Is ionized cyclopropylamine cyclic?

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Abstract

A combination of experiments based on proton transfer reactions monitored in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer and molecular orbital calculations up to the G2 and the CBS-Q levels demonstrates that the structure of the ions produced by electron ionization of cyclopropylamine, **1**, and relaxed at thermal energy, possess the ionized 1-propene amine structure $[CH_3CHCHNH_2]^{\cdot+}$, **3**$^{\cdot+}$. The experimental deprotonation enthalpy of ions **3**$^{\cdot+}$ is equal to 915.3 ± 3.2 kJ mol^{-1}. CBS-Q calculations are in good agreement with experiment. A value of 919–923 kJ mol^{-1} is calculated for the deprotonation enthalpy of ions **3**$^{\cdot+}$; 298 K heat of formation values of 852 kJ mol^{-1} and 783 kJ mol^{-1} are predicted from G2 atomization energies for ions **2**$^{\cdot+}$ and **3**$^{\cdot+}$, respectively. The heat of formation of $[CH_2CHCHNH_2]^+$ ions has been evaluated to 757.6 ± 5.7 kJ mol^{-1} from experiment and 755.8 kJ mol^{-1} from G2 atomization energy. (Int J Mass Spectrom 199 (2000) 59–69) © 2000 Elsevier Science B.V.

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1. Introduction

Proton affinity, i.e. the enthalpy change associated with the deprotonation reaction (1)

$$XH^+ \rightarrow X + H^+ \qquad (1)$$

may be determined by a variety of experimental methods [1]. Commonly, such experiments are conducted on even electron molecular species X. By contrast, proton affinity data for radicals is very limited. Obviously, the main reason for this situation is that radicals are highly reactive or unstable species that are not easily amenable to experiment. In particular, this excludes the possibility of proton affinity determination for a radical R$^{\cdot}$ by measurement of the equilibrium constant for the proton transfer reaction (2)

$$RH^{\cdot+} + B \rightarrow R^{\cdot} + BH^+ \qquad (2)$$

The few proton affinity values of radicals quoted in the compilation by Hunter and Lias [1] were obtained either from a thermochemical cycle, or by the "bracketing" technique. For example, three years ago, Audier et al. [2] used this latter method to estimate the deprotonation energies of several α-distonic ions $CH_2ZH^{\cdot+}$ ($Z = OH, OCH_3, NH_2$). At the same time
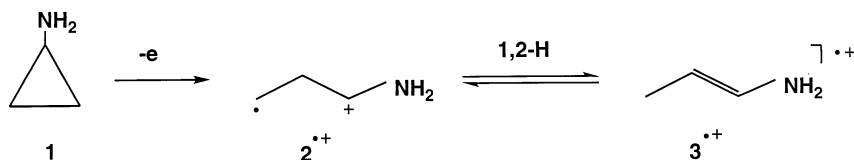
Scheme 1.

we developed a new method of determination of reaction thermochemistry based on the measurement of the corresponding proton transfer rate constant, called the "thermokinetic" method [3]. To the best of our knowledge, no experimental proton affinity determination of radicals has been made using this technique. The aim of the present study is to demonstrate that this method is particularly well suited for the determination of the gas phase basicity and the proton affinity of free radicals and for the characterization of the structure of the corresponding radical cations. An example application is that of the radical cation produced by ionization of cyclopropylamine.

We recently demonstrated [4] that, upon electron or photon ionization, cyclopropylamine, **1**, undergoes ring opening along the C(1)C(2) bond, thus giving rise to the distonic ion $[CH_2CH_2CHNH_2]^{\cdot+}$, $\mathbf{2}^{\cdot+}$ which, in turn, may rearrange to ionized 1-propene amine $[CH_3CH=CHNH_2]^{\cdot+}$, $\mathbf{3}^{\cdot+}$ (Scheme 1). The latter structure is at the origin of the dissociation products: $[CH_2=CH–CH=NH_2]^+ + H^\cdot$.

Arguments are based on MP4SDTQ/6-311G**// MP2/6-31G* + ZPE (zero point energy) molecular orbital calculations, dissociation threshold measurement, deuterium labeling, and dissociation rate constant determination. In particular, a statistical modeling of the reaction rate accurately reproduces the experimental data and the decrease in dissociation rate because of the passage through the stable structure $\mathbf{3}^{\cdot+}$. Another way to prove the occurrence of ring opening during the ionization of cyclopropylamine is to study the population of the nondissociated $[C_3H_7N]^{\cdot+}$ ions relaxed to thermal energies.

In principle, if the deprotonation energies of $\mathbf{2}^{\cdot+}$ and $\mathbf{3}^{\cdot+}$ are sufficiently different, the conclusions above may be checked by the determination of this thermochemical quantity for the $[C_3H_7N]^{\cdot+}$ ions pro-

duced by ionization of cyclopropylamine, **1**. Experiments involving proton transfer reactions (2) between the $[C_3H_7N]^{\cdot+}$ ions, formed by ionization of **1**, and a set of reference bases B has thus been undertaken in a Fourier transform ion cyclotron resonance (FTICR) spectrometer. The determination of the deprotonation energy of the ions has been made using the "thermokinetic" method. The structural assignment has been deduced from a comparison between the experimental data and the expectations based on molecular orbital calculations. For this purpose, G2 and CBS-Q calculations have been carried out on the relevant $[C_3H_7N]^{\cdot+}$ and $[C_3H_6N]^{\cdot}$ structures.

