come relatively more important. The ultimate limit will be roughly the ratios of the $A$ factors. For the rate equations estimated here the ratio of methylcyclopentadienes:cyclohexadiene:hexatrienes would be 1:4:10. As expected, the high energy chemical activation results lie between these limits and those observed at 600°K. Work is in progress to check the estimated Arrhenius parameters by comparing the RRKM predictions with the chemical activation results.[19]

## Conclusions

Chemically activated bicyclo[3.1.0]hex-2-ene isomerizes by both exocyclic and endocyclic cyclopropyl bond rupture. It is shown that the high activation energy for exocyclic rupture precludes isomerization by this pathway at temperatures around 170° despite the very large $A$ factor. At higher temperatures, 325°, the expected exocyclic bond rupture product is still not observed because of the high activation entropy associated with the hydrogen migration as well as a slightly higher activation energy. At very high energies, however, the products from both mechanisms are expected as observed in the experiment.

**Acknowledgment.** We gratefully acknowledge support of this research by the Robert A. Welch Foundation and by the Petroleum Research Fund administered by the American Chemical Society. We also thank Dr. Alan Rodgers for many helpful discussions and Miss Paula Crane and Miss Regina Carroll for their assistance in carrying out the irradiations.

(19) W. L. Hase, R. L. Johnson, and J. W. Simons, *Int. J. Chem. Kinet.*, **4**, 1 (1972), and references therein.

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# Gas-Phase Basicities of Amines. Hydrogen Bonding in Proton-Bound Amine Dimers and Proton-Induced Cyclization of $\alpha,\omega$-Diamines

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**Abstract:** The equilibrium constants for several gas-phase proton transfer reactions were determined as a function of temperature. This allowed the determination of $\Delta G°$, $\Delta H°$, and $\Delta S°$ of the reactions. One group of determinations dealt with the proton transfer $B_1H^+ + B_2 = B_1 + B_2H^+$, where $B_1$ and $B_2$ were various alkyl amines, substituted anilines, pyrrole, and other representative compounds. The findings follow trends reported in earlier publications. A second series of experiments dealt with the proton transfer $B_1H^+ + B_3 = B_1 + B_3H^+$, where $B_1$ indicates alkyl amines and $B_3$ indicates $\alpha,\omega$-diaminoalkanes. The measured $\Delta H$ values showed that the proton affinities of the diamines were very high. The reactions also showed large negative entropy changes. Both of these results are possible only if cyclization with a proton bridge occurs in the diamines. In a third series of experiments, measurement of the equilibria of $B_1H^+ + B_2 = B_1H^+B_2$ led to the enthalpy and entropy changes for these dimerization reactions. The amines involved were ammonia, methylamine, dimethylamine, and trimethylamine. The hydrogen bonds in the symmetric dimers ($B_1 = B_2$) were found not to change much with methyl substitution and were in the $\Delta H \approx 23$ kcal/mol range. Changes of the hydrogen bonds in $B_1H^+B_2$ could be qualitatively explained on the basis of the gas-phase basicities of $B_1$ and $B_2$. The hydrogen bond energies of the $B_1H^+B_1$ dimers are compared with those of the proton bridged diamines. This leads to an evaluation of ring strain in the proton-bridged diamines. The ring strain energies and the entropies of cyclization of the diamines were also compared with corresponding values for the cycloalkanes. The proton bridged 1,2-diaminoethane shows large strain energy, as would be expected for a four-membered ring. This means that the N–H$^+$–N bond tends to be linear. The $\Delta S_{\mathrm{cycl}}$ of the diamines generally follow the $\Delta S_{\mathrm{cycl}}$ of the cycloalkanes, but the correspondence is not complete. The rate constants for the forward and reverse components of the reaction $CH_3NH_3^+ + (CH_3)_2NH = CH_3NH_2 + (CH_3)_2NH_2^+$ were determined.

Measurements of gas-phase proton transfer equilibria (eq 1) were reported earlier.[1] B's were

$$B_1H^+ + B_2 = B_1 + B_2H^+ \qquad (1)$$

nitrogen containing organic bases which were mostly various monoamines. The equilibrium constants $K_1$ lead to the free energy changes $\Delta G° = -RT \ln K_1$, while van't Hoff plots of the temperature dependence of $K_1$ allowed evaluation of $\Delta H_1°$ and $\Delta S_1°$. Such measurements are of considerable interest since they permit an understanding of basicity on a molecular level, *i.e.*, without the complex interference of the liquid solvent. The measurements were done with a "high pressure" mass spectrometer.[2] Three other groups[3-5] have also reported independent measurements of gas-

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(1) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 5128 (1972).

(2) (a) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *ibid.*, **94**, 7627 (1972); (b) M. Arshadi, R. Yamdagni, and P. Kebarle, *J. Phys. Chem.*, **74**, 1475 (1970).

(3) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, D. Holtz, J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

(4) (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *ibid.*, **93**, 4314 (1971); (b) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972).

(5) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 471 (1972).

phase equilibria of type 1 observed near room temperature with ion cyclotron resonance mass spectrometers. The significance of the data was discussed in this work[1,3–5] and in earlier publications by Brauman[6] and Munson[7] based on qualitative measurements of gas-phase basicity orders. A determination of substituent effects on the basicity (proton affinity of acids), based on appearance potential measurements, was also reported earlier[8] from this laboratory.

The present work gives measurements for several new bases including some α,ω-diamines. The diamines are particularly interesting because they can cyclize after protonation as indicated in reaction 2.

$$BH^+ + NH_2(CH_2)_nNH_2 = B + \underline{NH_2(CH_2)_nNH_2\text{–}H^+} \qquad (2)$$

The ability for formation of a proton bridge should increase the basicity of the diamine. Thus, one would expect a larger (negative) enthalpy change for reaction 2 than for the proton transfer to a similar monoamine, *i.e.*, reaction 3. Furthermore, reaction 3

$$BH^+ + CH_3(CH_2)_nNH_2 = B + CH_3(CH_2)_nNH_3^+ \qquad (3)$$

should have a very small entropy change, typical for simple proton transfers, while (2) should have a substantial negative entropy change because of the loss of freedom caused by the cyclization.

