,1}$ equilibrium constant, with acetonitrile, had been determined in earlier work.[5] Since it is much larger than $K_{0,1}$ for ethylamine, only small concentrations of acetonitrile would be required to produce a prominent $K^+(CH_3CN)$ ion. An actual calculation using the equilibrium constant showed that the partial pressure of CH_3CN in the equilibrium chamber is only ~6% of the amine pressure. It could also be established that the yield of CH_3CN changed little with increase of the equilibration chamber temperature. Therefore the pyrolysis must be occurring on the surface of the potassium emitting filament, whose temperature (~600 °C) is much higher than that of the equilibration chamber and increases only relatively little with increase of the chamber temperature. In some runs, the composition of the equilibrium chamber gas was examined by a combination of analytical mass spectrometry and gas chromatography. Gas samples from the ion source were obtained by collection in a liquid nitrogen cooled glass trap. Such analysis showed that the amount of pyrolysis product is small. For example, when propylamine was used the analyzed ion source gas mixture contained 95% propylamine and 5% ethylnitrile. The failure to observe significant amounts of the aldimine formed by reaction 1 suggests that most often reactions 1 and 2 occur in rapid succession on the filament. The observed relatively low extent of thermal decomposition is probably due to the short contact time (seconds) of the gas with the filament. Since a temperature-independent error of ~5% in the partial pressure of the amine corresponds only 0.1 eu error in the entropy, the effect of pyrolysis was not considered in the evaluation of the amine $K_{0,1}$ equilibrium constants.

Since the temperature of the thermionic filament required to produce Na^+ and Li^+ becomes progressively higher, considerably more pyrolysis can be expected in clustering experiments with these ions. With the present apparatus such equilibria determinations would probably not be feasible. However, measurements should be possible with modified apparatus in which the contact of the clustering gas with the filament is minimized by the selection of suitable gas flow patterns in the ion source.

A second difficulty was encountered with some of the systems which were found to reach the (0, 1) equilibrium very slowly. Presumably this was due to low rate constants for the forward reaction involved in the (0, 1) equilibrium. The forward rate can be increased by increasing the pressure of the respective compounds. However, at higher ion source pressure stripping (collisional dissociation $K^+M \rightarrow K^+ + M$) begins to occur in the vacuum region outside the ion exit slit.[10] This stripping effect probably increases with size of the base M, i.e., size of the complex K^+M. In practice this meant that for two of the bases used (CH_3NH_2 and $(CH_3)_3N$) no pressure range could be found where $K_{0,1}$ could be measured directly. The equilibrium constants for these two compounds were obtained by means of the exchange reaction 3.

$$K^+OH_2 + M = K^+M + OH_2 \qquad (3)$$

The potassium hydrate is formed rapidly in the presence of water.[4,6] The exchange reaction 3, being independent of third bodies, occurs rapidly already at much lower pressure than the direct formation of $K^+(M)$ from $K^+ + M$. The $K_{0,1}(M^+)$ could then be evaluated from the temperature dependence of K_3 and the thermodynamic parameters[6,7] for reaction 4: $\Delta H°_4 = -16.9$ kcal/mol, $\Delta S°_4 = -19.9$ eu.

$$K^+ + OH_2 = K^+OH_2 \qquad (4)$$

Results and Discussion

The equilibrium constants $K_{0,1}(M)$ were determined at constant temperatures for several different pressures of M. An example of the pressure range covered and the results obtained is shown in Figure 1 where M = aniline. Several van't Hoff plots obtained from data like those in Figure 1 are shown in Figures 2, 3, and 4. The data obtained from the van't Hoff plots are collected in Table I. Included for comparison in the table are also results from earlier determination involving the $K^+(OH_2)$ complex.[5,6] Since the experimentally accessible temperature range was quite narrow the error in the slope derived ΔH and ΔS should be the largest. Of significance therefore are the direct data as displayed in the van't Hoff plots. The van't Hoff line which occurs higher belongs to the more stable (with respect to free energy) compound. To tabulate these stability differences we have included in Table I not only $\Delta G°_{300}$ which is obtained by downward extrapolation of the temperature but also the $\Delta G°_{600}$ which falls generally within the experimental range.