2. Experimental and computational

FTICR experiments were performed on a Bruker Spectrospin CMS 47X mass spectrometer equipped with an external ion source [5]. Cyclopropylamine was ionized in the external ion source (typical conditions were: filament current = 3 A, electron energy = 30 eV, ionizing pulse duration = 10 ms). All ions were transferred to the reaction cell located inside the 4,7 T superconducting magnet. Selection of the ion of interest (*m/z* 57) was done by ejection of unwanted ions by a combination of chirp and soft rf pulses. The reactants were relaxed to thermal energy (T = 300 K) by introducing argon inside the ICR cell at a pressure approximately one order of magnitude greater than the pressure of the neutral reactant. A relaxation delay of 2 to 6 s after selection of the reacting ions was typically used. Subsequently, the selected ions were allowed to react for a variable time with neutral B. Experiments were conducted at a constant pressure of neutral reactant in the range of 10^{-8} to 10^{-7} mbar. All the samples were commer-

cially available (Aldrich Chemical, St. Quentin Falla-vier, France).

Standard ab initio calculations have been carried out using the GAUSSIAN 94 series of programs [6]. Initially, the geometries of the different species inves-tigated were optimized at the HF/6-31G* level; the ZPE of the species considered has been calculated at this level after scaling by a factor 0.893 [7,8]. The HF/6-31G* geometries were then refined at the MP2/6-31G* level to take electron correlation effects explicitly into account. The corresponding harmonic vibrational frequencies were again calculated in order to verify that the stationary points found were local minima or transition structures on the potential energy surface. Standard G2 theory [9] employs a geometry optimized at the MP2(full)/6-31G(d) level and a scaled HF/6-31G(d) ZPE. A base energy calculated at the MP4/6-311G(d,p) level is corrected by several additivity approximations to QCISD(T) and to the 6-311+G(3df,2p) basis set. In an attempt to account for residual basis set deficiencies, G2 theory intro-duces higher-level corrections (HLC) that depend on the number of paired and unpaired electrons. In the G2(MP2) [10] variant, the basis set extension correc-tions are evaluated at the MP2 level, whereas energies are calculated at the QCISD(T)/6-311G(d,p) level. Finally, in the G2(MP2,SVP) [11] procedure the QCISD(T) calculations are carried out using the split-valence plus polarization (SVP) 6-31G(d) basis set.

G2 formalism yields, in general, reliable heats of formation, ionization energies, and proton affinities. However, for radicals with nonnegligible spin con-tamination, its performance can be unsatisfactory [12]. In such cases, it is advisable to use alternative methods such as the CBS family of procedures [13,14], that attempt to make an extrapolation to a complete basis set. For most of the species investi-gated here, the spin contamination was negligibly small and therefore the G2 calculations should per-form adequately. In the only species for which the spin contamination was found to be significant, namely structures **a** and **b** (vide infra), we have used instead the CBS-Q method [13,14].

Heats of formation of the species involved in the present study have been evaluated from G2 total energies via atomization reactions [15]. Thus, the heat of formation at 0 K of a given species X, $\Delta_f H_0^\circ(X)$, is given by

$$\Delta_f H_0^\circ(X) = \sum \Delta_f H_0^\circ(\text{atoms})$$
$$- \sum E[\text{G2}](\text{atoms}) + E[\text{G2}](X)$$

The heat of formation at 298 K is therefore given by

$$\Delta_f H_{298}^\circ(X) = \Delta_f H_0^\circ(X) + \Delta_{298} H^\circ(X)$$
$$- \sum \Delta_{298} H^\circ(\text{elements})$$

where the difference between the enthalpy at 298 K and 0 K is represented by the terms $\Delta_{298} H^\circ$ ($\Delta_{298} H^\circ = H_{298}^\circ - H_0^\circ$). For the elements, experi-mental $\Delta_{298} H^\circ$ values have been used (i.e., 8.468, 1.050, and 8.669 kJ mol^{-1} for $H_2(g)$, $C_{(s)}$, and $N_2(g)$, respectively), whereas, for the other species, the translational and rotational contributions were taken equal to 3 RT and the vibrational contribution estimated from the scaled (by a factor 0.893) HF/6-31G* vibrational frequencies.

3. Results and discussion

Deprotonation of ions $2^{\cdot+}$ and $3^{\cdot+}$ may lead to the radicals $CH_2CHCHNH_2$, **a**, $CH_3CHCHNH^{\cdot}$, **b**, or $CH_2CH_2CHNH^{\cdot}$, **c** (Scheme 2).

If a cyclization process is associated with the deprotonation of either $2^{\cdot+}$ or $3^{\cdot+}$, one may also expect formation of cyclic radicals such as **d**, **e**, or **f** (Scheme 3).

Thus, the two ion structures $2^{\cdot+}$ and $3^{\cdot+}$ and the six radicals **a–f** were examined by molecular orbital calculations.

3.1. Molecular orbital calculations

As noted in the Introduction, a molecular orbital study conducted at the MP4SDTQ/6-311G**//MP2/6-31G* + ZPE level on the $[C_3H_7N]^{\cdot+}$ ions $2^{\cdot+}$ and $3^{\cdot+}$ has been previously published [4]. We confirm here that, at the MP2/6-31G* level, the ionization of
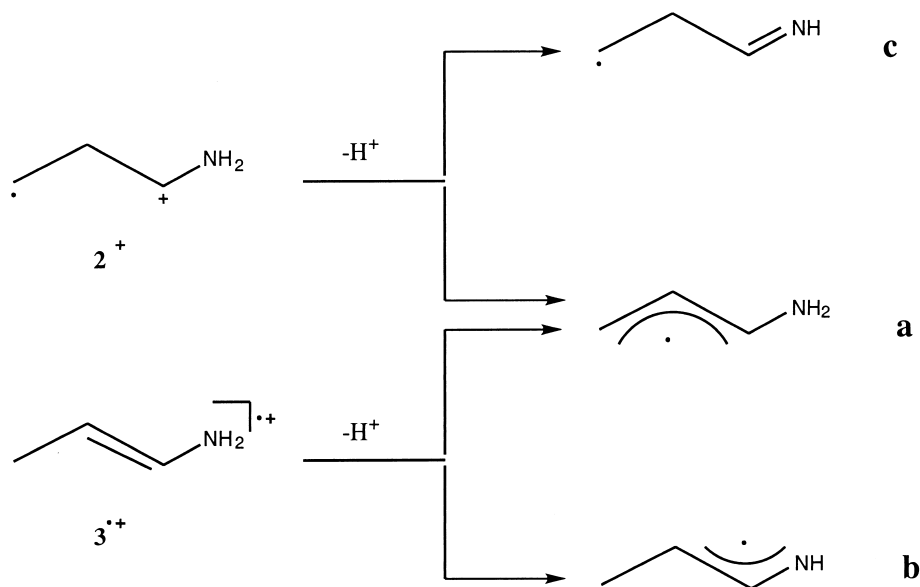
Scheme 2.

