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Gas Phase Ion Chemistry

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PREFACE

Fifteen years ago there was a handful of research groups involved in research on the chemistry of ions in the gas phase. Today there are hundreds of groups spanning a discipline that stretches from biochemistry to theoretical chemical physics. The growth has been dramatic, almost explosive, in the past decade, and the field is currently at the point where no one can even superficially keep up with all of it. There are three journals totally devoted to ion chemistry of one sort or another, and ion chemistry papers are making major contributions to most of the main line chemical journals.

The roots of gas phase ion chemistry, perhaps more than those of some disciplines, are found in technique development. The rapid technological advances in the post-Sputnik era provided the materials and vacuum and electronic capabilities to develop the sophisticated instrumentation we take for granted today. The chapter by Gentry on molecular beams in Volume 2 is illustrative of the inventive methods used to probe microscopic reaction mechanisms. Previous editors recognized this relationship and built their books around chapters that discussed the various techniques in use at that time.

The question arose, in attempting to put the present volumes together, of what topics should be emphasized and how they should be organized. In the end, the decision was to emphasize the topics I found most interesting and relevant, and to assign the organization of these topics to the various authors who graciously agreed to write the chapters. Each of the authors is a world leader in his respective area, and each area presents different requirements of both length and style of presentation. The areas I chose to emphasize are theory (3), kinetics and mechanism (6), ther-

mochemistry (3), and technique and applications (4). The numbers in
parentheses give the number of chapters in each section. The dominant
theme of the treatise is the chemical physics aspect of gas phase ion
chemistry; but a broad range of chemists should find most of the chapters
of interest, particularly those on thermochemistry, where comprehensive
compendiums of gas phase basicities, acidities, and electron affinities are
given.

Finally, I would like to thank the many people who made these volumes
possible. To the authors go the primary thanks for preparing high quality
chapters and forwarding them promptly. Members of my research group
all deserve thanks for carrying on during the editing process and for
helping to proofread the galleys. The helpful, competent, and professional
attitude of everyone at Academic Press minimized all of the difficulties
encountered, and my thanks go to them. Last, my family, and especially
my wife Diane, gave support and encouragement throughout, and I am
deeply grateful and thankful for their presence in my life.

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Chapter 9

Stabilities of positive ions from equilibrium gas-phase basicity measurements

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I. INTRODUCTION

Proton-transfer reactions are among the most important classes of chemical reactions and have been studied extensively in solution over a long period of time. We report here the results of recent gas-phase basicity measurements that derive from a study of equilibrium constants for proton-transfer reactions among positive ions. Negative ion stability data from electron affinity measurements are presented in Chapter 10 by Janousek and Brauman. Results of studies of proton-transfer equilibria among negative ions are found in Chapter 11 by Bartmess and McIver.

In summarizing the results of work on the stabilities of positive ions, we have tried to include all of the published data from accurate equilibrium studies through early 1978 along with some unpublished data from our laboratories. The data are presented with only a minimal interpretive discussion aimed at pointing out some of the major structural effects observed.

High-pressure mass spectrometer sources were first used to study proton-transfer reactions in the gas phase. By assuming that exothermic proton transfers should occur rapidly in the gas phase, these studies were used to qualitatively and semiquantitatively determine relative gas-phase basicities and proton affinities of various molecules by the reaction bracketing technique (Beauchamp, 1971). The gas-phase basicity (GB) is defined as the negative of the free-energy change for the protonation reaction (1), while the proton affinity (PA) is the negative of the enthalpy change for reaction (1).

