Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 227 (2003) 373–380

International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Proton affinity of some radicals of alcohols, ethers and amines

J. Fossey[a], P. Mourgues[a], R. Thissen[b], H.E. Audier[a,*]

[a] DCMR, UMR CNRS 7651, Ecole Polytechnique, 91128 Palaiseau, France
[b] LCP, Université Paris Sud, 91405 Orsay, France

Received 22 May 2002; accepted 29 May 2002

Abstract

Calculated proton affinities (PA) of the $CH_3{}^\bullet CHX$ ($X = OH, OCH_3$, and NH_2) α-radicals and of four β-radicals $^\bullet CH_2CH_2X$ ($X = OH, OCH_3, OCH_2CH_3$, and NH_2) confirm that PA of α-radicals lie far below those of the corresponding saturated molecules and indicate, as a first and rough evaluation, that a radical in the β-position, has a negligible influence on the PA at the heteroatom.

Experiments were performed to measure the PA of β-radicals both by measuring the rates of deprotonation of the corresponding β-distonic ions in a FT-ICR cell and by determining the $\Delta H_f[^\bullet CH_2CH_2XH^+]$, itself obtained by appearance energy (AE) measurements, using synchrotron radiation.

From these results and those of literature, the following values are proposed: $PA[^\bullet CH_2CH_2OH] = 185.8 \pm 0.5$ kcal/mol, $PA[^\bullet CH_2CH_2OCH_3] = 193.3 \pm 0.5$ kcal/mol and $PA[^\bullet CH_2CH_2NH_2] = 116 \pm 1$ kcal/mol.

Keywords: Gas basicity; Proton affinity; Distonic ions; VUV photoionisation; FT-ICR; Calculation

---

1. Introduction

Distonic ions are stable species which are isomers of ionised molecules [1–3]. They are currently of considerable interest as intermediates in the gas phase reactions of radical cations. For instance, the unimolecular reactions of long-chained alkanol [4], alkylether [5] or alkylamine [6] radical cations, often begin with the intramolecular protonation of the heteroatom leading to an intermediate $CH_3(CH_2)_n{}^\bullet CH(CH_2)_m XH^+$ ($X =$ OH, OCH_3, NH_2, etc.) distonic ion. The so formed distonic ion can, in turn, isomerise by long-distance H transfers into other distonic ions [6]. In the study of such reactions, it is in many cases necessary to estimate the ΔH_f of the putative intermediate distonic ions. These approximations are often based on the known thermochemistry of even-electron ions [7,8]. For instance, in order to evaluate ΔH_f, it is often assumed that the proton affinity (PA) at the heteroatom of the $CH_3(CH_2)_n{}^\bullet CH(CH_2)_m X$ radical is the same as of the corresponding saturated compound.

However, as pointed out by Holmes and Lossing [9], this assumption is frequently incorrect. This has been confirmed by the determination, both by experiment

---

[*] Corresponding author. Tel.: +33-169-33-4878; fax: +33-169-33-3041.
E-mail address: hea@dcmr.polytechnique.fr (H.E. Audier).

1387-3806/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00084-8

and by calculation [10], of the PA at the heteroatom site of several α-radicals, namely $^{\bullet}CH_2X$ ($X = OH$, OCH_3, and NH_2). In this study, the PA_X of α-radicals were found to be lower than those of the corresponding closed shell molecules by 10–17 kcal/mol [10]. This PA lowering was explained by the resonance between the unpaired electron and an adjacent lone pair in the α-radicals. The very good agreement between experiment and calculations observed in the previous work, lead us to proceed with other distonic ions.

In the present work, the PA of the $CH_3{}^{\bullet}CHX$ ($X = OH$, OCH_3, and NH_2) α-radicals and of four β-radicals $^{\bullet}CH_2CH_2X$ ($X = OH$, OCH_3, OCH_2CH_3, and NH_2) were calculated. For the β-radicals calculated results were compared to experiment. It is possible to define two PA, which we will denote $PA_C[^{\bullet}CH_2CH_2X]$ and $PA_X[^{\bullet}CH_2CH_2X]$, depending on the site of protonation. They are defined according to Eqs. (1) and (2).

$$PA_C[^{\bullet}CH_2CH_2X] = \Delta H_f[H^+] + \Delta H_f[^{\bullet}CH_2CH_2X] - \Delta H_f[CH_3CH_2X^{\bullet+}] \qquad (1)$$

$$PA_X[^{\bullet}CH_2CH_2X] = \Delta H_f[H^+] + \Delta H_f[^{\bullet}CH_2CH_2X] - \Delta H_f[^{\bullet}CH_2CH_2XH^+] \qquad (2)$$

In the first experimental method, PA_X is directly evaluated by measuring the rates of deprotonation of the corresponding α-distonic ions in the cell of an FT-ICR cell. In the second, PA_X is indirectly determined from the $\Delta H_f[^{\bullet}CH_2CH_2XH^+]$, itself obtained by appearance energy measurements (AE) by using VUV photoionisation by the synchrotron radiation. The results of the three methods will be compared and discussed in the light of previous results obtained by experiment [11–15] or by calculation [16–18].