The intramolecular formation of a proton bridge in the diamines can be compared with the bond formation in a proton-bound dimer, *i.e.*, the dimerization reaction 4. For cases where $k \approx n/2$, the enthalpy change for

$$C_kH_{2k+1}NH_3^+ + C_kH_{2k+1}NH_2 = (C_kH_{2k+1}NH_2)_2H^+ \qquad (4)$$

the dimerization reaction $\Delta H_4$ may be expected to give a measure of the proton bridge bond energy that would be observed in the cyclic protonated diamine

$$\underline{NH_2(CH_2)_nNH_3^+}$$

(provided that the ring strain was absent). A comparison of the two energies would lead to estimates of ring strain in the diamines.

The formation of proton held dimers in reactions like 4 and the formation of higher charge held aggregates have been the subject of extensive studies in this laboratory for the past several years in a program called "Ion solvent molecule interactions in the gas phase."[9] In the present work, results for the dimers of ammonia and several alkylamines will be presented. The effect of methyl substituents on the bond energy of the protonated alkylamine dimers will be considered first and then the results will be utilized in a comparison with bond energies observed in the protonated cyclic amines.[10]

## Experimental Section

**(a) Apparatus.** The measurements were done with the pulsed electron beam high-pressure ion source mass spectrometer used and described in earlier work.[2,9] Depending on the desired measurement either one or two amines were passed in slow flow through the ion source at a total pressure of some 3 Torr. Ionization was obtained with a 2000-V electron beam entering the ion source through a narrow slit. The beam was pulsed staying "on" for some 10 μsec and "off" for 8 msec. The created ions react with other molecules as they diffuse through the field free ion source. Some of the ions come to the vicinity of an ion exit slit (12 × 1500 μ) and escape into an evacuated region, with high pumping capacity, where they are accelerated, magnetically mass analyzed, and detected with a multiplier. The multiplier pulses for ions of a given mass are collected in a multichannel counter whose 8-msec sweep is synchronized with the electron beam pulse. Ions with different arrival times after the pulse are counted in different channels. After a large number of electron beam pulses, sufficient counts have been collected in each channel so that one obtains an intensity time profile for an ion of a given mass. The residence time of ions in the ion source is much longer than the time required for mass analysis so that the time coordinate represents the time available for reaction. The total ion current decays over some 6 msec to very low values.

Generally the concentrations of the neutral reactants are so chosen that the ion molecule reactions studied are fast, relative to the average residence time (~1 msec) of the ions in the ion source. When two ions have reached equilibrium their time dependent intensity ratio becomes constant.

The ion source was heated by means of heater elements embedded in the solid ion source block and the temperature measured by thermocouples embedded in the block.

The total pressure in the ion source was measured with a capacitance torr meter. When a two-amine mixture was used, the minor component was bled through a capillary calibrated with that component. The partial pressures of the two amines were then obtained from the total pressure measurement and flow rate considerations (see weight loss measurements[2a]).

In other cases a mixture of a major gas ($CH_4$) and one or two minor amine components was used. Typically the major gas was at 4 Torr while the amines were below 0.1 Torr. In one type of measurement two calibrated capillaries were used for the amines. In other measurements a gas mixture of the two amines was prepared and bled through one capillary (calibrated in moles/second gas mixture). The ratio of the amines was determined by using an auxiliary electron filament mounted in the low-pressure region immediately below the high-pressure ion source exit slit.

**(b) Reaction Conditions and Tests for Thermalization.** The exothermic proton transfer from $B_1H^+$ to $B_2$ probably proceeds with a rate constant $k_1 \approx 10^{-9}$ cm³ molecule⁻¹ sec⁻¹ (for an accurate value, see below). The excess energy due to the exothermicity of the reaction would initially reside in the reaction products $B_1$ and $B_2H^+$. In a typical experiment the $B_2$ pressure was around 100 mTorr. This corresponds to a number density of $B_2 \sim 3 \times 10^{15}$ molecules/cm³. Therefore the reaction frequency is $\nu_1 = k_1[B_2] = 3 \times 10^6$ sec⁻¹, which corresponds to a half-life around $10^{-6}$ sec for $B_1H^+$ before proton transfer. At equilibrium the rate of the reverse reaction (−1) will be equal to the forward rate. This means that the half-life of the $B_2H^+$ before reaction will be also around $10^{-6}$ sec. For a reaction mixture containing only the two amines at a total pressure around 3 Torr, one can calculate easily that $B_2H^+$ will suffer some 100 collisions (in $10^{-6}$ sec) before reacting (assumed rate constant for collisions is $10^{-9}$ cm³ molecule⁻¹ sec⁻¹). One may not be certain whether 100 collisions are enough to achieve thermalization of the $B_2H^+$. If some excitation is retained in the $B_2H^+$, *i.e.*, if the $B_2H^+$ energies are not thermal, the equilibrium assumption will not be justified.

In order to establish the validity of the measurements some special runs were made in the presence of a third gas ($CH_4$) and at very low concentrations of $B_1$ (methylamine) and $B_2$ (dimethylamine). The results are shown in Figure 1. Initially all ions are $CH_3NH_3^+$. The relative intensity of these ions decreases with time and there is a corresponding increase of $(CH_3)_2NH_2^+$. The two ion intensities become stationary after some hundreds of microseconds. The stationary concentrations substituted into the equilibrium constant quotient lead to $K_1 = 525$ and 508 and average to $\Delta G_1 = -7.44$ kcal/mol. The $\Delta G_1$ obtained in the absence of a third gas and pressures in the Torr range was 7.5 kcal/mol (see

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(6) J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, **93**, 3914 (1971).

(7) M. S. B. Munson, *ibid.*, **87**, 2332 (1965).

(8) E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.*, **58**, 1897 (1962).