A comparison between the present experimental results and the Bronsted gas phase basicities of the compounds M is provided by Table II. Also shown in Table II are the ΔH and ΔS changes of the gas phase reaction $(CH_3)_3B + M = (CH_3)_3BM$ studied extensively sometime ago by Brown and co-workers.[14] The formation of the trimethylboron M complex is a Lewis acid-base reaction which bears formal resemblance to the formation of the K^+M complex.

Before engaging in a comparison of the data in Tables I and II a consideration of the type of bonding occurring in the K^+M

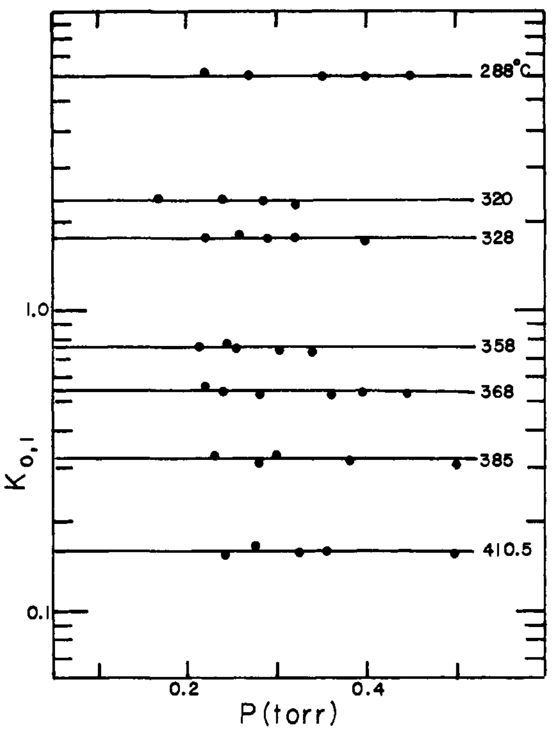

Figure 1. Pressure independence of equilibrium constant $K_{0,1}$ for reaction K^+ + aniline = K^+(aniline) at constant temperature and variable aniline pressures (standard state 1 Torr).

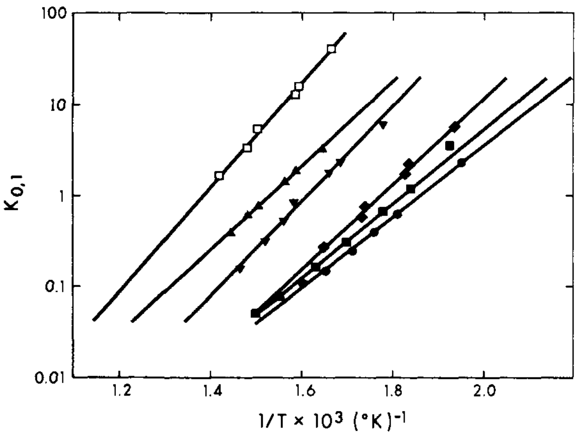

Figure 2. van't Hoff plots of equilibrium constants for reactions $K^+ + M = K^+M$: (●) NH_3, (■) CH_3NH_2, (♦) *n*-propylamine, (▼) pyridine, (▲) aniline, (□) ethylenediamine. Standard state 1 Torr.

complexes will prove to be useful. Recently ab initio SCF-MO calculations of the alkali ions water complexes M^+OH_2 were performed[15] which provided binding energies and $\Delta H_{0,1}$ data in good agreement with the experimental measurements from this laboratory.[4] These calculations showed that the bonding, particularly for the larger ions like K^+, was almost purely electrostatic. Thus the Mulliken population analysis showed a charge transfer of only 0.018, 0.013, and 0.004 electron from the water molecule to the Li^+, Na^+, and K^+ ions, respectively.[15b] In fact, the good accuracy of the calculated binding energies (the calculations did not include configurational interactions) was a consequence of the electrostatic nature of the bond. Since the number of electron pairs in the complex and the separated cation and water molecule are conserved and there is little electron transfer between molecule and cation in the complex the electron correlation error is expected to be small. Unfortunately, except[16] for Li^+NH_3, no MO calculations have been made for the alkali ions and other molecules like NH_3 and the other bases used in the present experimental work. However, it is quite safe to assume that also for these bases the bonding between potassium and the base M will be predominantly electrostatic.