2. Experimental

2.1. ICR experiments

The bimolecular reactions of ions **1** to **4** were studied with a Bruker (Bremen, Germany) CMX-47X FT-ICR spectrometer equipped with a superconducting magnet (4.7 T), an ASPECT 3000 computer, an external electron ionisation source [19] and an Infinity cell [20]. The neutral reactants were introduced into the cell through a leak valve at a pressure of 2×10^{-8} to 4×10^{-8} mbar depending on the experiment, and then diluted with argon, to give a total pressure of 2×10^{-7} mbar.

The ion–molecule reactions of the distonic ions were examined after isolation and thermalisation of the $^{\bullet}CH_2CH_2XH^+$ ions formed in the external source by fragmentation of $HYCH_2CH_2CH_2X^{\bullet+}$ [1]. After transfer into the cell, the ion of interest is first isolated by radio frequency (rf) ejection of all unwanted ions. After a 1 s delay, usually sufficient to thermalise the ions by successive collisions with argon, the isolation procedure was repeated by the use of low-voltage single rf pulses (soft shots) at the resonance frequencies of the product ions formed during the relaxation time.

The exact elemental composition of all ions produced in the reactions was checked by systematic high resolution mass measurements, during which the argon pressure was reduced to 8×10^{-8} mbar.

2.2. The deprotonation method

In order to determine $PA[^{\bullet}CH_2CH_2X]$, the distonic ion $^{\bullet}CH_2CH_2XH^+$ is allowed to react with different bases B [21–23]. The measured rate constant k_{exp} for reaction (3) leads to the efficiency of the reaction, defined as the k_{exp}/k_{coll}, where k_{coll} is the theoretical rate constant calculated by a standard trajectories method [24].

$$^{\bullet}CH_2CH_2XH^+ + M \rightarrow {}^{\bullet}CH_2CH_2X + MH^+ \qquad (3)$$

Since the entropy changes in the proton transfer reactions studied here are negligible [23], we assume that when the efficiency of the proton transfer process is close to 1, $PA_X[^{\bullet}CH_2CH_2X] < PA[B]$. Conversely when the efficiency is near zero, $PA_X[^{\bullet}CH_2CH_2X] > PA[B]$. In principle, this allows us to determine $PA_X[^{\bullet}CH_2CH_2X]$ but it is shown further below that the occurrence of competing reactions complicates the problem.

2.3. Appearance energy measurements

AE and ionisation energy (IE) measurements were performed at LURE (Orsay, France), using the synchrotron radiation from the Super-ACO storage ring and the CERISES [25] experimental setup. CERISES, making use of an octopolar ion guide gives access to transit times and detection of parent and fragment ions between 10^{-3} and 10^{-4} s. Results obtained on this setup give therefore information about metastable processes, as well as fragmentation thresholds with limited effects of kinetic shifts.

2.4. Calculations

Calculations were performed as described in previous work [10,26]. Standard ab initio molecular orbital calculations were carried out using the Gaussian 98 [27] program packages. Equilibrium geometries were calculated at the MP2(FU) [28] level of theory (second-order Møller–Plesset perturbation including all electrons) using the split-valence shell 6-31G(d,p) basis set [29].

Diagonalisation of the analytically calculated Hessian matrix at the MP2(FU)/6-31G(d,p) level using the MP2(FU)/6-31G(d,p) optimised geometries was performed to calculate harmonic vibrational frequencies, from which equilibrium geometries were characterised as minima. Thermal energies (E^{298}[radical] and E^{298}[distonic ion]) were determined at 298 K (1 atm) using MP2(FU)/6-31G(d,p) vibrational frequencies scaled by 0.95.

Finally PA and GB were calculated according to the G2′MP2 method [10] which is a slightly modified G2MP2 method [30].

