

Of other examples of torsionally strained double bonds studied by the X-ray methods, a torsion angle of only 12° has been found for the 4,5-double bond in 3-methoxy-5 β ,19-cyclo-5,10-secoandrosta-1(10)-2,4-trien-17 β -ol,^{18a} and 8.6° for bicyclo[5.3.1]undec-7-en-11-one-1-carboxylic acid.^{18b} The double bonds in the *trans*-cyclodecene-AgNO₃ complex¹⁹ and the *trans*-cyclooctene-CuCl complex²⁰ are reported to be twisted about 40° . The small (~ 5 kcal) strain energy of *trans*-cyclodecene¹⁹ when considered along with the recently observed rehybridization in olefin-transition metal complexes²¹ suggests that this 40° angle of twist does not exist in the pure olefin hydrocarbon.

(18) (a) H. Hope and A. T. Christensen, *Acta Crystallogr., Sect. B*, **24**, 375 (1968); (b) G. L. Buchanan, A. F. Cameron, and G. Jamieson, *Chem. Commun.*, 1145 (1969).

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Equilibrium Constants for Gas-Phase Ionic Reactions. Accurate Determination of Relative Proton Affinities¹

Sir:

Experimental techniques presently used to measure thermochemical quantities such as heats of formation, bond strengths, proton affinities, and electron affinities have been limited to an accuracy seldom better than ± 1 kcal/mol, yet more accurate values would be extremely useful for a wide variety of chemical problems. This communication describes the use of ion cyclotron resonance spectroscopy² for directly measuring equilibrium constants for proton-transfer reactions, permitting an accurate determination of relative proton affinities.

Most determinations of absolute proton affinities³ have been by appearance potential methods and by an empirical correlation of excess kinetic energies in ionic reactions.⁴ A qualitative method for the determination of relative proton affinities involves observation of the occurrence or nonoccurrence of ion-molecule reactions to place limits on proton affinities.^{4,5}

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(2) For a description of the icr technique see J. D. Baldeschwieler, *Science*, **159**, 263 (1968); J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971).

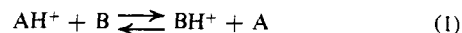
(3) The proton affinity of M, PA(M), is defined as the negative enthalpy change of the reaction $M + H^+ \rightarrow MH^+$.

(4) See M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969), and references therein.

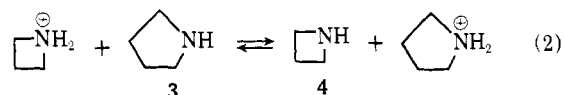
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Combinations of these techniques can give proton affinities with an uncertainty of about 2–5 kcal/mol. These uncertainties arise from inaccurate heats of formation of neutrals and ions, problems with internally excited ions, and the inherently qualitative nature of the relative proton affinity limits. In contrast, the equilibrium technique described here suffers none of these difficulties and provides relative proton affinities accurate to better than ± 0.2 kcal/mol.

The equilibrium constant for a proton-transfer reaction (1) is $K = [BH^+][A]/[AH^+][B]$. By measuring

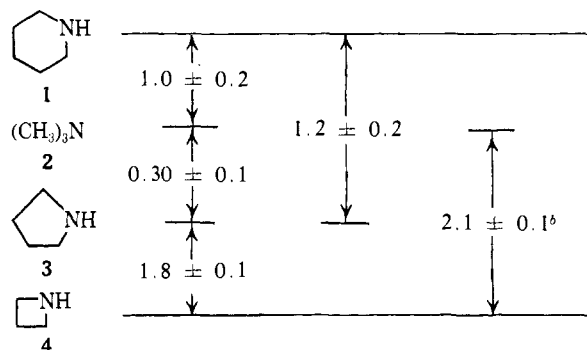


the ratios $[BH^+]/[AH^+]$ and $[A]/[B]$ at equilibrium, the equilibrium constant and ΔG for reaction 1 can be calculated. The ΔG for proton-transfer reactions should be nearly equal to ΔH , giving the relative proton affinities of A and B,⁶ hence $\Delta G \cong \Delta H = PA(A) - PA(B)$. Figure 1 illustrates an experiment in which a mixture of pyrrolidine, **3**, and azetidinium, **4**, was introduced into a standard ion cyclotron resonance spectrometer⁷ and the intensities of the azetidinium ions (m/e 58) and pyrrolidinium ions (m/e 72) were measured as the total pressure was raised. The ratio