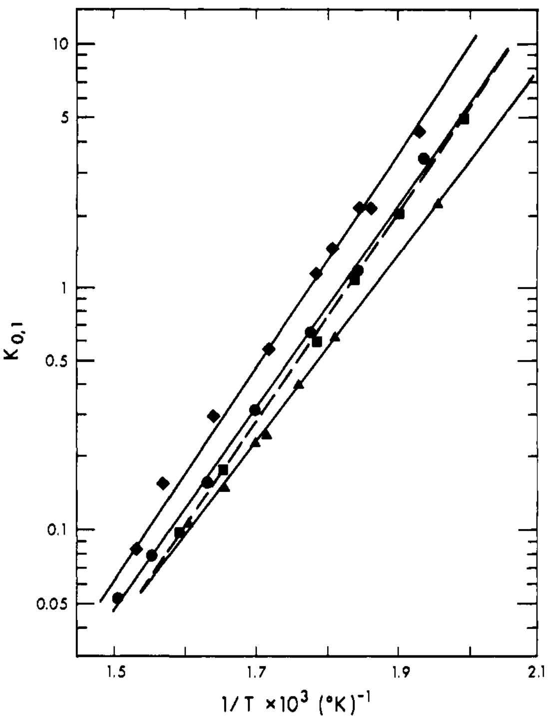

Figure 3. van't Hoff plots of equilibrium constants for reactions as in Figure 2 but involving: (▲) NH_3, (●) CH_3NH_2, (♦) $(CH_3)_2NH$, (■) $(CH_3)_3N$.

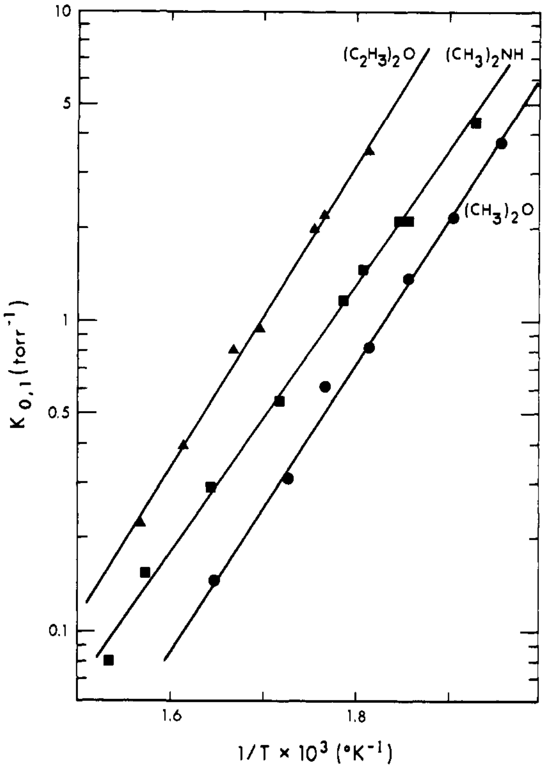

Figure 4. van't Hoff plots for reaction $K^+ + M = K^+M$ where M = $(C_2H_5)_2O$ (▲), $(CH_3)_2NH$ (■), $(CH_3)_2O$ (●).

Improved classical electrostatic calculations have recently been made[17,18] for the alkali and halide hydrates $M^+{\cdot}OH_2$ and $X^-{\cdot}H_2O$ which have reproduced quite well binding energies and other features. Such calculations, while inferior to the MO

Table I. Thermodynamic Functions for the Reactions $K^+ + M \rightleftarrows K^+(M)$

	$-\Delta H°^a$	$-\Delta S°^a$	$-\Delta G°_{298}{}^a$	$-\Delta G°_{600}{}^a$
Ammonia	17.8	20.0	11.8	5.8
Methylamine	19.1	21.8	12.7	6.2
Dimethylamine	19.5	21.4	13.1	6.6
Trimethylamine	20.0	23.4	13.0	6.0
n-Propylamine	21.8	25.5	14.2	6.5
Aniline	22.8	23.7	15.8	8.6
Pyridine	20.7	18.6	15.2	9.6
Ethylenediamine	25.7	22.3	19.0	12.3
HOH^b	16.9	19.9	10.93	4.9
CH_3OCH_3	20.8	24.8	13.4	5.89
$C_2H_5OC_2H_5$	22.3	24.7	14.9	7.51

[a] Values of ΔH and ΔG in kcal/mol, ΔS in eu subscript on ΔG refers to °K. Standard state 1 atm. Errors in ΔH and $\Delta G°_{300}$ estimated at ±1 kcal/mol, error in $\Delta G°_{400}$ estimated at ±0.2 kcal/mol. Error in ΔS estimated at ±2 eu. [b] From ref 5 and 6.

approach,[15,16] are much easier and can be useful in providing quantitative data and simple qualitative insights. We thought it therefore of interest to examine whether electrostatic calculations can reproduce the experimentally observed difference between OH_2 and NH_3 and the changes with methyl substitution in the bases NH_3 to $(CH_3)_3N$. The results from the electrostatic calculations for these systems are shown in Table III.