cyclopropylamine leads, by ring opening, to the distonic structure $2^{\cdot+}$. No stable cyclic structure may be identified for ionized cyclopropylamine on the MP2/6-31G* hypersurface. However, if a plane of symmetry perpendicular to the cyclopropane ring is imposed during the geometry optimization of ionized cyclopropylamine, a structure of symmetry C_S is obtained that, at the G2(MP2,SVP) level, is situated 8.74 eV above **1**. This energy difference is very close to the adiabatic ionization energy of **1** (8.86 eV, [4]). We note, however, that this $C_S-1^{\cdot+}$ structure has one negative vibrational frequency involving mainly the rotation of the amino group and the C(1)C(2) bond elongation. Thus, if the geometry of the $C_S-1^{\cdot+}$ structure is relaxed, it evolves spontaneously toward
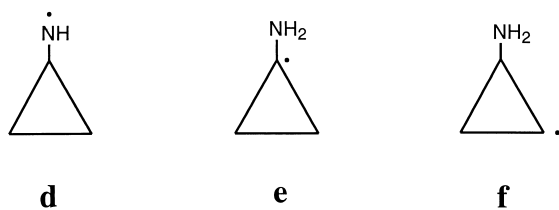
Scheme 3.

structure $2^{\cdot+}$. More precisely, the CC bond elongation generates the conformer $2b^{\cdot+}$ that is separated from the most stable conformation $2a^{\cdot+}$ by a barrier of ≈ 16 kJ mol^{-1} (MP2/6-31G* calculations) (Fig. 1). Structure $2a^{\cdot+}$ is more stable than $2b^{\cdot+}$ by ~ 5 kJ mol^{-1} at all the levels of theory considered. We note that both conformations take their stabilities from a favourable electrostatic interaction between the polarizable radical site and a positive centre: either an H atom of the NH$_2$ group in $2a^{\cdot+}$ or the carbon atom bearing the NH$_2$ group in $2b^{\cdot+}$.

Table 1 indicates that ionized 1-propene amine, $3^{\cdot+}$, is the most stable of the ions considered. G2 calculation shows that the distonic radical cation $2a^{\cdot+}$ is situated 68 kJ mol^{-1} above $3^{\cdot+}$, at 298 K. The heats of formation calculated from the G2 atomization energies of ions $2^{\cdot+}$ and $3^{\cdot+}$ are equal to 852 and 783 kJ mol^{-1}, respectively. These values are ~ 10 kJ mol^{-1} higher than our previous estimate based on a lower theoretical level of calculation [4]. An excellent agreement is found equally between experimental (757.6 $\pm$ 5.7 kJ mol^{-1}) and G2 (755.8 kJ mol^{-1}) heat of formation of the vinylimonium ion [CH$_2$=CH–CH=NH$_2$]$^+$. The experimental value has been cor-

2a$^{+\bullet}$

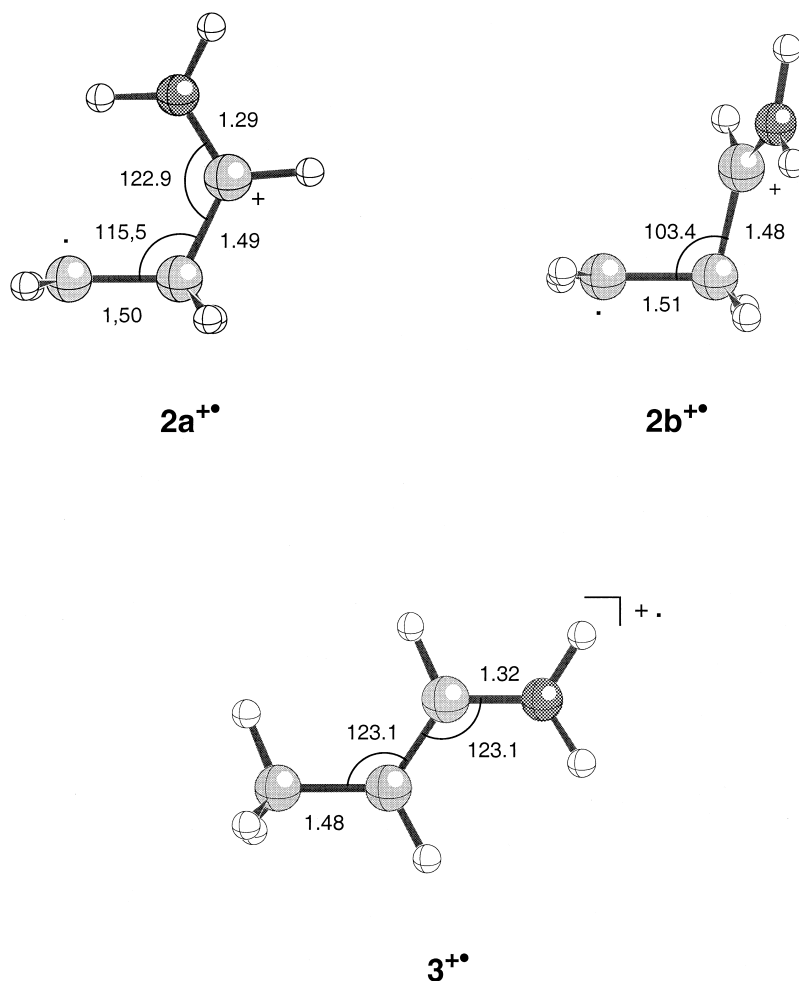**2b$^{+\bullet}$**

3$^{+\bullet}$

Fig. 1. Selected geometrical parameters (bond legths in Å, bond angles in degrees) of the MP2/6-31G* optimized geometry of ions **2$^{\cdot+}$** and **3$^{\cdot+}$**.

rected from the previous estimate as described in the Appendix.