$$A + H^+ \rightleftarrows AH^+, \quad -\Delta G^0 = GB(A) \\ -\Delta H^0 = PA(A) \tag{1}$$

$$AH^+ + B \rightleftarrows A + BH^+, \quad \Delta G^0 = GB(B) - GB(A) \\ \Delta H^0 = PA(B) - PA(A). \tag{2}$$
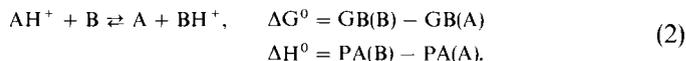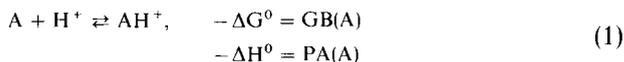
Thus, the direction of the proton-transfer reaction (2) gives the relative gas-phase basicities of A and B. The proton affinity of water was deduced to be between 163 and 172 kcal/mole by Tal'roze and Frankevich (1956) on the basis of the occurrence and nonoccurrence, respectively, of reactions (3)

and (4) and known heats of formation

$$H_2S^{+\cdot} + H_2O \rightarrow H_3O^+ + HS, \tag{3}$$

$$H_2C_2^{+\cdot} + H_2O \nrightarrow H_3O^+ + C_2H. \tag{4}$$
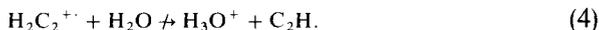
Munson (1965) determined the relative basicities of ammonia and the methylamines in the gas phase by such qualitative high-pressure mass spectrometric techniques. Later, using ion cyclotron double resonance techniques, Beauchamp and Buttrill (1968) and Brauman and Blair (1968, 1971) established relative basicities for some organic bases in the gas phase. Munson (1965) and Brauman and Blair (1968; Brauman *et al.*, 1971) observed that the order of gas-phase basicities of the methylamines was $NH_3 < MeNH_2 < Me_2NH < Me_3N$. This order differs from that observed in aqueous solution ($NH_3 < Me_3N < MeNH_2 < Me_2NH$), which indicated immediately that such gas-phase data could supply a set of *intrinsic* basicities that could be used to clarify our understanding of the origin of solution-phase basicity orders.

Ion–molecule reactions in the gas phase were first studied under equilibrium conditions in a high-pressure mass spectrometer by Kebarle and Godbole (1963) for an ion clustering reaction (5) involving the gas-phase solvation of H_3O^+,

$$H_3O^+ + nH_2O \rightleftarrows H_3O^+ \cdot nH_2O. \tag{5}$$

Since then, Kebarle's group has studied a wide variety of such clustering reactions for both positive and negative ions (Kebarle, 1972, 1977). The measurement of accurate equilibrium constants for these reactions provides valuable insight into the energetics of ionic solvation.

Equilibrium constants for proton-transfer reactions were first measured by Bowers, Webb, and Aue using an ion cyclotron resonance drift cell at high pressures (10^{-4}–10^{-3} torr). These reactions were also found, in collaboration with McIver, to reach equilibrium under the low-pressure (10^{-7}–10^{-6} torr) conditions of a trapped ion cell (Bowers *et al.*, 1971). These observations made possible, for the first time, the measurement of quantitative relative acidities or basicities from acid–base reactions of ions in the gas phase. Since 1971, ion cyclotron resonance studies by groups of Aue and Bowers at Santa Barbara, Taft and McIver at Irvine, and Beauchamp at California Institute of Technology have led to an extensive set of such basicity data for negative and positive ions. In addition, proton-transfer reactions have been investigated under equilibrium conditions by Kebarle's group at Alberta using high-pressure mass spectrometry (Briggs *et al.*, 1972) and by Bohme's group at York using flowing afterglow techniques (Bohme *et al.*, 1971, 1973a,b). This chapter will present the results of these studies on proton-transfer reactions of positive ions. Reactions of ions which involve

ligand transfer in clusters, halide transfer, hydride transfer, and electron transfer have also been studied in recent years and will be discussed, but in less detail.