The total stabilization energy E_t of the K^+M complex at equilibrium distance relative to the separated K^+ and M was calculated with the usual[17,18] eq 5

$$E_t = E_{dip} + E_{ind} + E_{dis} + E_{rep} \tag{5}$$

where

$$E_{dip} = 334 \sum_i Q_i/R_i \tag{6}$$

$$E_{ind} = -167 \sum_i \bar{\alpha}_i/R_i{}^4 \tag{7}$$

$$E_{dis} = -34.56 \frac{I_M I_{K^+}}{I_M + I_{K^+}} \frac{\alpha_M \alpha_{K^+}}{R_0{}^6} \tag{8}$$

$$E_{rep} = \sum_i C_{K^+-i} \exp(-a_{K^+-i} R_i) \tag{9}$$

where Q_i is the net charge on the atom i of molecule M, R_i is the atom-ion distance, α_M is the molecular polarizability of M, α_{K^+} is the potassium ion polarizability, $\bar{\alpha}_i$ is the polarizability of the atom i on the molecule M, I_M and I_{K^+} are the ionization potentials of M and the potassium ion, respectively, and C_{K^+-i} and a_{K^+-i} are repulsion potential parameters between the atom i of M and the potassium ion. Equation 6 for E_{dip} gives the ion-permanent dipole attractive energy which is obtained by summing over the coulombic potentials between the ion and net atomic charges on the molecules. The net atomic charges Q_i were obtained from the Mulliken electron populations of the molecules calculated by Hehre and Pople.[19] However, the calculated net atomic charges when combined with the experimental bond angles and distances[9,20,21] lead to a dipole moment which is lower by a factor of 1.6 than the experimental dipole moments.[21] Therefore, the Pople atomic charges multiplied by a correction factor of 1.6 were used in eq 6. Of course this procedure cannot correct for errors in the relative electron distribution that might be present in the Mulliken populations.[22] The induced dipole attractive energy E_{ind} was calculated on the basis of constituent atom contributions $\bar{\alpha}_i$ to the total polarizability of the molecule.[23] The attractive dispersion energy was evaluated by eq 8 which is a modified London equation.[24] The ionization potentials were multiplied by a factor of 2.5 as suggested by Pitzer[25] and Eliezer and Krindel.[18] R_0 corresponds to the distance between the geometrical center of the molecule and the ion. The repulsive energy E_{rep} was evaluated by eq 9. The repulsive parameters C_{K^+-i} and α_{K^+-i} were evaluated from data of Amdur[26] following the procedure used by Eliezer and Krindel.[18] The total energy E_t was minimized as a function of R. The values at the minimum are given in Table III. Comparison of the calculated E_t with the experimental $\Delta H_{1,0}$ in Table III shows quite good agreement[25] both for the absolute values and for the relative changes from compound to compound.

The potassium ion affinities ($-\Delta H_{0,1}$) of the nitrogen bases are seen to be somewhat larger than the affinities of the oxygen bases, but the difference is relatively small, compared with the differences of proton affinities of nitrogen and oxygen compounds (see Table II). Since the bonding to the potassium ion is predominantly electrostatic and occurs at relatively large distances, the permanent dipole of the bases M is important. The dipole of the oxygen compounds is larger because of the larger electronegativity of oxygen (compare OH_2 with NH_3 in Table III). On the other hand, the polarizability of the nitrogen bases is larger. This leads to larger induced dipole and dispersion interactions with the nitrogen compounds. The

Table II. A Comparison of Thermodynamic Properties[a] of the Gas Phase Reactions $A + M \rightleftarrows AM$