The corresponding deprotonated species $CH_2CHCHNH_2$, **a**, and $CH_3CHCHNH^{\cdot}$, **b**, are the only structures that exhibit a nonnegligible spin contamination of the unrestricted wavefunction. However, these two radicals are predicted to be of comparable stabilities (Table 1), both at the G2 (energy difference 2.4 kJ mol^{-1}) and the CBS-Q (energy difference 4.2 kJ mol^{-1}) levels of theory. The radicals **c–f** are by far less stable; their energies relative to **a** are from 60 to 150 kJ mol^{-1} higher, as indicated by the G2(MP2,SVP) calculations. Consequently, it is

clear that the most favourable deprotonation pathways from **2$^{\cdot+}$** and **3$^{\cdot+}$** correspond to the formation of radical **a** or a mixture of **a** and **b**, respectively.

The 298 K deprotonation enthalpies of $[C_3H_7N]^{\cdot+}$ ions determined from G2 calculations are summarized in Table 2. The CBS-Q results are also included for the deprotonation processes of **3$^{\cdot+}$**. First, the deprotonation of a hypothetical transient ion **1$^{\cdot+}$** has been considered. It should probably give rise to the radical **a** by deprotonation of a CH_2 group and simultaneous relaxation by ring opening. The corresponding deprotonation enthalpy (776 kJ mol^{-1}) may be estimated using the experimental heat of formation of cyclopro-

Table 1
Summary of calculated and experimental thermochemical data relevant to the various $[C_3H_6N]^{\cdot}$ and $[C_3H_7N]^{+\cdot}$ species discussed in the text (kJ mol^{-1})

Structure	0 K relative energies G2(MP2,SVP)	0 K relative energies G2	298 K $\Delta_f H°$ (G2)[a]	298 K $\Delta_f H°$ (exp)
1, cyclopropylamine	−688			77[b]
C_s-**1**$^{+\cdot}$ cyclopropylamine (C_s symmetry imposed)	155			932[c]
2a$^{+\cdot}$ $[CH_2CH_2CHNH_2]^{+\cdot}$	82	68	852.0	
2b$^{+\cdot}$ $[CH_2CH_2CHNH_2]^{+\cdot}$	86			
3$^{+\cdot}$ $[CH_3CHCHNH_2]^{+\cdot}$	0	0	783.3	
4$^{+\cdot}$ $[CH_2CHCHNH_2]^+ + H^{\cdot}$	207	186	973.8	975.6[d]
a, $[CH_2CHCHNH_2]^{\cdot}$	0	0	177.8	
b, $[CH_3CHCHNH]^{\cdot}$	3	2	179.8	
c, $[CH_2CH_2CHNH]^{\cdot}$	63	61	239.9	
d, $[c\text{-}CH_2CH_2CHNH]^{\cdot}$	88			
e, $[c\text{-}CH_2CH_2CNH_2]^{\cdot}$	102			
f, $[c\text{-}CH_2CHCHNH_2]^{\cdot}$	156			

[a] From G2 atomization enthalpies (see computational section).
[b] From [25].
[c] Adiabatic ionization energy $= 8.86 \pm 0.03$ eV [4,26].
[d] Using $\Delta_f H°[CH_2CHCHNH_2]^+ = 757.6$ kJ mol^{-1} (see Appendix) and $\Delta_f H°[H]^{\cdot} = 218.0$ kJ mol^{-1} [27].

pylamine and its adiabatic ionization energy (Table 1). Starting now, from the distonic ion **2**$^{\cdot+}$ the formation of the radical **a** requires 856 kJ mol^{-1}. Finally, the deprotonation of ionized 1-propene amine may lead to radicals **a** or **b** with a quasi-identical enthalpy variation of 925 and 927 kJ mol^{-1}, respectively, at the G2 level, and 919–923 kJ mol^{-1}, respectively, at the CBS-Q level. It appears, consequently, that the cation radicals **1**$^{\cdot+}$, **2**$^{\cdot+}$, and **3**$^{\cdot+}$ may be identified on the basis of their deprotonation enthalpies. Furthermore, the comparable stability of radicals **a** and **b** leads to the expectation that depro-

tonation of **3**$^{\cdot+}$ should originate from both a carbon or a nitrogen atom. In contrast, the deprotonation of **1**$^{\cdot+}$ or **2**$^{\cdot+}$ should mostly imply a carbon position. We will also take advantage of this fact to experimentally characterize the structure of ionized cyclopropylamine.