(9) (a) P. Kebarle in "Ions and Ion Pairs in Organic Reactions," Vol. I, M. Szwarc, Ed., Wiley, New York, N. Y., 1972, Chapter 2; (b) P. Kebarle, "Ion Molecule Reactions," Vol. 2, J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1972, Chapter 7.

(10) A study of the proton-bound dimers of ammonia and methyl-, dimethyl-, and trimethylamines had been nearly completed when M. T. Bowers (Dallas, May 1972) suggested the extension of the measurements to α,ω-diamines. D. H. Aue, H. M. Webb, and M. T. Bowers[11] had commenced earlier measurements of diamines using the icr technique and working at a constant temperature.

(11) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **95**, 2699 (1973).

**Table I**

(a) Proton Transfer Reactions: $B_1H^+ + B_2 = B_1 + B_2H^+$ [a]

| $B_1$ | $B_2$ | $-\Delta G°$ [b] | $B_1$ | $B_2$ | $-\Delta G°$ |
|---|---|---|---|---|---|
| $NH_3$ | $CH_3CONH_2$ | 3.4 | $C_6H_5NHCH_3$ | $C_6H_5NHC_2H_5$ | 3.4 |
| $NH_3$ | $CH_3NH_2$ | 10.8[d] | $C_6H_5NHCH_3$ | $C_6H_5N(CH_3)_2$ | 6.6 |
| $CH_3NH_2$ | $C_6H_5NHCH_3$ | 4.3[d] | $(CH_3)_2NH$ | Cyclohexylamine | 1.2 |
| $CH_3NH_2$ | *o*-Anisidine | 4.3 | $C_6H_5NHC_2H_5$ | Cyclohexylamine | 1.3 |
| $CH_3NH_2$ | $(CH_3)_2NH$ | 7.5[d] | $C_6H_5N(CH_3)_2$ | $(CH_3)_3N$ | 1.6 |
| $CH_3NH_2$ | Pyridine | 7.8[d] | $C_6H_5N(CH_3)_2$ | $C_6H_5N(CH_3)(C_2H_5)$ | 2.5 |
| $CH_3NH_2$ | $(CH_3)_3N$ | 12.5[d] | $C_6H_5N(CH_3)_2$ | Piperidine | 2.8 |
| $C_6H_5NH_2$ | $CH_3NH_2$ | 1.9[d] | $C_6H_5N(CH_3)_2$ | $C_6H_5N(C_2H_5)_2$ | 5.2 |
| $C_6H_5NH_2$ | $C_6H_5NHCH_3$ | 6.2 | Cyclohexylamine | Piperidine | 4.8 |
| $C_6H_5NH_2$ | *o*-Anisidine | 6.5 | Pyrrole | $C_6H_5NH_2$ | 1.75 |
| $C_6H_5NHCH_3$ | $(CH_3)_2NH$ | 3.5[d] | | | |

(b) Proton Affinity[b,c]

| Compd | This lab. | Other work | Compd | This lab. | Other work |
|---|---|---|---|---|---|
| $NH_3$ | 207.0[e] | | $C_6H_5NHC_2H_5$ | 225.5 | |
| $CH_3CONH_2$ | 210.4 | | Pyridine | 225.6[d] | |
| Pyrrole | 214.15 | | Cyclohexylamine | 226.7[d] | |
| $C_6H_5NH_2$ | 215.9 | | $C_6H_5N(CH_3)_2$ | 228.7 | |
| $CH_3NH_2$ | 217.8[d] | 216.5[3]<br>218.4[4b] | $(CH_3)_3N$ | 230.3[d] | 227.4[3]<br>229.1[4b] |
| $C_6H_5NHCH_3$ | 222.1[d] | | $C_6H_5NCH_3C_2H_5$ | 231.3 | |
| *o*-Anisidine | 222.1 | | Piperidine | 231.5 | 230.1[4] |
| $(CH_3)_2NH$ | 225.3[d] | 222.8[3]<br>224.9[4b] | $C_6H_5N(C_2H_5)_2$ | 234.0 | |

[a] All values in kcal/mol. [b] Gas-phase reactions at 600°K. [c] PA = proton affinity = $\Delta H$ for the reaction $BH^+ = B + H^+$. [d] Previous work, ref 1. [e] Haney and Franklin, ref 12.

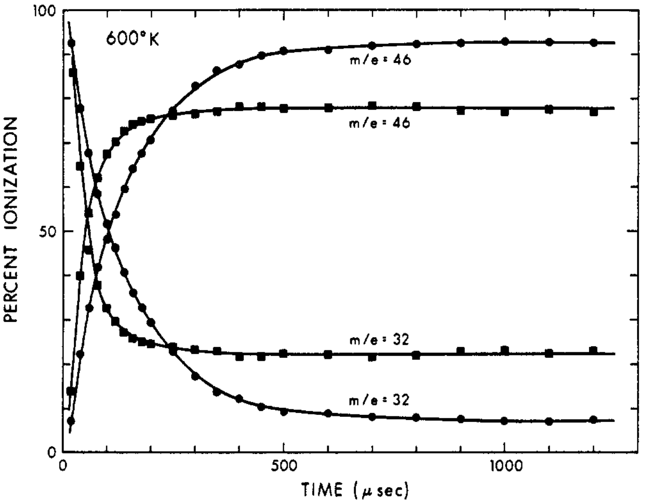

Figure 1. The time dependence of normalized ion intensities: *m/e* 46, $(CH_3)_2NH_2^+$; *m/e* 32, $CH_3NH_3^+$; (●) $CH_4$ at 4 Torr, methylamine at 31 mTorr, dimethylamine at 0.8 mTorr; (■) $CH_4$ at 4 Torr, methylamine at 340 mTorr, dimethylamine at 1.6 mTorr; 600°K.