II. TECHNIQUES FOR MEASUREMENT OF PROTON AFFINITIES

Measurements of equilibrium constants for proton-transfer reactions (2) give free energies equal to the difference in the gas-phase basicities of the molecules A and B. It has usually been assumed that these free energies differ from enthalpies for proton transfer by a $T \Delta S^0$ term approximately equal to that calculable from the symmetry changes in the reaction. Thus, the GBs and PAs differ by the entropy term for a free proton from the Sackur–Tetrode equation (7.75 kcal/mole) and the entropy term due to symmetry changes expressed in Eq. (6).

$$T \Delta S^0_{\text{sym}} = RT \ln(\sigma_{\text{AH}^+}/\sigma_A). \tag{6}$$

In a few cases these entropy terms have been determined by measuring equilibrium constants over a wide range of temperatures using a variable-temperature high-pressure mass spectrometer (Yamdagni and Kebarle, 1973) and variable-temperature ion cyclotron resonance drift and trapped ion cells (Wren et al., 1978; Wren, 1976). In such measurements, the entropy terms for proton-transfer reactions have been very small and about equal to those calculated except in cases where intramolecular hydrogen bonds are formed. Generally, gas-phase basicity measurements have been made at only one temperature and the entropy term has been calculated to give reported proton affinity values.

A. Absolute PAs

While the measurement of proton-transfer equilibrium constants can give *relative* GBs and PAs, only a few experimentally determined *absolute* PAs are required in order to set up a scale of absolute proton affinity values. Where absolute PAs have been measured for several compounds and these compounds related by a series of proton-transfer equilibrium measurements, the absolute and relative PA data may be compared to give a valuable check on the consistency of these independent measurements. Absolute proton affinity measurements are also very important for molecules not interconnected with others on the relative PA scale by equilibrium proton-transfer reactions.
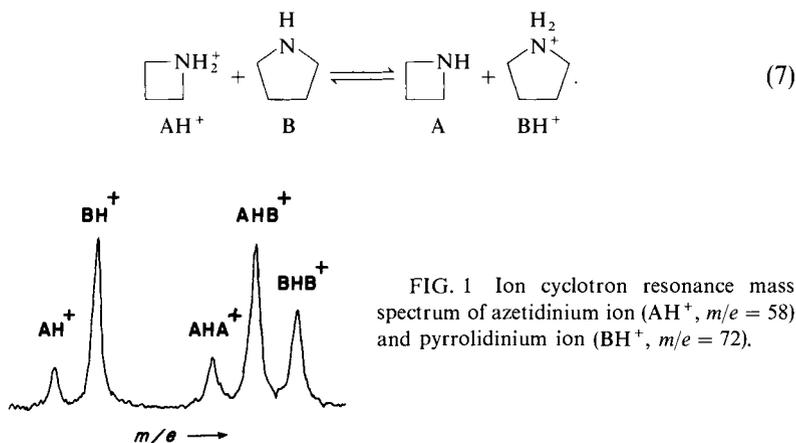
Absolute PAs have been most often measured by appearance potential measurements to give heats of formation of positive ions derived from photon- or electron-impact-induced molecular fragmentation or radical ionization. On the basis of such measurements for the heats of formation of t-butyl cation (Table XII) and ammonium ion (Ceyer et al., 1979), we have assigned the proton affinity scale such that the PA of isobutene is 196.9 kcal/mole and that of ammonia is 205.0 kcal/mole. Where PAs from other laboratories have been reported, we have adjusted them to be consistent with this absolute PA scale. These absolute PA assignments are somewhat arbitrary and agree only within error limits of several kilocalories per mole with absolute proton affinity measurements of formaldehyde and acetal-dehyde (Refaey and Chupka, 1968), water (Ng et al., 1977), propene, 1,3-butadiene, and cyclopentadiene (see Table XII). Absolute PAs from appearance potential measurements may suffer from errors in heats of formation of the molecules and radicals involved and lack of true adiabaticity in the threshold measurements. The heats of formation must also be corrected from 0 K to 298 K by estimation of heat capacity changes on ionization and fragmentation. As a result, the absolute assignment of the PA scale is still in doubt and errors up to several kilocalories per mole are possible. Usually this causes little problem in the interpretation of PA data, however, since comparisons of relative PAs are generally made.