	$A = K^{+b}$			$A = H^{+c}$		$A = B(CH_3)_3{}^d$		
M	$-\Delta H°$	$(\Delta H° \times 100)/\Delta H°(NH_3)$	$-\Delta G°_{298}$	$-\Delta H°$	$(\Delta H° \times 100)/\Delta H°(NH_3)$	$-\Delta H°$	$(\Delta H° \times 100)/\Delta H°(NH_3)$	$-\Delta G°_{298}$
H_2O	16.9	94.4	19.9	169	84			
$(CH_3)_2O$	20.8	116.2	24.8	189	94			
$(C_2H_5)_2O$	22.3	12.45	29.7	197	98			
NH_3	17.9	100	11.8	200.4	100	13.75	100	1.86
CH_3NH_2	19.1	106.7	12.7	210.8	105	17.15	129	5.54
$(CH_3)_2NH$	19.5	109	13.1	217.9	109	19.26	140	6.27
$(CH_3)_3N$	20.0	112	13.0	222.0	111	17.62	128	4.00
$CH_3CH_2CH_2NH_2$	21.8	122	14.2	214.9^e	107	18.14	132	5.33
$NH_2CH_2CH_2NH_2$	25.7	144	19.0	~228.3	114			
Pyridine	20.7	116	15.2	217.3	108	17.0	124	4.13
Aniline	22.8	127	15.8	207.6	103			

[a] All values in kcal/mol, standard state 1 atm. Subscript of ΔG corresponds to temperature in °K. [b] This work from Table I. [c] From ref 12 standardized to the new proton affinity ammonia,[13] $PA(NH_3) = 200.4$ kcal/mol. Proton affinities were obtained from $\Delta G°$ measurements of proton transfer assuming $\Delta H = \Delta G + T\Delta S_{rot}$ where ΔS_{rot} corresponds to entropy change due only to rotational symmetry numbers. [d] From ref 14. [e] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972).

Table III. Results from Electrostatic Calculations of Stabilization Energies for the Reactions[a] $K^+ + M \rightleftarrows K^+M$

M	R_{K^+N}[b]	$-E_{dip}$	$-E_{ind}$	$-E_{dis}$	E_{rep}	$-E_t$[d]	$-\Delta H_{0,1}$[e]	D[h]
H_2O	2.59[c]	17.79	3.36	1.72	5.95	16.92	16.9[f]	1.846
NH_3	2.58	17.48	6.05	2.97	8.98	17.53	17.9	1.468
CH_3NH_2[26]	2.52	16.06	8.16	5.23	11.19	18.26	19.0	1.343
$(CH_3)_2NH$[26]	2.46	15.96	10.51	7.56	13.90	20.12	19.5	1.03
$(CH_3)_3N$	2.43	16.08	12.62	8.90	15.68	21.89	20.0	0.612
$CH_3C\equiv N$[g]	2.57	21.31	6.56	2.46	7.90	22.4	24.4[g]	3.92

[a] All numerical values in kcal/mol. [b] Potassium–nitrogen distance in ångströms. [c] Potassium–oxygen distance in ångströms. [d] E_t corresponds to total stabilization energy of K^+M relative to $K^+ + M$. [e] Present experimental work except where noted. [f] From ref 4 and 5. [g] From ref 5. The electrostatic calculations used for acetonitrile were slightly different from those described in the present work. [h] Experimental dipole moments from ref 21, in debye units.

operation of these opposing effects results in small differences between the potassium ion affinities of the nitrogen and oxygen bases. With decrease of distance, the induced dipole interaction increases faster than the permanent dipole interaction. Therefore one can predict that the differences in alkali ion affinities between nitrogen and oxygen bases will increase as the radius is decreased, i.e., from K^+ to Li^+. This is in agreement with a recent theoretical[16] result of 40.3 kcal/mol and a recent experimental determination of 41.1 kcal/mol for the binding energy of Li^+NH_3. Both of these are much larger than 33.6 and 34 kcal/mol for the experimental[4] and theoretical[15] binding energy of Li^+OH_2.

Since the formation of MH^+ represents a true bonding interaction between the electron pair of the base and the totally devoid of electrons point charge hydrogen ion, a much larger amount of energy is released on reaction of M with H^+. Correspondingly the proton affinities are observed to be at least ten times higher than the potassium affinities (see Table II). Furthermore, as already mentioned, the proton affinities of the nitrogen compounds are found to be much larger both in absolute and relative terms than the proton affinities of the oxygen compounds. This difference can be understood when one considers that the lone pair of the base is involved in the bond formation. Since nitrogen is less electronegative than oxygen it has a more available lone pair. The much higher Bronsted basicity of the nitrogen bases over the oxygen bases also follows the relationship with the radius of the ion, i.e., K^+ to Li^+ to H^+, mentioned above.