In order to compare experimental and theoretical free energies of deprotonation it is necessary to estimate the entropy variation associated with reaction (1). For this purpose, the vibrational contribution to entropy has been calculated using the model of Pitzer for the internal hindered rotations [16,17]. Details of

Table 2
Theoretical enthalpies, entropies, and free energies of deprotonation of ions **1**$^{+\cdot}$–**3**$^{+\cdot}$

Deprotonation process	$\Delta H°_{298}$ (kJ mol^{-1})[a]	$\Delta S°_{298}$ (J mol^{-1} K^{-1})[d]	$\Delta G°_{298}$ (kJ mol^{-1})
1$^{+\cdot} \to$ **a** + H$^+$	776[b]		
2$^{+\cdot} \to$ **a** + H$^+$	856.4	99.2	826.8
3$^{+\cdot} \to$ **a** + H$^+$	925.2 [919.2][c]	104.5	894.1 [888.1][c]
3$^{+\cdot} \to$ **b** + H$^+$	927.2 [923.4][c]	107.9	895.0 [891.2][c]

[a] Estimated using $\Delta_f H°_{298}$ [H]$^+ = 1530$ kJ mol^{-1} and the G2 heats of formation presented in Table 1, unless otherwise specified.
[b] The heat of formation of the hypothetical ions **1**$^{+\cdot}$ has been deduced from $\Delta_f H°_{298}$ (**1**) $= 77$ kJ mol^{-1} and the adiabatic ionization energy of **1** (see Table 1).
[c] Values within brackets were obtained at the CBS-Q level of theory.
[d] Using S°[H]$^+ = 108.7$ J mol^{-1} K^{-1} at 298 K and S° calculated by the method described in the Appendix.

Table 3
Parameters relevant to proton transfer reactions involving $[C_3H_7N]^{\cdot+}$ ions produced by ionization of cyclopropylamine and several bases B

Base B	PA(B)[a] kJ mol^{-1}	GB(B)[a] kJ mol^{-1}	μ[b] D	α[c] Å^3	k_{exp} ($\times 10^{10}$) cm^3 mol^{-1} s^{-1}	k_{coll} ($\times 10^{10}$)[d] cm^3 mol^{-1} s^{-1}	RE[e] %
Methylamine	899.0	864.5	1.3	4.0	0.02	15.4 (11.7)	0.1 (0.2)
Cyclopropylamine	904.7	869.9	(1.4)	7.5	0.90	15.9 (13.0)	5.6 (7)
Ethylamine	912.0	878.0	1.1	5.8	0.61	14.2 (12.1)	4 (5)
Propylamine	917.8	883.9	1.4	7.7	2.61	16.3 (13.2)	16 (20)
Isopropylamine	923.8	889.0	(1.5)	7.7	7.73	16.3 (13.2)	47 (59)
Pyridine	930.0	898.1	2.2	9.5	11.16	19.4 (14.2)	58 (78)
Cyclohexylamine	934.4	899.6	(1.5)	12.5	10.72	17.0 (14.7)	63 (73)
Piperidine	954.0	921.0	(1.2)	10.6	11.21	15.4 (13.8)	73 (81)
Dipropylamine	962.3	929.3	(1.1)	13.2	13.09	15.8 (14.7)	83 (89)

[a] Proton affinities, PA, and gas phase basicities, GB, from the compilation by Hunter and Lias [28].
[b] Dipole moment in Debye, experimental values from [18] (in parentheses, calculated by the AM1 method [6]).
[c] Polarizabilities in Å^3 calculated using the method of Miller [19].
[d] Collision rate constant calculated using the ADO model [20] and, in parentheses, the VTST formalism [21].
[e] Reaction efficiency, RE $= k_{exp}/k_{coll}$.

these calculations are given in the Appendix. The corresponding free energies of deprotonation are also quoted in Table 2.

3.2. Proton transfer experiments

A series of proton transfer reactions (2′) has been experimentally studied in the FTICR spectrometer:

$$[\text{ionized } \mathbf{1}]^{\cdot+} + B \rightarrow C_3H_6N + BH^+ \qquad (2')$$

where "[ionized $\mathbf{1}]^{\cdot+}$" denotes the ions produced by ionization of cyclopropylamine.

To a first approximation, using thermalized reactants, reaction (2′) will occur if the enthalpy of deprotonation of [ionized $\mathbf{1}]^{\cdot+}$ is less than the proton affinity of B. We investigated a wide range of bases B of proton affinity (PA) between 752 kJ mol^{-1} (propene) and 962 kJ mol^{-1} (dipropylamine). The first observation was that no proton transfer is observed because PA(B) is lower than 890 kJ mol^{-1}. This is indication that structures $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ (whose enthalpies of deprotonation are 776 and 856 kJ mol^{-1}) are not present to a significant extent in the [ionized $\mathbf{1}]^{\cdot+}$ ions. Moreover, the reactions of [ionized $\mathbf{1}]^{\cdot+}$ with the bases B presented in Table 3 are essentially complete at long reaction times; this indicates that [ionized $\mathbf{1}]^{\cdot+}$

contains no ion of deprotonation enthalpy greater than 960 kJ mol^{-1}.

Deuterium labeling experiments have been undertaken by exchanging the hydrogen of the amino group of cyclopropylamine with D_2O in the inlet system of the external ion source of the FTICR spectrometer. The $[C_3H_4D_2N]^{\cdot+}$ ions were then selected and allowed to react with base B. In all the cases examined, a transfer of D and H is systematically observed. This confirms that $\mathbf{3}^{\cdot+}$ is present in the [ionized $\mathbf{1}]^{\cdot+}$ ions and that it deprotonates from two sites to generate both radicals $\mathbf{a}$ and $\mathbf{b}$.

