ELSEVIER

International Journal of Mass Spectrometry 190/191 (1999) 295–302

Intra- and intermolecular isotope effects for hydrogen loss from protonated aniline and the barrier to hydrogen transfer between the ring and substituent

Yasmin A. Ranasinghe, Gary L. Glish*

Department of Chemistry, CB# 3290, University of North Carolina, Chapel Hill, NC 27599, USA

Received 2 October 1998; accepted 17 February 1999

Abstract

Protonated aniline was generated by reacting ammonia or ammonia-d_3 with phenylium ($C_6H_5^+$) in a quadrupole ion trap and in a chemical ionization (CI) source of a double focusing mass spectrometer. Significant intramolecular isotope effects are observed for the loss of $H^\cdot(D^\cdot)$ in the mass spectra obtained from each instrument. Intramolecular isotope effects are also observed for the metastable dissociation of the adduct ion ($C_6H_5NH_3^+$) in the sector instrument and for the collision-induced dissociation (CID) of the adduct ion in the quadrupole ion trap. The relative magnitudes of these isotope effects are consistent with the different energy and time scales of the experiments. An intermolecular isotope effect is also observed for the rate of dissociation in the quadrupole ion trap. Hydrogen/deuterium (H/D) exchange between the nitrogen and ring is observed when protonated aniline is formed by reacting ammonia-d_3 with phenylium. This allows bracketing of the energy barrier for this intramolecular H/D exchange. Semi-empirical molecular orbital calculations of transition states for hydrogen exchange are consistent with the experimentally observed energy barrier. (Int J Mass Spectrom 190/191 (1999) 295–302) © 1999 Elsevier Science B.V.

Keywords: Quadrupole ion trap; Ion/molecule reaction; Isotope effect; Tandem mass spectrometry; H/D scrambling

---

1. Introduction

Understanding the dissociation mechanisms that occur for gas phase ions can be complicated by the fact that different mass spectrometers operate on different time scales and therefore different portions of the ion's internal energy distribution may be sampled. This means that different mass spectra and MS/MS spectra may be obtained from studies of the same compound using different mass spectrometers. The effect of internal energy and time scales is reflected in competitive reactions by different rates of dissociation. Such differences can even be observed in some cases for dissociations containing different isotopes, especially hydrogen and deuterium.

For intramolecular isotope effects, the rates of dissociation (k_H and k_D) for loss of a hydrogen or equivalent deuterium atom are affected due to differ-

---

* Corresponding author. E-mail: glish@unc.edu

Dedicated to Ray March and John Todd on the occasion of their retirement and for their support and encouragement to all us newcomers in quadrupole ion trap research.

PII S1387-3806(99)00048-2

ences in critical energies [1]. Replacement of hydrogen with deuterium causes a change in the zero point energy, increasing the critical energies. For intramolecular isotope effects, if the isotope bond is involved in the reaction, then the heavier isotope should have a slower rate of dissociation because there is less excess internal energy in the ion and thus the isotope effect should be greater than one. It should be noted that in most cases k_H and k_D are not measured, but instead, the abundance of the product ions (e.g. $[M - H]^+$ and $[M - D]^+$) is measured. In addition to being a function of k_H (k_D), which is a function of the internal energy of the ion, the abundance is a function of other instrumental parameters and the time frame of the experiment. If k_H and k_D are insensitive to internal energy over the internal energy range of the reacting ions, or if the rates are parallel over the internal energy range, then the relative abundance of the two products is a good estimate of the isotope effect [1].

For intermolecular isotope effects, ion abundances are not a good reflection of isotope effects. Not only do critical energies change, but the density of states in the transition state and in the reactant also changes. Typically, though, k_H/k_D is expected to be greater than one. This is because the increase in critical energy for the reaction of the heavier isotope should be more than counterbalanced by its increase in the density of states [1].