The potassium ion affinities of the oxygen and nitrogen bases are seen to increase with alkyl substitution. However, the increase is relatively small. For example, in the methylamine series $NH_3 \cdots (CH_3)_3N$ the changes of $-\Delta H_{0,1}$ with methyl substitution are so small that they are soon overshadowed by trends in the entropy changes. Since the entropy changes become progressively less favorable, the increase of stabilities ($-\Delta G^\circ_{0,1}$) is not continuous but reaches a maximum for $(CH_3)_2NH$ and then falls off with $(CH_3)_3N$. The electrostatic calculations reproduce the small increases of $-\Delta H_{0,1}$ with methyl substitution quite well (see Table III).[29] It is important to note that the net negative charge on the nitrogen atom (from the Mulliken population analysis[19]) decreases with methyl substitution. This is in line with the experimentally observed lowering of the permanent dipole moment (see Table III). Another unfavorable factor is the increase of repulsive forces with methyl substitution. The operation of this effect can be seen in the E_{rep} values shown in Table III. The net increase of binding energy is a result of the relatively large increase of induced dipole and London dispersion energies which occur with methyl substitution and overcome, but barely, the unfavorable dipole and repulsion energy change.[30]

The absolute increase of proton affinity with methyl substitution in the methylamines is much larger than that of the corresponding potassium ion affinities; however, when the values are normalized to ammonia proton affinity = ammonia potassium ion affinity = 100 (see Table II) the relative changes are seen to be quite similar. The proton affinities should also be adversely affected by the increasing negative charge on nitrogen with methyl substitution; however, since after the addition of the proton a significant positive charge is transferred to the nitrogen, the large increase of internal polarizability by the introduction of the methyl groups is decisive and leads to large increases in Bronsted basicity.

It can be noted from Tables I and II that *n*-propylamine is a considerably weaker Bronsted base than trimethylamine but interacts more strongly with K^+ than trimethylamine. This behavior is in line with the bonding factors just considered. The increase of polarizability due to the methyl groups is not as important for the long-range interactions with K^+ as for the bonding with H^+; therefore the lower steric repulsion and the higher dipole moment of the *n*-propylamine lead to the higher potassium ion affinity.

The binding energies ($-\Delta H$ values) of the Lewis acid $(CH_3)_3B$ with the alkylamines obtained by determinations of Brown and co-workers[14] are seen to be numerically quite close to the potassium ion affinities observed in the present work (Table II). The bonding of the trimethylboron to the bases M is significantly different from the electrostatic bonds involved with K^+. With boron, as with H^+, a true electron pair bond is formed; however, the acid is uncharged, bulky, and must initially undergo the energetically unfavorable $sp^2 \rightarrow sp^3$ rehybridization. This leads to a much weaker binding than observed when the proton is involved. The $-\Delta H$ changes with methyl substitution of the methylamine series do not follow completely the changes of the potassium ion affinities. With trimethylboron the increase stops at dimethylamine and is followed by a decrease between dimethylamine and trimethylamine. An explanation of this behavior was given[14] on the basis of increasing steric strain between the bulky trimethylboron acid and the increasingly bulky methylamines. It is interesting to note that the entropy changes in trimethylboron reactions are very much less favorable than the corresponding entropy changes with the potassium ion. This is probably due to a considerable loss of freedom (vibration and internal rotation) on formation of the trimethylboron complexes and is thus also related to steric constraints.

The experimental $-\Delta H_{0,1}$ for pyridine and aniline (Table II) are considerably higher than those for ammonia and the alkylamines. Electrostatic calculations for aniline and pyridine were not made, however, considering the sizable dipole moments[21] of 1.5 and 1.2 D, respectively, and from the very high polarizabilities, due to the π electrons in the aromatic ring, it can be expected that electrostatic type interactions will be sufficient to account for the observed binding energies. The dipole axis in aniline, passing through the nitrogen and pointing away from the partially positive H atoms of the NH_2 group, makes an angle of ~43° with the benzene ring plane.[31] Since the potassium ion may be expected to approach aniline approximately along the dipole axis, it is evident that the π cloud of the aromatic ring would come quite close to the ion and a particularly favorable induced dipole and dispersion interaction should result. This effect would further explain the large potassium ion affinity observed for aniline.