Our determination of the free energy of deprotonation and the enthalpy of deprotonation of [ionized $\mathbf{1}]^{\cdot+}$ is based on the semiempirical "thermokinetic" method developed in this laboratory [3]. It may be briefly recalled that this method of determination of gas basicity and proton affinity uses a correlation between the reaction efficiency, RE, and the standard free energy change, $\Delta G°$, or the standard enthalpy variation, $\Delta H°$, of a proton transfer process. For a reaction of the type (2) the expected correlation is expressed as Eq. (3)

$$\text{RE} = k_{exp}/k_{coll} = 1/[1 + \exp((\Delta G_2^\circ + \Delta G_a^\circ/RT)] \qquad (3)$$

where k_{exp} and k_{coll} are the experimental and collision rate coefficients, respectively, ΔG_2° is the standard free energy change, and ΔG_a° is an apparent energy barrier for reaction (2). As long as ΔG_2° is equal to the difference in gas phase basicities $GB(R^\cdot) - GB(B)$, $GB(R^\cdot)$ (i.e., the free energy of deprotonation of $RH^{\cdot+}$) can be deduced by plotting the RE of reaction (2), for a series of bases B of known basicities, as a function of $GB(B)$, and by fitting the data with a parametric function accounting for the theoretical relationship [Eq. (4)]

$$RE = a/[1 + \exp(b(c - GB(B)))] \qquad (4)$$

It has been empirically established [3] that $\Delta G_a^\circ = RT$, thus $GB(R^\cdot)$ may be calculated according to Eq. (5)

$$GB(M) = c - 1/b \qquad (5)$$

In a similar way $PA(R^\cdot)$ (i.e., the deprotonation enthalpy of $RH^{\cdot+}$) can be deduced from a correlation between reaction efficiency of reaction (1) and $PA(B)$ [Eq. (6)]

$$PA(M) = c - 1/b + \langle T\Delta S_2^\circ \rangle \qquad (6)$$

where $\langle T\Delta S_2^\circ \rangle$ is the mean value of the $T\Delta S_2^\circ$ term of reaction (2).

The results concerning [ionized **1**]$^{\cdot+}$ and various bases B in the 860–930 kJ mol^{-1} basicity range are gathered in Table 3. The collision rate constants k_{coll} were calculated using the average dipole orientation (ADO) theory [20] or a variational transition state theory calculation (VTST) [21] in order to evaluate the relative efficiencies, $RE = k_{exp}k_{coll}$. The curve fitting procedure used to solve Eq. (4) and its PA counterpart uses a nonlinear iterative least squares method (Levenberg–Marquardt algorithm) implemented in the IGOR Pro 3.1 package (Wavemetrics Inc., Lake Oswego, OR, 1996). One example of the correlation observed between RE and $GB(B)$ or $PA(B)$ is presented in Fig. 2.

The "thermokinetic" treatment of the data reported in Table 3 allows the determination of the free energy of deprotonation of [ionized **1**]$^{\cdot+}$, the RE versus $GB(B)$ correlation leads to a value of 883.8 ± 2.8 kJ

mol^{-1}. Similarly, using the $\langle T\Delta S_2^\circ \rangle$ term deduced from Table 3 and $S^\circ(R^\cdot) - S^\circ (RH^{\cdot+} = S^\circ(\mathbf{a}) - S^\circ (\mathbf{3}^{\cdot+}) = -4.2$ J mol^{-1} K^{-1} (Table 2) the correlation between RE and $PA(B)$ leads to a deprotonation enthalpy value of 915.3 ± 3.2 kJ mol^{-1}.

Examination of Table 2 reveals that these experimental values compare only with the theoretical estimate obtained for the deprotonation processes $\mathbf{3}^{\cdot+} \rightarrow \mathbf{a} + H^+$ and $\mathbf{3}^{\cdot+} \rightarrow \mathbf{b} + H^+$. These results, combined with the observations that no proton transfer is observed if $PA(B)$ is less than 890 kJ mol^{-1} and that all [ionized **1**]$^{\cdot+}$ ions are deprotonated if $PA(B)$ is greater than 960 kJ mol^{-1}, lead to the conclusion that the $[C_3H_6N]^{\cdot+}$ ions sampled under our experimental conditions are exclusively of structure $\mathbf{3}^{\cdot+}$.

3.3. Discussion

As described in the experimental section, the ions studied are produced in the electron impact external source of the FTICR mass spectrometer. The $[C_3H_6N]^{\cdot+}$ ions thus correspond to [ionized **1**]$^{\cdot+}$ species undissociated at observation time $\approx 10^{-6}$ s. A summary of the potential energy profile associated with the ionization/dissociation processes of cyclopropylamine is presented in Fig. 3 [4].