B. Relative PAs from Drift-Cell Ion Cyclotron Resonance Spectrometry

In ion cyclotron resonance spectrometry, a signal results when the cyclotron frequency of an ion, $\omega = qH/mc$, equals the frequency ω_0 of the marginal oscillator detector. At this point the ions of a particular mass m and charge q are in resonance, and they absorb power from the marginal oscillator when the magnetic field is fixed at H. The power absorbed is proportional to the number of ions and is thus a measure of ion intensity. The relative intensities of ions in an ICR cell can be measured in two ways. The first involves operating the marginal oscillator at constant frequency and varying the magnetic field. The cyclotron frequency of an ion is directly proportional to the magnetic field. As the magnetic field is varied, ions of different masses come into resonance. In the second method, the instrument is operated at a constant magnetic field and the frequency of the marginal oscillator is varied until it matches the cyclotron frequency of an ion.

In the course of carrying out double resonance experiments to determine qualitatively the direction of proton-transfer reactions of some heterocyclic amines, we discovered that equilibrium is reached in these proton-transfer

reactions at pressures above $(1-2) \times 10^{-4}$ torr (Bowers *et al.*, 1971). When the pressure ratio of A and B is kept fixed but the total pressure increased through the 10^{-5} torr range, the relative intensities of the AH^+ and BH^+ ions are found to approach a constant value as the pressure increases above 1×10^{-4} torr. This behavior was interpreted as an indication that the proton-transfer reaction between A and B had reached equilibrium with an equilibrium constant $K = [BH^+][A]/[AH^+][B]$ for the reaction $AH^+ + B \rightleftharpoons BH^+ + A$. The ratio of the pressures of A and B can be measured directly using a Baratron capacitance manometer. The relative ion intensities can be measured by the cyclotron resonant power absorption at the appropriate marginal oscillator frequencies, as indicated above. A typical experimental trace of the ion intensities is shown for reaction (7) between azetidine (A) and pyrrolidine (B) in Fig. 1.

$$
\left[\begin{array}{c} -NH_2^+ \end{array}\right] + \left\langle\begin{array}{c} H \\ N \end{array}\right\rangle \rightleftharpoons \left[\begin{array}{c} -NH \end{array}\right] + \left\langle\begin{array}{c} H_2 \\ N^+ \end{array}\right\rangle . \tag{7}
$$

$$
\begin{array}{cccc} AH^+ & B & A & BH^+ \end{array}
$$

FIG. 1 Ion cyclotron resonance mass spectrum of azetidinium ion (AH^+, $m/e = 58$) and pyrrolidinium ion (BH^+, $m/e = 72$).

The equilibrium constant for this reaction can thus be calculated simply from the peak area ratio and the pressure ratio. The results of a number of such determinations over a wide pressure range are presented in Fig. 2. This figure shows the formation of AH^+ and BH^+ at low pressures by irreversible proton transfer from the radical cations $A^{+\cdot}$ and $B^{+\cdot}$ and the equilibration of AH^+ and BH^+ at high pressures. The drift time in a drift-cell ion cyclotron resonance spectrometer is usually ~ 2 msec, which permits hundreds of ion–molecule collisions to occur at the highest pressures shown in Fig. 2. The ratio of AH^+ to BH^+ remains essentially constant above 2×10^{-4} torr, although both ions are decreasing in intensity rapidly in this pressure range. At high pressures, the proton-bound dimers at m/e 115, 129, and 143 form corresponding to the structures AHA^+, AHB^+, and BHB^+, respectively.
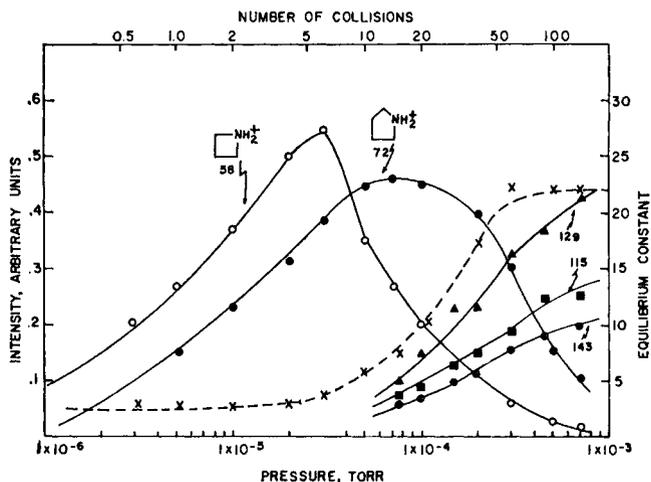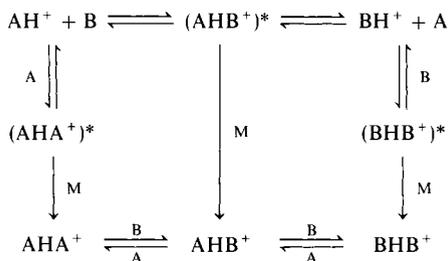
NUMBER OF COLLISIONS