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(22) The Mulliken populations tend to overemphasize centers with larger basis functions, thus, for example, the calculated Mulliken electron populations on hydrogen generally are lower than they should be.

(23) The atomic polarizabilities $\alpha_N = 0.98$, $\alpha_C = 1$, and $\alpha_H = 0.44$ Å^3 were used for ammonia and the methylamines. These values were obtained from the molecular polarizabilities of the above compounds (determined by Le Fevre^8) by assuming that the molecular polarizabilities can be expressed as a sum of the polarizabilities α_N, α_C, and α_H of the constituent atoms.

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(27) Strictly speaking the E_t are not directly comparable with $\Delta H_{0,1}$. The difference between the two values is largely composed of the zero-point energies for the three new vibrations in the ion–molecule complex. These amount to about 2 kcal/mol^{18} such that $E_t + 2 \approx \Delta H_{0,1}$. Since the purpose of the present calculations is to obtain qualitative insights this small difference is not taken into consideration.

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(29) The geometry for the methylamine series $NH_3 \cdots (CH_3)_3N$ was not optimized in the electrostatic calculation. The axis between the K^+ and the N atom was assumed to pass symmetrically through the NH_3 molecule. The methyl groups were then introduced by replacing H with CH_3 without changing the angle of the NH_3 molecule to the N–K^+ axis. Thus, the calculations for CH_3NH_2 and $(CH_3)_2NH$ which have no threefold symmetry axis are somewhat in error. The geometry optimized binding energies for these two molecules are expected to be somewhat larger.

(30) It should not be forgotten that the changes of the experimental $\Delta H_{0,1}$ with methyl substitution particularly between dimethylamine and trimethylamine are essentially within experimental error. Therefore a small lowering rather than a small increase of the $-\Delta H_{0,1}$ cannot be excluded on the basis of the present experiments. Considering the assumption made in the electrostatic calculations a similar error could exist there also. Therefore the important point is that because of the operation of the mentioned opposing factors the increases are very small, so small that they might even reverse for the last pair.

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MCD Spectra of Diphenylmethyl Cation and Anion. A Test of the Pairing Theorem[1]

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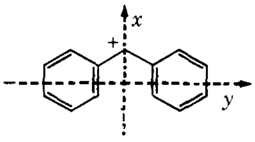
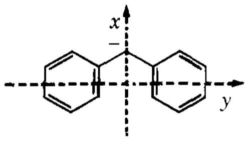
Abstract: Magnetic circular dichroic spectra of the $(C_6H_5)_2CH^+$ and $(C_6H_5)_2CH^-$ ions are approximate mirror images of each other as predicted by the pairing theorem within the framework of the π-electron Pariser-Parr-Pople (PPP) model. The spectra reveal the existence of two transitions in what appears to be the first absorption band in each ion. The observed absolute MCD signs are in agreement with results of PPP calculations and also with simple arguments based on inspection of Hückel orbitals of the ions.

A general theorem[2] valid for the Pariser-Parr-Pople (PPP) model[3] states that π-electron contributions to the magnetic circular dichroic (MCD) spectra of two species paired in the sense of alternant symmetry[4] should be mirror images of each other (their absorption spectra should be identical[4,5]). Since this a priori prediction follows from the fundamental structure of the PPP model and is independent of the choice of parameters and most other calculational details, an experimental test will provide important indications of the extent to which the model is valid for π electrons and of the role which σ electrons play in codetermining the MCD spectra of π chromophores. This is of particular interest in view of the recent questioning of the validity of the concept of alternant symmetry and pairing based on ab initio calculations on benzene.[6]

It is known[7] that the differences of experimental absorption spectra of the members of a cation–anion pair are small for ions with well delocalized charge, such as radical ions of even alternant hydrocarbons, and somewhat larger for ions with charge largely localized at one atomic center, such as polyarylmethyl ions. This has been tentatively attributed to the larger sensitivity of anions of the latter kind to effects of pairing with the counterion but could also be due to deficiencies in the PPP model. We have selected the diphenylmethyl ions (Ic, Ia) as a fairly demanding case for testing



Ic



Ia

the PPP prediction and used solvents believed to minimize ion association. Ions Ic and Ia are well known,[7-9] and their