An isomerization barrier $\mathbf{2}^{\cdot+} \rightarrow \mathbf{3}^{\cdot+}$ of ~ 100 kJ mol^{-1}, and a dissociation barrier $\mathbf{3}^{\cdot+} \rightarrow [CH_2CHCHNH_2]^+ + H^\cdot$, $\mathbf{4}^{\cdot+}$, of 190 kJ mol^{-1}, have been predicted by the MP4SDTQ/6-311G**//MP2/6-31G* + ZPE calculations [4]. Another important point is that the energy level of the isomerization barrier closely corresponds to the energy level attained after adiabatic ionization of cyclopropylamine. Considering these elements, it appears that the undissociated [ionized **1**]$^{\cdot+}$ species should correspond to a mixture of interconverting structures $\mathbf{2}^{\cdot+}$ and $\mathbf{3}^{\cdot+}$ of internal energy situated between 160 and 190 kJ mol^{-1} with respect to the ground state of $\mathbf{3}^{\cdot+}$. This corresponds to the hatched area in Fig. 3. At the low pressure used in the external ion source, essentially no collisions may deactivate the $[C_3H_6N]^{\cdot+}$ ions. Their distribution is thus given by the corresponding densities of vibrational states. It is expected that the large energy difference between $\mathbf{2}^{\cdot+}$ and $\mathbf{3}^{\cdot+}$ (68 kJ mol^{-1}
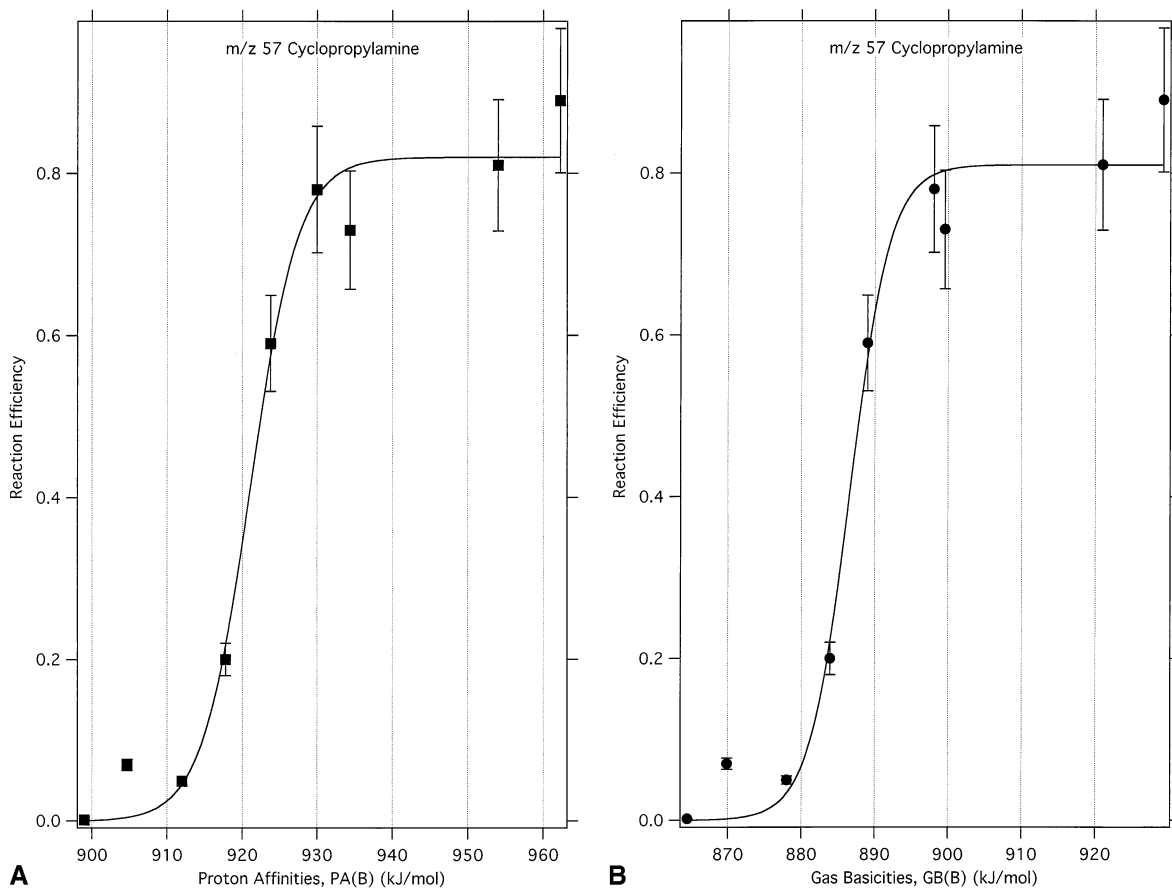
Fig. 2. Proton transfer reaction efficiency vs. PA(B) or GB(B) for deprotonation of ionized cyclopropylamine by the reference bases B.

at the G2 level) will tremendously favour the latter structure in the mixture. This has been confirmed by a computation of the densities of vibrational states, $N(E)$, using the Beyer–Swinehard algorithm [22] and the scaled HF/6-31G* frequencies of $2^{\cdot+}$ and $3^{\cdot+}$. In the internal energy range situated between the top of the isomerization barrier $2^{\cdot+}$ and $3^{\cdot+}$ and the dissociation threshold $3^{\cdot+} \rightarrow 4^{\cdot+}$, the ratio $N_3(E)/N_2(E')$ ($E = E' + 68$ kJ mol^{-1}) is situated around 100 (more precisely, $N_3(E)/N_2(E') = 160$ for $E = 160$ kJ mol^{-1} and $N_3(E)/N_2(E') = 80$ for $E = 190$ kJ mol^{-1}). It is consequently clear that the mixture of $[C_3H_6N]^{\cdot+}$ ions emerging from the external source of the FTICR mass spectrometer contains essentially ($\approx 99\%$) structure $3^{\cdot+}$. The selection and the thermalization of the $[C_3H_6N]^{\cdot+}$ ions done in the ICR cell

give a picture of this distribution that is revealed by the measurement of the basicity properties.