FIG. 2 Relative ion intensities versus pressure of the product ions in a 5.1:1.0 mixture of $(CH_2)_3NH$ and $(CH_2)_4NH$ 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 $K = [(CH_2)_4NH_2^+][(CH_2)_3NH]/[(CH_2)_3NH_2^+][(CH_2)_4NH]$. The number of collisions was approximated from the orbiting limit. K was determined directly from the ionic intensities without mass correction. [Reprinted with permission from Bowers et al. (1971). Copyright by the American Chemical Society.]

They form according to the detailed kinetic scheme I in a mechanism

$$AH^+ + B \rightleftharpoons (AHB^+)^* \rightleftharpoons BH^+ + A$$

$$A \Updownarrow \qquad\qquad M \qquad\qquad \Updownarrow B$$

$$(AHA^+)^* \qquad\qquad\qquad (BHB^+)^*$$

$$\downarrow M \qquad\qquad \downarrow M \qquad\qquad \downarrow M$$

$$AHA^+ \underset{A}{\overset{B}{\rightleftharpoons}} AHB^+ \underset{A}{\overset{B}{\rightleftharpoons}} BHB^+$$

scheme I

involving collisional stabilization of the vibrationally excited species $[AHA^+]^*$, $[AHB^+]^*$, and $[BHB^+]^*$. This kinetic scheme for formation of proton-bound dimers has been confirmed in these laboratories by extensive kinetic studies on such dimerization reactions of amines (Neilson et al., 1978). The intensity ratios of the ions AHA^+, AHB^+, and BHB^+ remain constant over the range of pressures shown, indicating that they too are in equilibrium as a result of base-transfer reactions among them. These reactions will be discussed in detail later.

The marked disappearance of AH^+ and BH^+ to proton-bound dimers presents some potential experimental and kinetic problems to the measurement of accurate equilibrium constants. We have analyzed these problems and discussed them in detail elsewhere (Davidson *et al.*, 1977). Problems caused by measurements at constant oscillator frequency are due to the variation in magnetic field which causes a change in drift times of the ions in the cell. This problem has now been solved by the development of techniques for the calibration of the marginal oscillator sensitivity at different frequencies, making it possible to operate at fixed magnetic field and variable frequency (Kemper and Bowers, 1977a).

A more serious problem is caused by the possibility that proton-bound dimer formation from AH^+ and BH^+ may occur at rates competitive with proton transfer and disrupt the attainment of proton-transfer equilibrium in the kinetic scheme II. This kinetic scheme has been analyzed and the