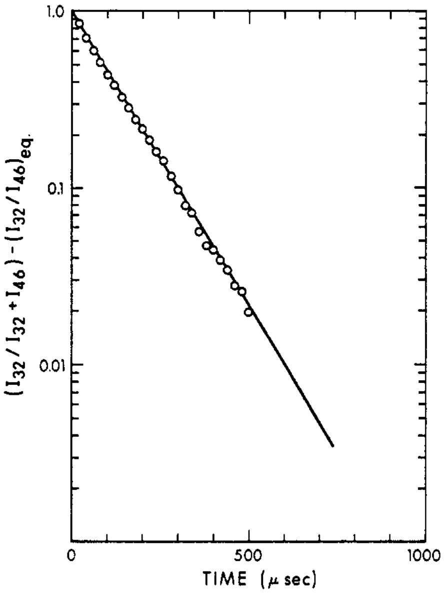

Figure 2. The determination of the rate constant for the reaction $CH_3NH_3^+ + (CH_3)_2NH = CH_3NH_2 + (CH_3)_2NH_2^+$: $CH_4$ at 4 Torr, $CH_3NH_2$ at 31 mTorr, $(CH_3)_2NH$ at 0.8 mTorr; 600°K.

Table I). Thus the third gas data are in good agreement with the pure amine mixtures.

Time-dependent intensity changes like that shown in Figure 1 can be used for determination of the rate constants for the forward and reverse reaction $k_1$ and $k_{-1}$. Figure 2 shows a plot of log $\{I_{32}/(I_{32} + I_{46}) - (I_{32(eq)}/I_{46(eq)})\}$ *vs.* time. $I_{32}$ and $I_{46}$ are the time-dependent counts per channel for the ions $CH_3NH_3^+$ and $(CH_3)_2NH_2^+$ while $I_{(eq)}$ are the corresponding counts after a stationary (*i.e.*, equilibrium) intensity has been achieved.

Treating the relative intensities as if they were relative concentrations in the ion source, one can use standard kinetic expressions. For a reversible (pseudo-first order) reaction the slope of the straight line in Figure 2 should be equal to $\nu_1 + \nu_{-1}$ where $\nu_1$ and $\nu_{-1}$ are the reaction frequencies (pseudo-first-order rate constants) $\nu_1 = k_1[(CH_3)_2NH]$ and $\nu_{-1} = k_{-1}[CH_3NH_2]$. The ratio $\nu_1/\nu_{-1}$ is given by the equilibrium expression $\nu_1/\nu_{-1} = [B_2H^+]/[B_1H^+]$ at equilibrium. Thus from the slope and the equilibrium concentrations one can evaluate $k_1$ and $k_{-1}$. The values obtained are $k_1 = 5.5 \times 10^{-10}$ and $k_{-1} = 1.08 \times 10^{-12}$ cm³ molecule⁻¹ sec⁻¹. The rate constants are probably accurate only to some 20–30% which corresponds to the expected inaccuracy of the concentrations of the amines in methane. Since $\nu_{-1} = 0.54 \times 10^3$ sec (for the run shown in Figure 2) the half-life of $(CH_3)_2NH_2^+$ before reaction is about 1 msec. In this time it suffers some $10^5$ collisions with the third gas. The reacting $(CH_3)_2NH_2^+$ species must be thermal under these conditions. The agreement between the equilibrium constant obtained under these conditions and the experiments where the amines were used by themselves indicates that thermalization is also achieved in the latter runs.

The dimerization equilibria, $B_1H^+ + B_2 = B_1H^+B_2$, were generally measured in the absence of a third gas since the partial pressures of the base ($B_1 = B_2$) or bases ($B_1 \neq B_2$) can be determined more easily under these conditions. In order to check that thermalization is also achieved in these reactions some runs were

**Table II.**[a] Energy Changes for Proton Transfer, $B_1H^+ + B_3 = B_1 + B_3H^+$

| $B_1$ | $B_3$ | $-\Delta H°$ | $-\Delta S°$ | $-\Delta G°_{298}$ | PA[b] |
|---|---|---|---|---|---|
| Dimethylamine | 1,2-Diaminoethane | 9.6 | 12.7 | 5.8 | 234.9 |
| Trimethylamine | 1,3-Diaminopropane | 13.0 | 20.6 | 6.8 | 243.3 |
| Trimethylamine | 1,5-Diaminopentane | 13.0 | 20.0 | 7.1 | 243.3 |
| Trimethylamine | 1,7-Diaminoheptane | 12.9 | 20.0 | 6.9 | 243.2 |

[a] $\Delta H°$ and $\Delta S°$ values approximately temperature independent are valid for the experimental temperature range of Figure 3, $\Delta H°$ and $\Delta G°$ in kcal/mol, $\Delta S°$ in eu. [b] The proton affinity corresponding to $\Delta H$ change for reaction $\alpha,\omega$-diamine·$H^+$ = $\alpha,\omega$-diamine + $H^+$, in the gas phase (kcal/mol).

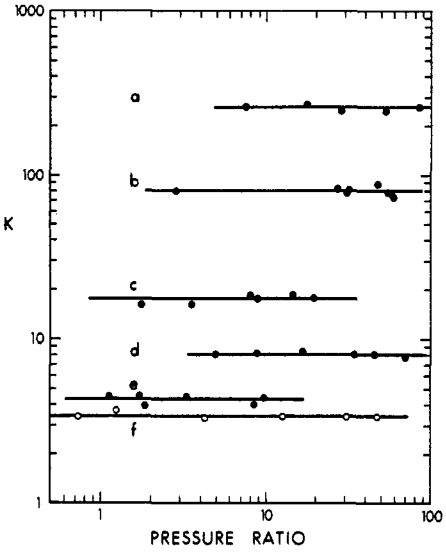

Figure 3. A plot showing that the equilibrium constant $K$ for reaction $B_1H^+ + B_2 = B_1 + B_2H^+$ is independent of the pressure ratio of neutral reactants ($B_1$, $B_2$): (a) *N*-methylaniline, *N*,*N*-dimethylaniline; (b) *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline; (c) *N*-methylaniline, *N*-ethylaniline; (d) *N*,*N*-dimethylaniline, *N*-ethyl-*N*-methylaniline; (e) pyrrole, aniline; (f) *N*-ethylaniline, cyclohexylamine. Pressure ranges: major component, 1–4 Torr; minor component, 20–200 mTorr.