of their intensities becomes constant at about 1×10^{-4} Torr, indicating that equilibrium in the proton-transfer reaction 2 is established after about 30–50 collisions with $K = 22 \pm 2$ and $\Delta G^{25^\circ} = -1.8 \pm 0.1$ kcal/mol. Double-resonance experiments were performed at high pressures and indicated that indeed reaction 2 proceeds in both directions. Similar experiments were performed on all systems reported here. Equilibrium data for mixtures of piperidine (**1**), trimethylamine (**2**), pyrrolidine (**3**), and azetidinium (**4**) are presented in Chart I. The reproducibility obtained in several runs and the internal consistency of the over-

Chart I. Changes in Free Energy, ΔG^{25° (kcal/mol), for Proton Transfer Reactions such as Reaction 2^a



^a Piperidine (**1**) has the highest proton affinity in this series.

^b Determined by pulsed icr only because at high pressure the ions at m/e 58 and 60 were not resolved.

(1968); D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5913 (1969).

(6) Proton affinities are defined as enthalpies (ref 3), but for large molecules the ΔS for proton transfer should be negligible. Temperature-dependence studies are planned to verify this.

(7) M. T. Bowers and P. R. Kemper, *J. Amer. Chem. Soc.*, in press.

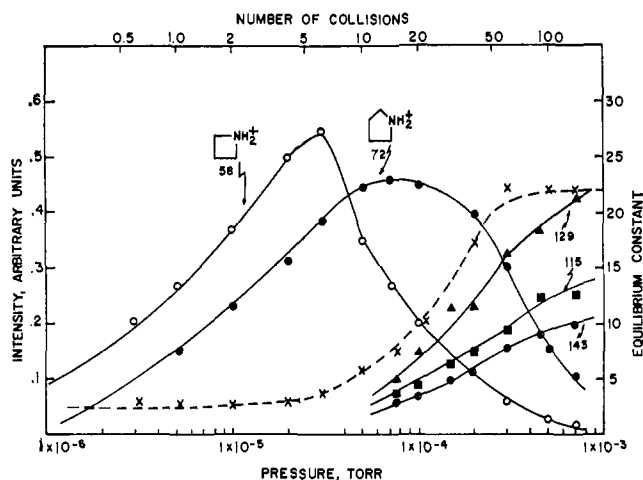


Figure 1. Relative ion intensities vs. pressure of the product ions in a 5.1:1.0 mixture of $(\text{CH}_2)_3\text{NH}$ and $(\text{CH}_2)_4\text{NH}$ at 9 eV. The protonated species (m/e 58, 72) were formed by proton transfer from the parent ions (m/e 57, 71) to the two neutral molecules. The dashed line denotes $K = [(\text{CH}_2)_4\text{NH}_2^+][(\text{CH}_2)_3\text{NH}]/[(\text{CH}_2)_3\text{NH}_2^+][(\text{CH}_2)_4\text{NH}]$. The number of collisions was approximated from the orbiting limit. K was determined directly from the ionic intensities without mass correction.

lapping data provide free energies with an uncertainty of less than ± 0.2 kcal/mol.⁸

At high pressures, collision-stabilized proton-bound dimers (m/e 115, 129, 143) are formed (Figure 1). These dimers rapidly come to equilibrium and the resulting equilibrium constants directly yield quantitative relative stabilities of the dimers.⁹

Concern that the formation of the proton-bound dimers might affect the equilibrium between the protonated parent ions led us to perform experiments on the same mixtures using a pulsed ion cyclotron resonance spectrometer fitted with a trapped ion analyzer cell.¹⁰ With this new technique, gaseous ions are formed by a short pulse of an electron beam and then trapped within the analyzer cell for times variable from 1 to 500 msec. As the ions react with the neutral molecules, the abundance of each mass ion can be monitored as a function of the reaction time. At pressures below 10^{-5} Torr the proton-bound dimers are not observed because the time between collisions is long relative to the lifetime of the unstabilized proton-bound dimer. For the pulsed icr experiments equilibrium was studied by trapping the ions for reaction times of 100 msec at low pressures. A typical experiment is shown in Figure 2 for a mixture of azetidine (4) and pyrrolidine (3). Equilibrium is reached in about 40 collisions with a ΔG^{25° of 1.9 ± 0.1 kcal/mol. Each determination of ΔG by the high-pressure technique was confirmed (± 0.1 kcal) by the pulsed icr technique.