Protonated aniline is an ion that has generated substantial interest over the years because of the possibility of both nitrogen and ring protonation [2–9]. The lowest energy pathways for the dissociation of protonated aniline are via loss of $H^{\cdot}$ and loss of NH_3, which are 73 and 81 kcal mol^{-1} endothermic, respectively [10]. Thus, even when aniline is protonated by reagent ions with low proton affinities, e.g. CH_5^+, little fragmentation is observed. Also, even when protonated aniline is formed via a very exothermic proton transfer reaction, exchange between the ring and substituent is not observed [7]. As an alternative method to a proton transfer reaction between a gas phase acid and aniline to generate protonated aniline, phenylium can be reacted with $NH(D)_3$ [Eq. (1)].

$$C_6H_5^+ + NH(D)_3 \xrightarrow{k_a} C_6H_5NH(D)_3^+ \qquad (1)$$

In this reaction, k_a is the overall reaction rate constant and the reaction should produce only the nitrogen protonated aniline. The enthalpy of reaction for Eq. (1) is -81 kcal mol^{-1} [10]. Thus, the energy in the product exceeds the critical energy for $H^{\cdot}$ loss by 8 kcal mol^{-1}. For the product in Eq. (1), we have observed both intra- and inter-molecular isotope effects for the loss of $H^{\cdot}$ versus loss of $D^{\cdot}$. Intramolecular isotope effects were observed in both the mass spectra and MS/MS spectra. Intramolecular H/D exchange between the ring and substituent was also observed when protonated aniline is formed by Eq. (1). From these experiments, it has been possible to bracket the energy required for intramolecular hydrogen exchange between the ring and substituent in protonated aniline.

2. Experimental

2.1. Quadrupole ion trap

The theory, instrumentation, and methodology of quadrupole ion trap mass spectrometry have been discussed in detail elsewhere [11–14]. All experiments were performed in a Finnigan ion trap mass spectrometer mounted in a custom vacuum system. All chemicals were used as supplied except for chlorobenzene, which was subject to multiple freeze–pump–thaw cycles, to remove any noncondensable gases. Ammonia and ammonia-d_3 were introduced into the vacuum system through a Varian leak valve. A constant pressure of 2.3×10^{-6} Torr, determined with a Bayard–Alpert ionization gauge, was used.

Phenylium ions were formed by the following procedure. Chlorobenzene was pulsed into the ion trap vacuum system using a General Valve Corporation (Fairfield, NJ) Series 9 pulsed solenoid valve. The pulse valve was opened for 300 μs and the chlorobenzene pressure maximized approximately 50 ms after triggering the pulse valve. Ionization was affected with a 1 ms electron pulse, 50 ms after the pulse valve was triggered. The $C_6H_5^+$ (*m/z* 77) ion was isolated by ramping the rf to a value that ejected ions with mass-to-charge ratios less than 77 and concurrently resonantly ejecting ions with mass-to-charge ratios greater than 77. The isolated *m/z* 77 was then allowed to react with $NH(D)_3$, introduced into the vacuum system through the leak valve. Helium was used as a buffer gas at pressure of 1.4×10^{-3} Torr, and also served as the collision gas for the MS/MS experiments. The mass and MS/MS spectra were obtained by ramping the 1.1 MHz rf voltage on the ring electrode at a hardware set rate of 5555 Da s^{-1}. A 530 kHz, 5 V_{p-p} signal was applied to the endcaps to resonantly eject the ions to the detector during the data acquisition rf ramp.

MS/MS experiments using collision-induced dissociation (CID) were performed by kinetically exciting the parent ions with a resonant excitation voltage of a few hundred millivolts applied to the endcap electrodes for 20 ms. Optimum conditions were determined by adjusting the voltage and the frequency to obtain the maximum total conversion of parent ions to product ions. Parent ions were isolated using the procedure described above for $C_6H_5^+$. Typically, ten scans were averaged to obtain a spectrum and ten spectra were averaged to obtain the data presented.

2.2. High pressure chemical ionization

A Finnigan MAT 900 mass spectrometer (EB geometry) was used for the high-pressure chemical ionization (CI) experiments. Chlorobenzene was introduced via the solids probe or a heated inlet system. Ammonia was introduced into the source via the CI reagent gas line. The ion source pressure cannot be measured directly but was estimated to be 0.5 Torr based on the manufacturer's specifications. The desired reacting species ($C_6H_5^+$ and NH_3) cannot be selected for reaction as in the quadrupole ion trap. However, based on quadrupole ion trap experiments it is not expected that any other reactions other than that shown in Eq. (1) occurred to form ions corresponding to the masses of protonated aniline and the various deuterated analogs. Mass spectra were obtained by a standard magnetic field scan. Metastable spectra were obtained by a linked scan at constant *B/E*, to detect dissociations occurring in the first reaction region (i.e. between the ion source and electric sector).