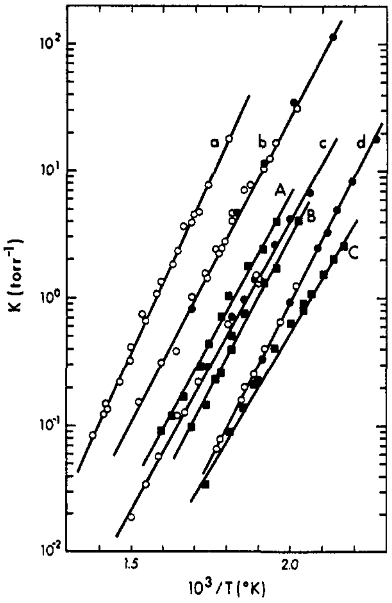

Figure 4. van't Hoff plots of equilibrium constants for reactions $B_1H^+ + B_2 = B_1H^+B_2$: ($B_1$, $B_2$); (a) $NH_3$, $NH_3$; (b) $CH_3NH_2$, $CH_3NH_2$; (c) $(CH_3)_2NH$, $(CH_3)_2NH$; (d) $(CH_3)_3N$, $(CH_3)_3N$; (A) $CH_3NH_2$, $NH_3$; (B) $(CH_3)_2NH$, $CH_3NH_2$; (C) $(CH_3)_3N$, $(CH_3)_2N$. (○) $B_1 = B_2$, total pressure due to amine only. (●) $B_1 = B_2$, major gas $CH_4$.

done in the presence of a major third gas. These runs gave the same results for the equilibrium constants. Runs with a third gas are indicated in the van't Hoff plots to be shown below.

The results of some runs in which the reactant ratio $B_1/B_2$ was varied are shown in Figure 3. They show that the equilibrium constant $K_1$ is independent of the concentration ratio of the anilines. These experiments were done in the absence of a third gas. $B_1$ was the major gas and large variations of the concentration ratio were achieved largely by a change in the partial pressure of $B_2$.

## Results and Discussion

**(a) Results.** The results from the measured equilibria of reactions 1 are given in Table Ia. $B_1$ and $B_2$ are aliphatic and aromatic amines. The table gives the $\Delta G°_1 = -RT \ln K_1$ results for the reactions at 600°K. Some of the equilibria included in the table were measured earlier.[1] The temperature dependence of several equilibria was also examined at that time. It was found that the free energy changes $\Delta G°_1$ were nearly independent of temperature; *i.e.*, the $\Delta S°_1$ values were very small, mostly less than 3 eu. Therefore, $\Delta G°_1$ (600°) ≈ $\Delta G°_1$ (300°) and $\Delta G°_1 \approx \Delta H_1$ within about 1 kcal/mol.

Table Ib gives the proton affinities of the compounds involved in equilibria 1 calculated on the basis of the above assumptions and PA($NH_3$) = 207 kcal/mol.[12] Values obtained with the ion cyclotron technique at 300°K are also given in the table. Comparison of these literature data with the present results shows that agreement is generally within 1–2 kcal. Considering the very different nature of the experiments and particularly the difference in temperature and pressure this agreement is as good as could be expected.

Results from the proton transfer reactions to $\alpha,\omega$-diamines are given in Table II. Used as acids were $(CH_3)_2NH_2^+$ and $(CH_3)_3NH^+$ since their conjugate bases were of similar strength but somewhat weaker than the diamines. The free energy changes for these reactions showed considerable temperature dependence, which means that the reactions proceeded with significant entropy changes. Therefore, $\Delta G°$, $\Delta H°$, and $\Delta S°$ are given in the table. The $\Delta H°$ and $\Delta S°$ values were obtained from the van't Hoff plots of the equilibrium constants. These plots are given in Figure 4.

Results for the formation of proton-bound dimers corresponding to reactions 5 and 6 are given in Table III. Since these reactions proceed with significant entropy changes, $\Delta G°$ and $\Delta H°$ are given in the table. The van't Hoff plots from which the data were evaluated are shown in Figure 5.

$$B_1H^+ + B_1 = (B_1HB_1)^+ \qquad (5)$$

$$B_1H^+ + B_2 = (B_1HB_2)^+ \qquad (6)$$

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(12) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2029 (1969).

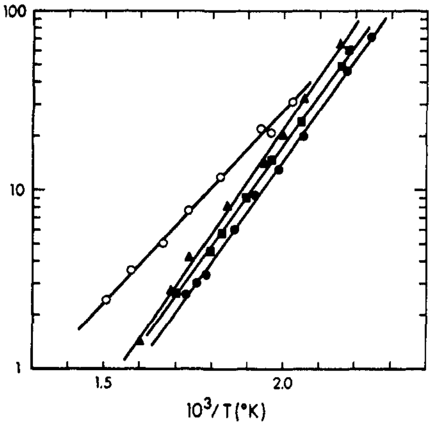

Figure 5. van't Hoff plots of proton transfer reactions $B_1H^+ + B_3 = B_1 + B_3H^+$ where $B_1$ is a monoamine and $B_3$ an $\alpha,\omega$-diamine capable of proton induced cyclization: (○) dimethylamine, 1,2-diaminoethane; (●) trimethylamine, 1,3-diaminopropane; (▲) trimethylamine, 1,5-diaminopentane; (■) trimethylamine, 1,7-diaminoheptane.