$$AH^+ + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH^+ + A$$

$$A_2H^+ \qquad ABH^+ \qquad B_2H^+$$

scheme II
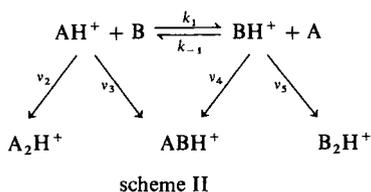
differential equations solved exactly. The solution can also be conveniently approximated using a digital numerical integration technique developed at Santa Barbara (Shindell *et al.*, 1978). From the measurement of the dimerization rates v_2 and v_5 in scheme II and from experimental rate constants k_1 and k_{-1} for proton-transfer reactions, we are able to use this kinetic scheme to demonstrate how closely our experimentally measured equilibrium constants approximate the true equilibrium constant k_1/k_{-1}. The errors in the equilibrium measurements are likely to be largest when one of the two ions AH^+ or BH^+ dimerizes much more rapidly than the other and when this dimerization rate becomes competitive with proton transfer. We have shown experimentally that these dimerization reactions do not generally cause errors in ΔG^0 of more than 0.2 kcal/mole for equilibria involving amines. For hydrocarbons and oxygenated compounds, the dimerization rates are sometimes slow enough for rapid proton transfer to permit the measurement of equilibria using drift-cell techniques (Davidson *et al.*, 1977). In other cases, however, such measurements are not possible without substantial errors. In these cases, low-pressure trapped-ion-cell techniques may be often applied, since at lower pressures the proton-bound dimer formation is often slower because of the higher order of pressure dependence frequently seen in the dimerization rates versus proton-transfer rates. When

applicable, the drift-cell technique for measurement of equilibrium constants is rapid, convenient, and less susceptible to experimental errors due to noise and pressure measurement than the trapped-ion-cell technique. Where errors from the dimerization kinetics are a potential problem, however, we use the trapped-ion-cell technique to measure equilibrium constants. This cell has an added advantage for molecules where the parent ions $A^{+\cdot}$ or $B^{+\cdot}$ or P-1 ions are unreactive and contribute to the intensity of the broad AH^+ or BH^+ peaks at high pressures in the drift cell or where AH^+ and BH^+ have nearly the same mass. The low-pressure trapped-ion spectra suffer from little collisional line broadening so that unit mass resolution is readily achievable.

C. Relative PAs from Trapped-Ion-Cell Ion Cyclotron Resonance Spectrometry

Proton-transfer equilibrium techniques on the McIver trapped ion cell (McIver, 1970) were developed in collaboration with McIver for the same reactions that had been studied by drift-cell techniques, in order to confirm the contention that equilibrium was being achieved in these systems (Bowers et al., 1971). A somewhat different type of trapped ion cell was later developed by McMahon and Beauchamp (1972). In these cells, the ions do not drift out of the cell within a few milliseconds as in the drift cell. Instead, they are trapped within the cell for periods in excess of 1000 msec. Such long ion trapping times permit hundreds of collisions to occur and result in proton-transfer equilibrium at lower pressures ($\sim(1-4) \times 10^{-6}$ torr) than in the drift cell. At higher pressures, however, ion loss from the trapped ion becomes a major problem, so that the total number of ion–molecule collisions attainable is comparable to that in the drift cell. Absolute pressure measurement in the trapped ion cell must be accomplished indirectly using an ion gauge calibrated against a capacitance manometer at higher pressures. An example of an experimental equilibrium constant determination by this technique for the azetidine and pyrrolidine equilibrium (7) studied in the drift cell is shown in Fig. 3. Here the intensities of the azetidinium and pyrrolidinium ions reach a constant ratio after about 30 collisions to give an equilibrium constant in good agreement with the value obtained from drift-cell measurements. Because of the limitations on the total number of collisions attainable by either ICR technique, using current technology, the largest equilibrium constants that can be reliably measured are less than 50, corresponding to ΔG^0 values less than 2.0 kcal/mole at 25°C. Occasionally larger values of K can be measured in very well behaved systems, but these cases are not usual.
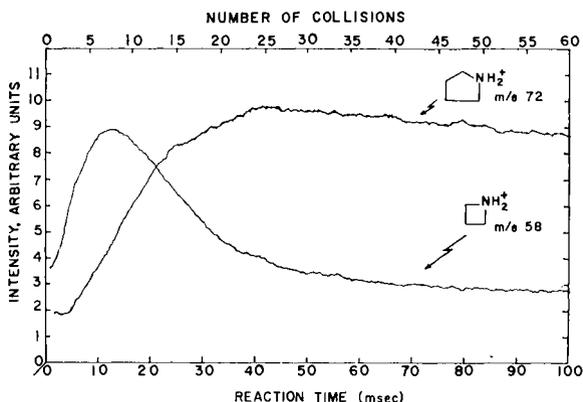
FIG. 3   Pulsed ICR data for the $(CH_2)_3NH_2{}^+$ and $(CH_2)_4NH_2{}^+$ peaks in a 6.4:1.0 mixture of $(CH_2)_3NH$ and $(CH_2)_4NH$ at 10 eV and approximately 1×10^{-5} torr. The protonated species ($m/e = 58, 72$) were formed by proton transfer from the parent ions ($m/e = 57, 71$) to the two neutral molecules. Each measured ionic intensity was multiplied by the mass of the ion to obtain K. [Reprinted with permission from Bowers et al. (1971). Copyright by the American Chemical Society.]
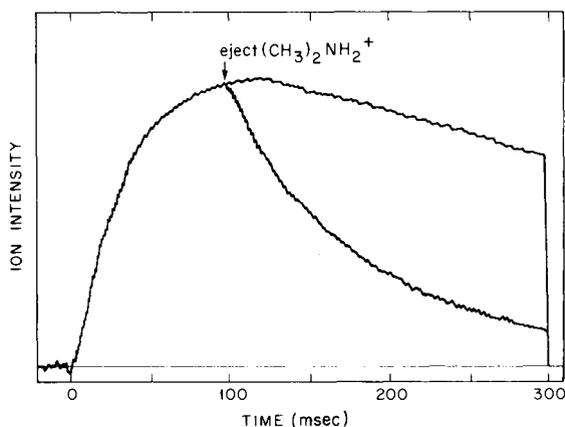