2.3. Molecular orbital calculations

Semi-empirical molecular orbital calculations using the MOPAC package, version 6.0, were used in conjunction with the molecular modeling software program, PCMODEL (Serena Software), to estimate the heat of formation for protonated aniline with different sites of protonation. PCMODEL software was first used to generate a structure based on molecular mechanics. This structure was then used as the starting structure for MOPAC, in which the AM1 (Austin Model 1) Hamiltonian was used [15]. Heats of formation for transition states for intramolecular proton transfer from the nitrogen to the ring were also calculated using MOPAC.

3. Results and discussion

3.1. Formation of protonated aniline

Eq. (1) shows the general overall reaction for the formation of protonated aniline. In actuality, there are several reactions involved, as shown in Eq. (2), in which

$$\begin{aligned} &C_6H_5^+ + NH(D)_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (C_6H_5NH(D)_3^+)^* \xrightarrow[[N]]{k_s} C_6H_5NH(D)_3^+ \\ &\qquad\qquad \downarrow k_d \\ &\qquad C_6H_5NH(D)_2^{+\cdot} + H(D)^{\cdot} \end{aligned} \tag{2}$$

k_f is the forward reaction rate constant for formation of the phenylium/ammonia adduct, k_b is the rate constant for dissociation of this adduct back to reactants, k_s is the rate constant for collisional stabilization of the intact adduct, k_d is the rate constant for dissociation of the adduct by loss of $H^{\cdot}$, and $[N]$ is the number density (pressure) of the buffer gas. From this equation it can be seen that the overall rate constant [k_a in Eq. (1)] for formation of $C_6H_5NH_3^+$ depends upon the system pressure [N] and k_d. If k_d is ignored for the moment, because it should be constant, at some pressure the rate of collisional stabilization of the adduct ion is much greater than the rate of the back dissociation ($k_s[N] \gg k_b$). Under these conditions the reaction will be second order, independent of [N], and $k_a = k_f$. For pressures at which $k_b \gg k_s[N]$, the system is operating under third order kinetics and k_a will be a function of the pressure. If k_d is of similar magnitude or less than $k_s[N]$, k_f can be determined by the decrease in $C_6H_5^+$ as a function of time at a constant pressure. A set of such experiments was performed in the quadrupole ion trap, varying the helium pressure. Plotting k_f versus [He] allows for the determination of when the system is operating under conditions of second order kinetics. Such a plot indicates that under typical quadrupole ion trap conditions used here, the system [Eq. (2)] is well into the second order kinetic range. This is important in the intermolecular isotope effects discussed later.

Whereas the cyclic phenylium ion is the most stable $C_6H_5^+$ isomer, it has been reported that a fraction of the $C_6H_5^+$ ions formed by electron ionization of chlorobenzene have the acyclic structure [16]. An isomerically pure population of $C_6H_5^+$ ions can be generated in the quadrupole ion trap via CID MS/MS of the molecular ion of chlorobenzene [17]. In the sector instrument the purity of the $C_6H_5^+$ ions cannot be controlled or measured. It is not known whether the acyclic $C_6H_5^+$ ions will react with NH_3, because attempts to form the acyclic $C_6H_5^+$ isomer to test this in the quadrupole ion trap were unsuccessful. This lack of success in forming the acyclic $C_6H_5^+$ isomer may be the result of collisional stabilization to the most stable form, phenylium. If this is the case, stabilization should also occur in the chemical ionization source of the sector instrument because it is operating at a much higher pressure, which leads to a faster rate of collisional stabilization. Thus, the adduct ions formed by Eq. (2) should all be the result of reaction of cyclic $C_6H_5^+$ (phenylium) and these adduct ions should have the structure of protonated aniline.