**Table III.** $\Delta H°$ and $\Delta G°$ Changes for Reactions $B_1H^+ + B_2 = B_1H^+B_2$ in the Gas Phase

| | $B_2$ | | | |
|---|---|---|---|---|
| $B_1H^+$ | $NH_3$ | $CH_3NH_2$ | $(CH_3)_2NH$ | $(CH_3)_3N$ |
| | $-\Delta G°_{550}$[a] | | | |
| $NH_4^+$ | 10.6 | 17.9 | (23.3) | (27.3) |
| $CH_3NH_3^+$ | 7.1 | 8.7 | 13.8 | (17.0) |
| $(CH_3)_2NH_2^+$ | 5 | 6.3 | 6.65 | 9.4 |
| $(CH_3)_3NH^+$ | (4) | (4.5) | 4.8 | 4.9 |
| | $-\Delta H°$[b] | | | |
| $NH_4^+$ | 24.8[c] | ~32.0 | (38.9) | (43.3) |
| $CH_3NH_3^+$ | 21.4 | 21.7 | 27.5 | (32.5) |
| $(CH_3)_2NH_2^+$ | 20.6 | 22.4 | 20.8 | 23.3 |
| $(CH_3)_3NH^+$ | (20) | (20) | 20.5 | 22.5 |

[a] Values in kcal/mol. Standard state, 1 atm. 550°K represents an average temperature in the experimental temperature range utilized in the equilibria studies. Numbers in parentheses are predicted values. [b] $\Delta H°$ values in kcal/mol. Numbers in parentheses are predicted values. [c] This value is lower than an earlier determination (S. K. Searles and P. Kebarle, *J. Phys. Chem.*, 72, 792 (1968)) which led to 27 kcal. The difference is believed to be due to somewhat faulty temperature measurement in the earlier work. Details on new $NH_4^+(NH_3)_n$ and $NH_4^+(H_2O)_n$ measurements will be published later.

(b) **Proton Transfer to the Monoamines.** The basicities of alkylamines were discussed earlier.[1,3-7] The data in Table I include several anilines. The basicity of the aniline increases with substituents in the following order: H, *N*-methyl, *o*-methoxy, *N*-ethyl, *N,N*-dimethyl, *N*-methyl-*N*-ethyl, *N,N*-diethyl. Thus we see that the *N*-alkyl substituents have the same effect as in ammonia.[1-7] The higher basicity of the *o*-methoxyaniline relative to that of the unsubstituted compound is also to be expected.

It is noteworthy that the gas-phase basicity of pyrrole is higher than that of ammonia. The reverse order is observed in aqueous solution. Comparing the gas-phase basicity of pyrrole (PA = 214.15 kcal, Table Ib) with that of pyrrolidine (PA = 228.7)[4] one finds that pyrrolidine is a much stronger base. The low (aqueous) basicity of pyrrole is generally explained by the existence of a partial positive charge on the nitrogen atom due to some bonding participation of the two lone p electrons. We see that this effect is confirmed by the gas-phase results, but only when the comparison is made with a compound of similar structure, *i.e.*, pyrrolidine. The traditional comparison with ammonia in which the higher aqueous basicity of ammonia is explained on the basis of electronic effects in the molecules is thus, strictly speaking, incorrect. Ammonia on the molecular level is a weaker base because it lacks the strong charge stabilizing effect of the polarizable hydrocarbon groups. It happens to be the stronger aqueous base because of more favorable interactions with water, *i.e.*, solvation. Similar considerations are also valid for pyridine, aniline, and acetamide.

(c) **Proton Bound Dimers of Alkylamines.** The free energy, enthalpy, and entropy changes for reactions 5 and 6 by which the symmetric $B_1H^+B_1$ and the mixed $B_1H^+B_2$ dimers are formed are shown in Table III. The corresponding van't Hoff plots are in Figure 4. The thermodynamic relationship in eq 8 connects the free energies for reactions 6 and 7

$$B_1H^+ + B_2 = (B_1HB_2)^+ \qquad (6)$$

$$B_1 + B_2H^+ = (B_1HB_2)^+ \qquad (7)$$

$$B_1H^+ + B_2 = B_1 + B_2H^+ \qquad (1)$$

$$\Delta G°_6 - \Delta G°_7 = \Delta G°_1 \qquad (8)$$

with that for the proton transfer reaction 1.

Identical relationships hold for the $\Delta H°$ and $\Delta S°$ values. $\Delta G°_6$ and $\Delta G°_7$ were determined in the same experiment. Their difference (see Table II) is in fair agreement with $\Delta G°_1$ from Table I which was generally determined in separate experiments under somewhat different conditions, *i.e.*, concentrations and temperatures favoring the observation of ions involved in (1).

The $\Delta G°_{550}$ values given in Table III show some interesting trends. A decrease is observed as one moves vertically down in any column. Thus in the first column the formation of $NH_3H^+NH_3$ from $NH_4^+ + NH_3$ releases 10.6 kcal while the formation of $(CH_3)_2NHH^+NH_3$ from $(CH_3)_2NH_2^+$ and $NH_3$ releases only 5.1 kcal. One may view the formation of the proton bound dimer as a partial proton transfer reaction from the proton donor (*i.e.*, the onium ion, to the proton acceptor (the free base)). According to this view a large free energy will be released in the dimer formation if the proton donor is a strong acid and the acceptor a strong base. In the first column the acceptor remains the same ($NH_3$) while the proton donors change from donors of high acidity ($NH_4^+$) to donors of low acidity $(CH_3)_2NH_2^+$. The decrease in the released free energy thus follows the decreasing acidity of the donors. Moving along the top row of the table we notice that the released energies increase from left to right. In this case we have a fixed proton donor $NH_4^+$ and different proton acceptors with increasing basicity ($NH_3$ to progressively substituted amines). Again the observed increase of energy released follows the notion of a partial acid–base reaction. It should be noted that the values of the top row are related to the values of the first column by the relationship in eq 8. Thus in this case the agreement with the acid–base picture is largely a consequence of the thermodynamic requirement of eq 8. The value for $(CH_3)_3NH^+NH_3$ (bottom left corner Table III) given in parentheses is not a measured value but a predicted number. The prediction is based on the gradual decrease observed when one goes down the first column and the very slight increase when one moves from left to right in the bottom row.

The change in the bottom row is very slow. This effect can be understood when it is considered that the proton in $(CH_3)_3NH^+$ is already strongly stabilized by the methyl groups. The additional stabilization obtained by attaching the (neutral) base cannot be very large and will not change much (in absolute terms) with the nature of the base, which in the series considered is always weaker than $(CH_3)_3N$. The rapid change in the top row illustrates the opposite phenomenon. Since $NH_4^+$ is not too well stabilized the additional stabilization achieved by the addition of the base is important, and the strength of the incoming base has a strong effect on the energies.