FIG. 4   Plot of ion intensity versus time of protonated pyridine, $C_5H_5NH^+$, in a mixture of 4×10^{-7} torr pyridine and 9×10^{-7} torr $(CH_3)_2NH$. The rate constant was determined from the decrease in pyridinium ion signal when protonated dimethylamine is ejected from the cell. [From Davidson et al. (1977).]

An important feature of the trapped ion cell is the possibility of measuring reaction rates for proton transfer by ejection of the ions and observation of the decay of the other ion (McIver and Dunbar, 1971; McMahon et al., 1976). Such an experiment is illustrated in Fig. 4 for the disappearance of the pyridinium ion after ejection of dimethylammonium ion for equilibrium (8) (Davidson et al., 1977).

$$Me_2NH_2^+ + \text{(pyridine)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{(pyridinium)} + Me_2NH \tag{8}$$
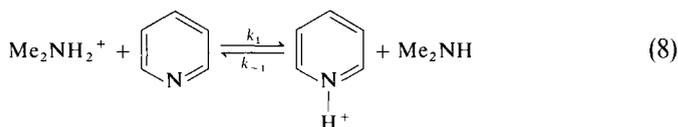
$$k_1 = 5.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}, \qquad K = 1.6$$
$$k_{-1} = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Assuming that ion loss before ejection is negligible relative to that after ejection, the exponential decay of the pyridinium ion is equal to the pseudo-first-order rate constant k_{-1}. Similarly, the rate constant k_1 can be measured by ejection of the pyridinium ion. The equilibrium constant obtained from the ratio k_1/k_{-1} agrees well with that obtained from the ion intensity ratios of the drift- and trapped-ion-cell experiments.