Table 1
Relative intensities for ions in the region of the intact adduct when phenylium is reacted with ammonia-d_3

			% Relative intensity	
Ion formula	Neutral	*m/z*	Ion trap	Sector
$C_6H_5D_3N$		97	73	85
$C_6H_4D_3N$	H	96	23	10
$C_6H_5D_2N$	D	95	4	5

3.2. Intramolecular isotope effect

When ammonia-d_3 is used as the neutral gas to form protonated aniline, three peaks are observed in the molecular ion region of the mass spectra obtained with both instruments. These peaks are at *m/z* 95, 96, and 97. MS/MS of the ions at *m/z* 97 indicates that it is the intact adduct (protonated aniline-d_3). Tandem mass spectra of the ions at *m/z* 95 and 96 indicate that these ions correspond to $D^{\cdot}$ and $H^{\cdot}$ loss, respectively, from the ions at *m/z* 97. Table 1 lists the relative abundances of these peaks in the mass spectrum of the two instruments used in this study.

There are several features to note in the data in Table 1. First, more of the intact adduct, protonated aniline, is observed in the sector instrument. Two factors, pressure and time, contribute to this result. The sector instrument's CI source has a pressure more than 100 times greater than the quadrupole ion trap; thus the rate of collisional stabilization should be faster. This means that within a given time window, more adduct ions should be collisionally stabilized before they can dissociate by $H^{\cdot}$ loss. Additionally, the ions in the quadrupole ion trap have more than 1000 times longer to dissociate, assuming standard ion residence times in the sector CI source of a few microseconds. Both these factors would be expected to cause more fragmentation of the adduct ions to be observed in the quadrupole ion trap, which is what is observed.

The second observation in Table 1 is that the ratio of $H^{\cdot}$ to $D^{\cdot}$ loss is substantially different between the two instruments (5.75:1 in the quadrupole ion trap and 2:1 in the sector). The significance of this, however, is difficult to interpret. First, if the adduct remains protonated on the nitrogen, it might be assumed that the H(D)$^\cdot$ loss only occurs from the nitrogen. Loss of a ring hydrogen would generate a distonic ion, which for some species can be quite stable [18]. MOPAC calculations indicated that the ion structure resulting from loss of a nitrogen H should be greater than 1 eV more stable than any of the distonic ions that could be formed by loss of a ring H. Thus, it seems reasonable to expect the H$^\cdot$ lost to be from the nitrogen. However, if this is the case for protonated aniline-d_3 formed by Eq. (2), a ring hydrogen and nitrogen deuterium must exchange before fragmentation occurs. The data in Table 1 indicates that this in fact does happen in both instruments, although to different extents (vide infra). Assuming the energy barrier to H/D exchange between the ring and nitrogen is less than the exothermicity of Eq. (2), intramolecular exchange can occur until the adduct ion is collisionally cooled below that energy barrier. Because the rate of cooling is faster in the sector CI source (higher $[N]$), less exchange may occur in ion generated in the sector instrument. This would explain the lower ratio of H$^\cdot$ to D$^\cdot$ loss observed in the sector.

Given that intramolecular H/D exchange occurs, it is also possible that some of the fragmenting ions are ring protonated. In this case the H(D) loss would occur from the ring. This seems to be a less likely possibility. If the exchange completely randomizes the hydrogens and deuteriums, a 5:3 ratio of H:D loss would be expected in the absence of an isotope effect. Although the sector result is not far from this (2:1), the quadrupole ion trap ratio is almost 6:1. Thus, a definite isotope effect is present for the loss of H$^\cdot$/D$^\cdot$ from protonated aniline-d_3.

Because of the longer time frame and slower rate of collisional cooling in the quadrupole ion trap versus the sector, a lesser degree of H/D randomization may be expected, and in fact, is observed (vide infra). Because the degree of scrambling in the fragmenting ions cannot be determined, the absolute magnitude of isotope effect cannot be determined. The minimum isotope effect can be calculated, though. If complete randomization occurs and the H(D) loss occurs from the nitrogen, a ratio of 5:3 for H:D loss would result if there were no isotope effect. As the degree of randomization decreases, this ratio should get smaller. The observed H:D ratio in the sector instrument experiments means that an isotope effect of at least 1.2 (2:1/5:3) is present. For the quadrupole ion trap the observed H:D ratio of 5.75:1 indicates an isotope effect of at least 3.4 (5.75:1/5:3). Because these are only minimum effects it cannot be said for sure that the quadrupole ion trap has a greater isotope effect. This is because the quadrupole ion trap should sample ions with a greater degree of H/D randomization because of the longer time frame of the experiment and slower rate of collisional stabilization. However, this longer time frame should also favor a greater isotope effect because the kinetic shift will be less and therefore ions with less excess internal energy will be able to fragment, which will favor H$^\cdot$ loss.