Similar but intermediate trends are observed or predicted in the intermediate columns and rows of the $\Delta G°$ table. The diagonal from top left to bottom right shows a decrease of released energy with increased substitution in the symmetric dimers.

The $-\Delta H°$ values given in Table III follow somewhat similar but not identical trends. There is a decrease in the first column but the decrease is small. This means that the decrease of the corresponding $-\Delta G°$ values is due mostly to the progressive loss of entropy. The top row in the enthalpy table again shows a large increase (from left to right) which is due to the relationship in (8) and reflects the big changes of proton affinities of the bases. The trend in the bottom row is not very pronounced, the values indicating a small increase from left to right. The diagonal containing the symmetric dimers does not show a clear trend. Initially from $(NH_3)_2H^+$ to $((CH_3)_2NH)_2H^+$ there is a decrease; then the value for the trimethylamine dimer becomes higher. We do not believe that this reversal of $\Delta H$ values is due to experimental error. It is clear that the simple partial acid–base reaction model considered in the discussion is not too well suited to predictions for the symmetric dimers where the strength of the acid partially losing the proton is equal to the strength of the (identical) base partially gaining the proton.

In an earlier study of the hydrogen bonding to negative ions[13] the reactions $Cl^- + HR = (ClHR)^-$ were examined. It was found that the energy released ($-\Delta G°$ and $-\Delta H°$) increased with the gas-phase acidity of HR. In another series HR was kept constant (HR = HOH) and the bases ($F^-$, $Cl^-$, ..., $NO_2^-$, etc.) were changed. Again the energy released increased with the gas-phase basicity of the base, *i.e.*, the negative ion. Thus both the H-bonding energies in the negative dimers $(R_1HR_2)^-$ and in the positive bases $B_1H^+B_2$ do qualitatively follow predictions based on the partial acid–base reaction concept. The earlier study indicated that the hydrogen bond in the symmetric dimers $(RHR)^-$ increased with the gas-phase basicity of $R^-$. Thus $I_2H^-$, $Br_2H^-$, $Cl_2H^-$, and $F_2H^-$ were expected to have progressively stronger hydrogen bonds, although the expected spread was not very large.[13] In the present case, *i.e.*, the positive symmetric amines, the spread is not very large, also the overall trend of the $\Delta H$ change is not very clear.

**(d) Proton Bound Cyclic Diamines.** The thermodynamic data obtained for the proton transfer equilibria

$$B_1H^+ + B_3 = B_1 + B_3H^+ \qquad (2)$$

where $B_1$ is dimethyl- or trimethylamine and $B_3$ is an $\alpha,\omega$-diamine, are shown in Table II. The reactions proceed with appreciable negative entropy changes. Proton transfer between monoamines does not involve significant entropy changes. Therefore, we can conclude that the observed entropies are due to the formation of proton bound cyclic diamines. We can imagine that the reaction proceeds in two steps.

$$B_1H^+ + NH_2(CH_2)_nNH_2 = B_1 + NH_3^+(CH_2)_nNH_2 \qquad (9)$$

$$NH_3^+(CH_2)_nNH_2 = \underline{NH_3^+(CH_2)_nNH_2} \qquad (10)$$

Step 9 should involve no significant $\Delta S°$ while step 10 involves the entropy loss due to cyclization. We may therefore put $\Delta S°_2 \approx \Delta S°_{10}$ which corresponds to $\Delta S$ cyclization.

The enthalpy changes for the proton transfer reactions given in Table II can be used in conjunction with the known proton affinities of $B_1$ (dimethyl- or trimethylamine; see Table I) for the evaluation of the proton affinity of the diamines. The resulting proton affinities are given in the last column of Table II. We see that the proton affinities of the diamines are considerably larger than those for monoamines of comparable structure. Thus the proton affinity of 1,3-diaminopropane equals 243.3 while PA(*n*-propylamine)[11] = 222.3 and PA(*n*-butylamine)[11] = 222.8 kcal/mol are lower by more than 20 kcal/mol. This again indicates that additional energy is released because of cyclization. We may obtain a fairly close estimate for the enthalpy change of the cyclization reaction, $\Delta H_{cycl}$, by assuming that the first step in the proton transfer, *i.e.*, reaction 9, involves a $\Delta H$ which is equal to the $\Delta H$ change for proton transfer to the monoamine $CH_3(CH_2)_nNH_2$. The $\Delta H_{cycl}$ is then given by eq 11. The

$$\Delta H_{cycl} = \Delta H_{10} = PA(NH_2(CH_2)_nNH_2) - PA(NH_2(CH_2)_nCH_3) \qquad (11)$$

$\Delta H_{cycl}$'s obtained by eq 11 are shown in Table IV together with $\Delta S_{cycl}$.

We may compare these evaluated $\Delta H_{cycl}$ values with the $\Delta H$ results for the formation of proton-bound dimers involving two alkylamines. One may expect that in the absence of ring strain $\Delta H_{cycl} \approx \Delta H_4$, where

$$C_kH_{2k+1}NH_3^+ + C_kH_{2k+1}NH_2 = (C_kH_{2k+1}NH_2)_2H^+ \qquad (4)$$

$k \approx n/2$. Unfortunately values for all $\Delta H_4$ are not available. We must rely only on the dimerization of methylamine and the general trends observed in Table III. It was pointed out in the preceding section that the enthalpy values for the symmetric dimers do not change much with $k$. Therefore, we can take an average value for $\Delta H_4 = -23$ kcal/mol (see Table III). With this value and eq 12 one can estimate the strain

$$\text{strain energy} = \Delta H_{cycl} - \Delta H_4 = \Delta H_{cycl} + 23\ \text{kcal} \qquad (12)$$

energy in the cyclic protonated diamines. The resulting values are shown in Table IV.