Accurate relative proton affinities are very useful in correlation with chemical reactivity, solution basicity,

(8) The runs were done on several different neutral mixtures at high observing frequency and long drift times to ensure minimal differential pumping or adsorption effects.

(9) D. H. Aue, H. M. Webb, and M. T. Bowers, details to be published. Similar equilibria have been observed in a high-pressure mass spectral study of ammonia, water, and methanol: S. K. Searles and P. Kebarle, *J. Phys. Chem.*, **72**, 742 (1968), and references therein.

(10) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); K. C. Smyth, R. T. McIver, Jr., J. I. Brauman, and R. W. Wallace, *J. Chem. Phys.*, in press; R. T. McIver, Jr., and M. A. Haney, submitted for publication.

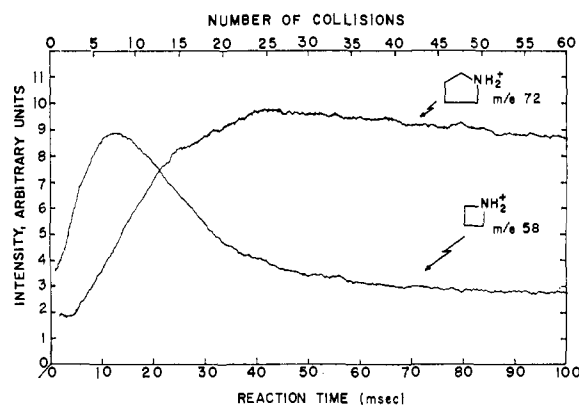


Figure 2. Pulsed icr data for the $(\text{CH}_2)_3\text{NH}_2^+$ and $(\text{CH}_2)_4\text{NH}_2^+$ peaks in a 6.4:1.0 mixture of $(\text{CH}_2)_3\text{NH}$ and $(\text{CH}_2)_4\text{NH}$ at 10 eV and approximately 1×10^{-5} Torr. The protonated species (m/e 58, 72) were formed by proton transfer from the parent ions (m/e 57, 71) to the two neutral molecules. Each measured ionic intensity was multiplied by the mass of the ion to obtain K .

structure, molecular orbital calculations, and other physical data. We have examined some of these correlations for a large number of amine proton affinities determined by this technique.¹¹ The scope of the technique for proton affinities of other classes of molecules and for equilibrium studies in a variety of other gas phase reactions is also under investigation.

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(11) D. H. Aue, H. M. Webb, and M. T. Bowers, manuscript in preparation.

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Alkyl Substituent Effects on Gas-Phase Acidities. The Influence of Hybridization

Sir:

The problem of the effect of alkyl substituents on reaction rates and equilibria continues to be a vexing one.¹ We have shown previously that in the gas phase, in saturated systems, alkyl groups appear to stabilize both positive and negative charges, in accordance with a polarization stabilization mechanism.^{2,3} In general, for those systems thus far examined, the dipole moment associated with the varying alkyl portion of the molecule would be expected to be small and fairly constant in a given series. Thus, replacing a hydrogen with methyl in the parent saturated system simply increases

(1) For example, see M. J. S. Dewar, *Tetrahedron*, **17**, 123 (1962); P. von R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, **90**, 6528 (1968), and references cited therein. Also, see E. M. Arnett and J. W. Larsen, *ibid.*, **91**, 1438 (1969); W. M. Schubert and D. F. Gurka, *ibid.*, **91**, 1443 (1969); A. Himoe and L. M. Stock, *ibid.*, **91**, 1452 (1969).

(2) J. I. Brauman and L. K. Blair, *ibid.*, **92**, 5986 (1970); **90**, 6561 (1968).

(3) J. I. Brauman and L. K. Blair, *ibid.*, **93**, 3911 (1971); **91**, 2126 (1969); J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).