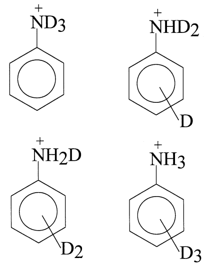

Fig. 1. Possible distribution of H and D between ring and substituent in protonated aniline-d_3.

With the quadrupole ion trap it is possible to monitor changes in the isotope effect as a function of the helium buffer gas pressure. When the helium buffer gas pressure was increased, not only was there an increase in the number of intact adduct ions formed relative to fragmentation, but there was also an increase in the isotope effect. In the limit, only H$^\cdot$ loss is observed. At this point, the signal to noise is such that H$^\cdot$ loss is at least 20 times greater than D$^\cdot$ loss. Thus the isotope effect is at least 12.

An intramolecular isotope effect is also observed in the tandem mass spectra of the stabilized adduct ions. The degree of H/D scrambling can be determined in this case so the absolute isotope effect can be measured. Fig. 1 shows the four possible isotopomers that can be formed by the H/D exchange between the

Table 2
Theoretical[a] and experimental result for loss of $N(H,D)_3$ from *m/z* 97 $(C_6H_{5-n}D_nNH_{3-m}D_m)^+$ $n + m = 3$

	$-ND_3$	$-ND_2H$	$-NDH_2$	$-NH_3$
Theoretical	2%	27%	54%	17%
Ion trap	7%	29%	46%	19%
Sector	9%	36%	46%	9%

[a] The theoretical distribution is based on complete randomization of the hydrogens and deuteriums and no isotope effect for $(NH,D)_3$ loss.

ring and nitrogen (disregarding possible positional isomers). MS/MS of the adduct ions shows the general dissociations: loss of $N(H,D)_3$ and loss of $H(D)^{\cdot}$. Table 2 shows the theoretical distribution for loss of $N(H,D)_3$ (assuming a negligible isotope effect) and that observed in the two instruments. The data indicate that more randomization occurs in the quadrupole ion trap (a greater percentage of NH_3 loss) than in the CI source of the sector mass spectrometer. This would be expected because of the longer time frame and lower pressure (slower rate of collisional stabilization) in the quadrupole ion trap.

Using the distribution of the isotopomers determined from the experimental $N(H,D)_3$ loss, the expected distribution for $H(D)^{\cdot}$ loss can be calculated. (This assumes that the internal energy of the protonated aniline has been reduced below the critical energy for H/D exchange between the ring and substituent by collisional stabilization, which should be valid for stable ions trapped for this period of time). The expected ratios without an isotope effect are given in Table 3, along with the experimental ratios of H and D loss. It can be seen that loss of $H^{\cdot}$ is greater than would be expected. For the quadrupole ion trap the isotope effect is 2.7 and for the sector instrument it is 3.0. Thus, compared to what is observed in the mass spectrum, for the MS/MS experiment in the quadrupole ion trap the isotope effect decreases from 3.4–2.7, whereas in the sector MS/MS experiment the isotope effect may increase (from 1.2–3.0, where the 1.2 measured in the mass spectrum is a minimum value).

Table 3
Theoretical and experimental ratios for H and D loss from MS/MS of the isotopomers distribution determined by $N(H,D)_3$ loss