4. Conclusion

FTICR experiments demonstrate that the deprotonation enthalpy of ions produced by electron ionization of cyclopropylamine, **1**, and relaxed to thermal energy is equal to 915.3 $\pm$ 3.2 kJ mol^{-1}. This finding is compatible only with the formation of the 1-propene amine structure $[CH_3CHCHNH_2]^{\cdot+}$, $3^{\cdot+}$, for which the theoretical estimate of this thermodynamic quantity is in the range 919–923 kJ mol^{-1}. Heat of formation values of 783.3 kJ mol^{-1} and 852.0 kJ mol^{-1} have been calculated from G2 atomization
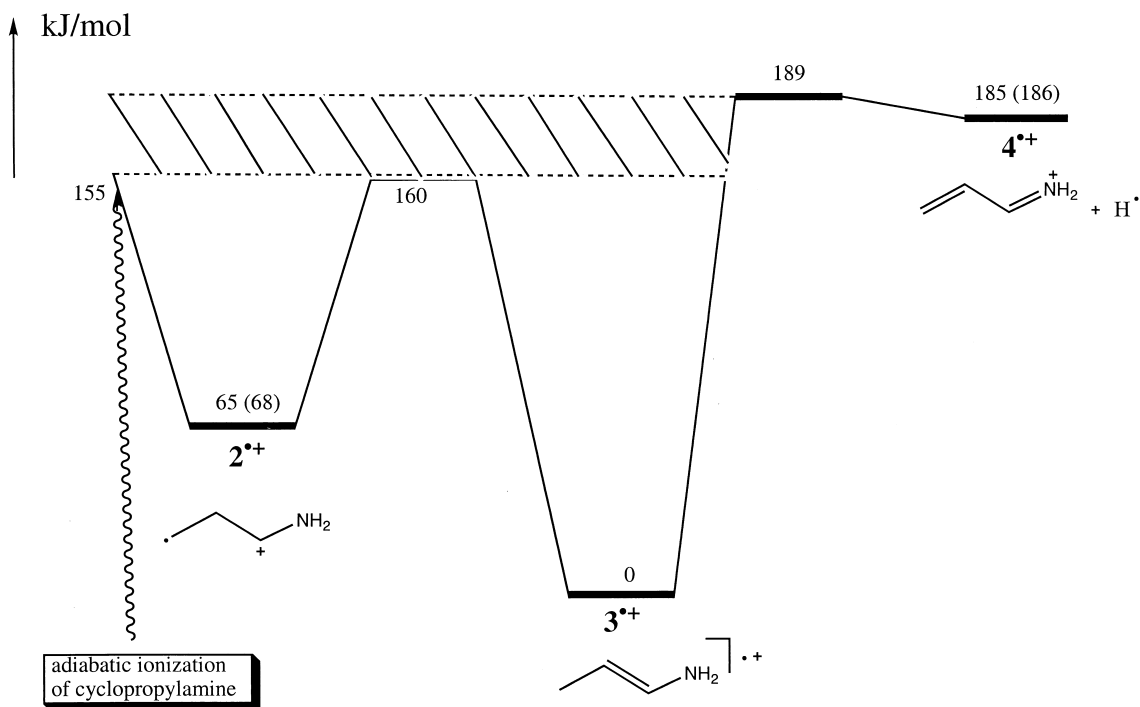
Fig. 3. MP4SDTQ/6-311G**//MP2/6-31G* + ZPE energy profile for isomerization/dissociation of $[C_3H_7N]^{\cdot+}$ ions [in parentheses, G2(0 K) results].

energies of ions $2^{\cdot+}$ and $3^{\cdot+}$. The same procedure applied to the immonium ion $[CH_2CHCHNH_2]^+$ leads to $\Delta_f H_0^\circ[CH_2CHCHNH_2]^+ = 755.8$ kJ mol^{-1} in good agreement with the corrected experimental value of 757.6 ± 5.7 kJ mol^{-1}.

Appendix

Entropies of radicals **a** and **b** and of ions $2^{\cdot+}$ and $3^{\cdot+}$ have been estimated using the usual statistical thermodynamic functions. The vibrational contributions have been calculated using the harmonic oscillator approximation with the HF/6-31G* calculated vibrational frequencies scaled by the factor 0.893 already used in the ZPE calculation. The only exceptions to this treatment were the low frequency torsion modes for which the method developed by Pitzer has been used [17]. This procedure has been applied to the methyl group rotation in **b** and $3^{\cdot+}$, the torsion of the

NH$_2$ group in **a**, and the two internal rotations around the CC bonds in ion $2^{\cdot+}$. For each case, the rotational barriers V_0 have been estimated at the MP2/6-31G* level. The method is comparable to the E2 method employed recently by East and Radom [16]. The resulting third law entropies of **a**, **b**, $2^{\cdot+}$, and $3^{\cdot+}$ were: 300.7 J mol^{-1} K^{-1} ($V_0 = 20$ kJ mol^{-1}); 304.1 J mol^{-1} K^{-1} ($V_0 = 2$ kJ mol^{-1}); 310.2 J mol^{-1} K^{-1} ($V_0[C1–C2] = 16$ kJ mol^{-1}, $V_0[C2–C3] = 8$ kJ mol^{-1}); 304.9 J mol^{-1} K^{-1} ($V_0 = 2$ kJ mol^{-1}), respectively.

The heat of formation of the immonium ion $[CH_2CHCHNH_2]^+$ has been previously deduced from the appearance energy of $[C_3H_6N]^+$ ions produced by photodissociation of cyclopentylamine [23]. In our original treatment we take into consideration only the initial internal energy of the precursor molecule before estimating $\Delta_f H_{298}^\circ[CH_2CHCHNH_2]^+$. In fact, if we follow the reasoning of Traeger and McLoughlin

[24], the translational energy of the precursor molecule must be conserved during the dissociation and the heat of formation of the fragment ion must be deduced from the relationship (7)

$$\Delta_f H^\circ_{298}[CH_2CHCHNH_2]^+ = AE_{298}[C_3H_6N]^+$$

$$- \Delta_f H^\circ_{298}[C_2H_5] + \Delta_f H^\circ_{298}[cyclopentylamine]$$

$$- \Delta H^\circ_{0\rightarrow298}[C_2H_5] + \Delta H^\circ_{0\rightarrow298}[CH_2CHCHNH_2]^+$$

$$- 5/2\ RT \tag{7}$$

Using the experimental appearance energy value $AE_{298}[C_3H_6N]^+ = 9.42 \pm 0.05$ eV [23] and $\Delta_f H^\circ_{298}[C_2H_5] = 118.0$ kJ mol^{-1} [15]; $\Delta_f H^\circ_{298}[cyclopentylamine] = -54.9 \pm 0.9$ kJ mol^{-1} [14]; $\Delta H^\circ_{0\rightarrow298}[C_2H_5] = 13.0$ kJ mol^{-1} (calculated G2 contribution to enthalpy between 0 K and 298 K); $\Delta H^\circ_{0\rightarrow298}[CH_2CHCHNH_2]^+ = 14.8$ k mol^{-1} (calculated G2 contribution to enthalpy between 0 K and 298 K); we get $\Delta_f H^\circ_{298}[CH_2CHCHNH_2]^+ = 757.6 \pm 5.7$ kJ mol^{-1}.

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