The results show that there is a significant strain energy (10.4 kcal) for the protonated 1,2-diaminoethane. The higher diamines, 1,3-diaminopropane, etc., show strain energies which are much lower,

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(13) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **93**, 7139 (1971).

**Table IV.** Cyclization of Protonated $\alpha,\omega$-Diamines

| | $-\Delta S_{\mathrm{cycl}}$[a] | $-\Delta H_{\mathrm{cycl}}$[b] | Strain[c] | PA diamine | PA[g] monoamine |
|---|---|---|---|---|---|
| 1,2-Diaminoethane | 12.7 | 12.6 | 10.4 | 234.9 | 222.3 |
| 1,3-Diaminopropane | 20.6 | 20.5 | 2.5 | 243.3 | 222.8 |
| 1,4-Diaminopentane | 20.0 | 20.1 | 2.9 | 243.3 | 223.2 |
| 1,6-Diaminoheptane | 20.0 | 20.0 | 3.0 | 243.2 | 223.2 |

| | $\Delta S$[d] | $\Delta H_c$[e] | Strain[f] |
|---|---|---|---|
| (c-Propane)–(*n*-propane) | −7.8 | 37.5 | 27 |
| (c-Butane)–(*n*-butane) | −10.7 | 36.5 | 26 |
| (c-Pentane)–(*n*-pentane) | −13.4 | 16.5 | 6 |
| (c-Hexane)–(*n*-hexane) | −21.5 | 10.5 | (0) |
| (c-Heptane)–(*n*-heptane) | −20.5 | 16.4 | 6 |
| (c-Octane)–(*n*-octane) | −23.9 | 19.8 | 9.3 |

[a] $\Delta S$ cyclization in eu estimated by assuming $\Delta S$ for reaction $\mathrm{B_1H^+ + B_3 = B_1 + B_3H^+}$ (see Table III) equal to $\Delta S_{\mathrm{cycl}}$. [b] $\Delta H_{\mathrm{cycl}}$ = PA($\mathrm{NH_2(CH_2)_nNH_2}$) − PA($\mathrm{CH_3(CH_2)_nNH_2}$) (kcal/mol). [c] Strain = 23 + $\Delta H_{\mathrm{cycl}}$ (see the discussion) (kcal/mol). [d] $S°$(cycloalkane) − $S°$(*n*-alkane) at 298°K (eu). [e] $H°$(cycloalkane) − $H°$(*n*-alkane) (kcal/mol). [f] Strain obtained by the difference $\Delta H_c$(alkanes) − $\Delta H_c$(hexane), *i.e.*, assuming that cyclohexane is strain free (kcal/mol). [g] References 4b and 11.

~2.5–3.0 kcal, and which appear not to change much with increasing carbon number. The high-strain energy for the diaminoethane shows that the resulting ring structure corresponds more to a four-membered ring, *i.e.*, that the $\mathrm{N{-}H^+{-}N}$ hydrogen bond tends to be linear. The entropy decrease for that reaction is also significantly smaller than those for the higher diamines.

For the purposes of comparison some thermodynamic data for the *n*-alkanes and cycloalkanes[14] are also given in Table IV. In the $\Delta S$ column the entropy difference ($\Delta S° = S°$(cycloalkane) − $S°$(*n*-alkane)) is given. This difference may be expected to be fairly close to the entropy change for the cyclization reaction (reaction 13) of the hydrocarbon biradical. Thus the

$$\mathrm{CH_2(CH_2)_nCH_2\cdot} = \underbrace{\mathrm{CH_2(CH_2)_nCH_2}} \qquad (13)$$

compilation by Benson and O'Neal[15] gives estimates of $\Delta S°_{13} \approx -10$ eu for cyclopropane and $\Delta S°_{13} \approx -12$ eu for cyclobutane. On the other hand $\Delta H°_{\mathrm{C}} = H°$(cycloalkane) − $H°$(*n*-alkane) cannot be expected to come close to $\Delta H_{13}$. However, if it is asssumed that cyclohexane is essentially strain free, then the strain energy in the other cycloalkanes can be estimated by eq 14.

$$\Delta H_{\mathrm{strain}} = \Delta H_{\mathrm{cycl}}(\text{cycloalkane}) - \Delta H_{\mathrm{cycl}}(\text{cyclohexane}) \qquad (14)$$

The resulting values for the strain energy are shown in Table IV.

In cyclopentane there is only some 6 kcal of strain while cyclobutane and propane show strain energies of some 26 and 27 kcal. Taking the C–C bond in the cycloalkanes as ~80 kcal one finds that the strain in these compounds amounts to some 30% of the C–C bond. It is interesting to note that the strain energy in the 1,2-diaminoethane appears larger if expressed as a percentage of the hydrogen bond strength, namely $10.4/23 \times 100 = 45\%$ (see Table IV).

The proton bonded higher cyclic amines do not reproduce completely the increase of strain energy observed in the cycloalkanes past the six-membered ring. In the cycloalkanes this increase of strain is believed to be due to repulsions between the partially eclipsed $\mathrm{CH_2}$ groups in the rings. Similar increases could be expected also for the diamines, but the experimental data indicate that they are considerably lower. The amine strain energies were evaluated with the assumption that $\Delta H_4$ was constant. A small increase of $-\Delta H_4$ with chain length would lead to a corresponding increase of calculated strain energies.

It is interesting to note that the entropies of the diamine cyclization ($\Delta S_{\mathrm{cycl}}$, Table IV), while generally close to those for the corresponding cycloalkanes, do not completely follow them. The large strain energy in the 1,2-diaminoethane suggested that the ethane should be considered to lead to a quasi-four-membered and the propane to a quasi-five-membered ring. However, the entropy change for the diaminopropane at 20.6 eu is already up to the entropy values observed with cyclohexane while the cyclopentane has a value of only 13.4 eu. This shows, provided that the present experimental entropies are correct, that the cyclic diamines behave somewhat differently. This is not surprising considering the difference between the C–C and $\mathrm{N{-}H^+{-}N}$ bonds.

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[14] D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., (1969).

[15] S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," National Bureau of Standards, Washington, D. C., 1970.