	Ion trap H:D	Sector H:D
Theoretical	3:2	1:1
Experimental	4:1	3:1

The change in the isotope effect in opposite directions when comparing the mass spectral results with the MS/MS results for each of the two different instruments is consistent with the nature of the respective MS/MS experiments. In the quadrupole ion trap MS/MS experiment, the ions are being collisionally activated, which will increase their internal energy. In fact, it might be considered surprising that an isotope effect is observed at all in a CID experiment. However, this just emphasizes the nature of the CID experiment in the quadrupole ion trap, in which multiple collisions with low center of mass collision energy lead to small, incremental gains in internal energy. Because of the relatively long time frame of the experiment, the kinetic shift for dissociation should be small; thus, little energy in excess of the critical energy is required for dissociation to occur. As the amount of excess internal energy in the dissociating ion decreases, the isotope effect should increase. Because the isotope effect is smaller for the CID experiment in the quadrupole ion trap than in the mass spectrum when phenylium reacts with ammonia in the same instrument, it can be concluded that the average excess internal energy in the parent ion in the CID experiment is greater than the 8 kcal mol^{-1} excess internal energy that is in the adduct ion.

In contrast to the quadrupole ion trap MS/MS experiment, in the sector the tandem mass spectrum is from the dissociation of metastable ions. These metastable ions are longer-lived, and thus lower in internal energy, than the ions that fragment in the ion source. This should lead to an increase in the isotope effect because the kinetic shift is reduced.

3.3. Intermolecular isotope effect

As discussed above, under the normal operating range of helium pressure in the quadrupole ion trap, the reaction in Eq. (2) proceeds under second order kinetics, i.e. k_b can be neglected. If, under these conditions, the helium pressure is adjusted to obtain equal intensity signals of the stabilized adduct ion, $C_6H_5NH(D)_3^+$, and the fragment ion due to loss of $H(D)^{\cdot}$, $k_s[He] = k_d$, and k_d, the unimolecular dissociation rate constant, can be determined if k_s and [He] are known. The collisional stabilization rate constant, k_s, is taken as the Langevin collision constant, and was calculated to be 7.6×10^{-10} cm^3 mol^{-1} s^{-1}. For the adduct formed by reaction with NH_3, a unimolecular dissociation rate constant of 2.0×10^3 s^{-1} was determined. Similarly, for the reaction with ND_3, the unimolecular dissociation rate constant, k_d, was calculated to be 3.0×10^2 s^{-1}. Thus, an intermolecular isotope effect of almost seven is observed, which is the expected direction of an intermolecular isotope effect.

3.4. Energy barrier to H/D exchange between the ring and substituent

Previous studies of protonated aniline using deuterated reagent gases [3] or deuterium labeled aniline in a chemical ionization experiment [8] noted that no exchange is observed between the ring and substituent hydrogens and deuteriums. In fact, a method was developed to determine the number of active hydrogens using bimolecular H/D exchange that depended upon the lack of exchange between the ring and substituent [19]. One recent study [20] suggested the possibility of ring/substituent exchange but noted that this could be the result of collisional activation. The exchange in that study is far less than observed in the present work by forming protonated aniline by the ion/molecule reaction in Eq. (2). Thus, the question arises as to why there is this apparent discrepancy.

The most exothermic proton transfer reaction that has been used in chemical ionization to form protonated aniline is with CH_5^+ as the reagent ion [8,20]. The exothermicity of proton transfer from this reagent ion to aniline [proton affinity (PA) = 210 kcal mol^{-1}] [10] is 78 kcal mol^{-1}. If this energy is statistically partitioned between the two products, neutral CH_4 and protonated aniline, the protonated aniline should have approximately 63 kcal mol^{-1} of this energy. The reaction in Eq. (2) is 81 kcal mol^{-1} exothermic. All this energy, along with the center of mass collision energy, must remain in the protonated aniline ion until the ion undergoes a collision or dissociates (assuming no radiative emission) [21]. This suggests that the barrier to transfer of a hydrogen from the nitrogen to the ring is somewhere between these values.

Table 4
Calculated heats of formation (kcal mol^{-1}) for protonation of aniline at different sites