For many reactions involving oxygenated species and hydrocarbons, the ion loss rates are rapid and competitive with proton-transfer rates. At low pressures in the trapped ion cell, we have found that ion loss processes by various condensation reactions have the same pressure dependence as proton transfer, so that operation at even the lowest pressures does not serve to suppress these reactions relative to proton transfer. In these cases we have attempted to assess the effect of these interfering reactions on the experimental determination of equilibrium constants by a kinetic analysis employing experimental rate constants. Rate constants for ion loss can be approximated from ion loss curves for each pure compound and for the mixture at long reaction times. The ion ejection technique in such cases gives traces, as illustrated in Fig. 5, that do not fit the assumption of slow ion loss relative to
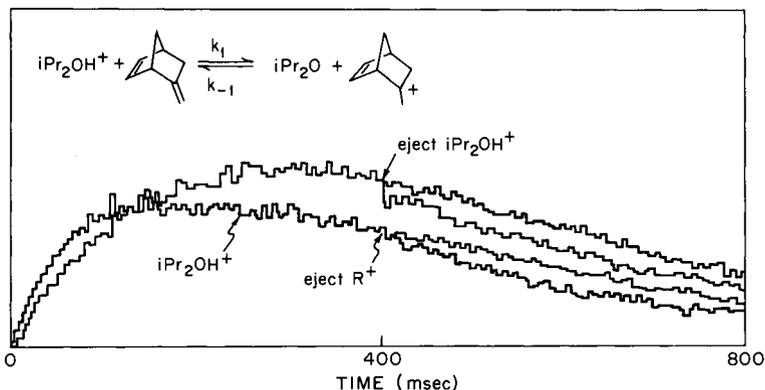

FIG. 5 Trapped ion ICR data showing approximate proton-transfer rate constants (in units of cm^3 molecule^{-1} sec^{-1}) derived from continuous ion ejection at 400 msec reaction time. $k_1 = 1.4 \times 10^{-10}$, $k_1 = 1.0 \times 10^{-10}$, $\Delta G^0 = -0.3$, error $= -0.2$ kcal/mole.

the loss after ejection. To get proton-transfer rates from such data, these traces have been fit by an interactive digital kinetic simulator developed by Shindell *et al.* (1978) at Santa Barbara. Figure 5 shows an extreme case where the proton-transfer rates k_1 and k_{-1} are unusually small as indicated by the small effect observed on ejection. A computer fit of these ionic concentration curves can be obtained with the k_1 and k_{-1} values of about 10^{-10} cm^3 molecule^{-1} sec^{-1} and pseudo-first-order ion loss rates of 2–3 sec^{-1}. This fit is not unique and there can be significant errors in the k's derived, but it gives a reasonable estimate of the degree to which such a reaction can approach equilibrium. In this case, the equilibrium constant is nearly one, and the error in ΔG^0 is ~ 0.2 kcal/mole. With proton-transfer rates this small, however, the measurement of larger equilibrium constants would have large errors. In these cases, double resonance data are sometimes required to ascertain the PAs within ~ 2 kcal/mole error limits.

Thus, trapped-ion-cell ion cyclotron resonance spectrometer and drift-cell instruments are complementary in their application to thermochemical measurements. The drift-cell instrument is best for rapid determination of equilibrium constants for rapid proton-transfer reactions with moderately slow ion loss pathways. It is ideal for the study of base exchange reactions between proton-bound dimers, which occur at high pressures, and it is useful for semiquantitative double resonance experiments for the determination of relative gas-phase basicities. The drift-cell instrument is also well suited for the determination of reaction rates for many types of reactions (see, e.g., Anicich and Bowers, 1974; Kemper and Bowers, 1977b; Neilson *et al.*, 1978).

The trapped ion cell is very valuable for studying equilibria where the low pressures can slow down rapid third-order dimerization or condensation reactions relative to second-order proton-transfer reactions and where the higher resolution obtainable at low pressures is important. Resonant ion ejection experiments can be used to determine proton-transfer rates most conveniently in many cases and can be used in semiquantitative determinations of GBs when proton-transfer rates become small.

Extensive comparisons of data for the same sets of experiments and compounds demonstrate that the two techniques give closely comparable gas-phase basicities. Agreement is within a few tenths of a kilocalorie per mole for comparisons between drift- and trapped-cell results obtained at Santa Barbara and between results obtained at Santa Barbara by both techniques and those trapped-cell measurements at Irvine and California Institute of Technology (Taft, 1975; Wolf *et al.*, 1977a). Furthermore, all of these results agree well with those obtained by Kebarle by high-pressure mass spectrometric techniques (Briggs *et al.*, 1972; Yamdagni and Kebarle, 1973, 1976; Lau and Kebarle, 1977) and by the flowing afterglow technique (see, e.g., Staley and Beauchamp, 1975).