Protonation site	Heat of formation
N	177
C-1	218
C-2	182
C-3	204
C-4	179

To investigate this possibility, semi-empirical molecular orbital calculations (MOPAC) were done to determine the heats of formation of aniline protonated on the nitrogen and the various ring carbon atoms. Then calculations were performed to determine the energies of the transition states for transfer of a hydrogen from the nitrogen to the ring. Table 4 lists the heats of formation determined by the MOPAC calculations for protonation at various sites on aniline. It should be noted that the value obtained for the N protonated species, 177 kcal mol^{-1} is in agreement with the experimental value [10]. For the transfer of a hydrogen from the nitrogen to C-1, a heat of formation for the transition state was calculated to be 241 kcal mol^{-1}. This is the lowest energy transition state of all the possibilities calculated. Thus, a minimum of 64 kcal mol^{-1} of excess internal energy is required to transfer the hydrogen from the nitrogen to the ring. This is right at the value of the excess internal energy for protonated aniline formed by proton transfer from CH_5^+. Given the kinetic shift associated with reactions, this is consistent with the observation that there is no exchange between the ring and substituent when protonated aniline is formed by proton transfer from CH_5^+ or other reagent gases that undergo even less exothermic proton transfer reactions [8,20]. Conversely, the energy of the system when protonated aniline is formed by reacting phenylium with ammonia is sufficient to transfer a proton from the nitrogen to the ring. This result also explains the slight amount of exchange previously observed under collisional activation conditions [20]. Under the conditions used in that study, the collisional activation could add up to 16 kcal mol^{-1} of internal energy to the protonated aniline. This energy, combined with the excess energy from ionization, would raise the internal energy of the reactant ion higher than the 64 kcal mol^{-1} necessary for transfer of a hydrogen from the nitrogen to the ring.

References

[1] P.J. Derrick, Mass Spectrom. Rev. 2 (1983) 285.

[2] Y.K. Lau, P. Kebarle, J. Am. Chem. Soc. 98 (1976) 7452.

[3] D.P. Martinsen, S.E. Buttrill, Jr., Org. Mass Spectrom. 11 (1976) 762.

[4] S.K. Pollack, J.L. Devlin, III, K.D. Summerhays, R.W. Taft, W.J. Hehre, J. Am. Chem. Soc. 99 (1977) 4583.

[5] K.D. Summerhays, S.K. Pollacks, R.W. Taft, W.J. Here, J. Am. Chem. Soc. 99 (1977) 4585.

[6] J. Catalan, M. Yanez, Chem. Phys. Lett. 60 (1979) 499.

[7] J. Catalan, M. Yanez, J. Chem. Soc., Perkin Trans. 2 (1979) 741.

[8] R.L. Smith, L.J. Chyall, B.J. Beaseley, H.I. Kenttamaa, J. Am. Chem. Soc. 117 (1995) 7991.

[9] M.J. Nold, C. Wesdemiotis, Proceedings of the 43rd ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, GA, May 1995, p. 1030.

[10] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) 1.

[11] R.E. March, R.J. Hughes, Quadrupole Storage Mass Spectrometry, Wiley, New York, 1989.

[12] J.F.J. Todd, A.D. Penman, Int. J. Mass Spectrom. Ion Process 1 (1991) 106.

[13] R.G. Cooks, G.L. Glish, S.A. McLuckey, Chem. Eng. News 69 (1991) 26.

[14] S.A. McLuckey, G.J. Van Berkel, D.E. Goeringer, G.L. Glish, Anal. Chem. 66 (1994) 689A.

[15] R.C. Bingham, M.J.S. Dewar, D.H. Lo, J. Am. Chem. Soc. 97 (1975) 1285.

[16] P. Ausloos, S.G. Lias, T.J. Buckley, E.E. Rogers, Int. J. Mass Spectrom. Ion Processes 92 (1989) 65.

[17] Y.A. Ranasinghe, G.L. Glish, J. Am. Soc. Mass Spectrom. 7 (1996) 473.

[18] S. Hammerum, Mass Spectrom. Rev. 7 (1988) 123.

[19] D.F. Hunt, S.K. Sethi, J. Am. Chem. Soc. 102 (1980) 6953.

[20] N.N. Dookeran, A.G. Harrison, J. Am. Soc. Mass Spectrom. 6 (1995) 19.

[21] The kinetic energy of the reacting phenylium ion varies with the phase of the trapping rf field. Whereas the well depth is such that ions with 10 s of eV of kinetic energy can be trapped, the helium buffer gas damps the ion motion to the center of the trap and minimizes the ion kinetic energy. Additionally, the reaction cross section should decrease with increasing kinetic energy. Thus, it is expected that contributions to the ion internal energy from formation of the collision complex should be small.