3. Results and discussion

The results of this work as well as those of literature [11–18] are summarised in Tables 1–3 in order to appreciate the precision of each method, to discuss the validity of the approximations done in this work, and to compare the results obtained for each β-radical and β-distonic ion with those of previously published results.

Table 1
Calculated PA of α- and β-radicals in kcal/mol

	PA_{cal}	$PA_{rad} - PA_{mol}$
CH_3CH_2OH	185.7 (185.4)[a]	
$^{\bullet}CH_2CH_2OH$	186.0	+0.3
$CH_3{}^{\bullet}CHOH$	174.3	−11.4
$CH_3CH_2OCH_3$	193.5 (193.4)[a]	
$^{\bullet}CH_2CH_2OCH_3$	194.5	+1.0
$CH_3{}^{\bullet}CHOCH_3$	183.8	−9.7
$CH_3CH_2NH_2$	218.5 (218.0)[a]	
$^{\bullet}CH_2CH_2NH_2$	216.6	−1.9
$CH_3{}^{\bullet}CHNH_2$	205.9	−12.6
$CH_3CH_2OC_2H_5$	200.0 (198.0)[a]	
$^{\bullet}CH_2CH_2OC_2H_5$	195.0	−5.0

[a] Measured value of the NIST Table [7].

3.1. Calculated GB and PA

Calculations, using the method proposed by Radom to determine PA, give very reliable results. For neutral molecules, the differences are very small between our calculated values compared to the NIST Table [7]: 0.3 kcal/mol for PA of ethanol, 0.1 kcal/mol for methylethyl ether and 0.3 kcal/mol for ethylamine. In all cases, the calculated PA lies slightly above the PA of the NIST Table [7] (Table 1). In contrast, the difference is not negligible for diethylether: 2 kcal/mol. This may be due to the fact that diethylether possesses a greater number of conformations than the preceding molecules. The distribution of the conformations involved in the experimental protonation process could be different in the neutral and in the protonated species. On the other hand, calculations are based on the energies of the most stable structure of the initial molecule and of its protonated counterpart.

The results shown in Table 1 first confirm, for the $CH_3{}^{\bullet}CHX$ ($X = OH, OCH_3$, and NH_2) α-radicals, the results previously obtained for the $^{\bullet}CH_2X$ series [10]: PA at the heteroatom site of the $CH_3{}^{\bullet}CHX$ α-radicals lies about 9.5–12.5 kcal/mol below that of the corresponding saturated molecule.

For the β-radicals, calculated PA_X are found to be very close to those of the saturated molecules. They are

Table 2
Measured and calculated values for PA of β-radicals in kcal/mol

	PA (AE)	PA (ICR)	PA (calc.)	PA (exp.)	PA (calc.)
CH_3CH_2OH		(185.4)[a]	185.7[b]		
$^{\bullet}CH_2CH_2OH$	185.8 ± 1[b]	185.0 ± 0.5[b]	186.0[b]	177.4[c], 183.6[d]	183.4[e], 180.5[f]
$CH_3CH_2OCH_3$		(193.4)[a]	193.5[b]		
$^{\bullet}CH_2CH_2OCH_3$	193.3 ± 1[b]	192.7 ± 0.5[b]	194.5[b]	189.4[g], 197.3[h]	
$CH_3CH_2NH_2$		(218.0)[a]	218.5[b]		
$^{\bullet}CH_2CH_2NH_2$		214.5 ± 1[b]	216.6[b]	215.6[i]	215.9[e]
$CH_3CH_2OC_2H_5$		(198.0)[a]	200.0[b]		
$^{\bullet}CH_2CH_2OC_2H_5$			195.0[b]		

[a] Ref. [7].
[b] This work.
[c] Ref. [11].
[d] Ref. [12].
[e] Ref. [16].
[f] Ref. [17].
[g] Ref. [13].
[h] Ref. [14].
[i] Ref. [15].

slightly higher for $^{\bullet}CH_2CH_2OH$ and $^{\bullet}CH_2CH_2OCH_3$ and 1.9 kcal/mol lower for $^{\bullet}CH_2CH_2NH_2$. The only significant difference is found for $^{\bullet}CH_2CH_2OC_2H_5$, which has a PA_X that lies 5 kcal below that of diethyl ether.

3.2. Proton transfer in the FT-ICR cell

Proton transfer from the distonic ion $^{\bullet}CH_2CH_2XH^+$ to the neutral reactant (Eq. (3)) reflects the PA of the radical $^{\bullet}CH_2CH_2X$ at the heteroatom site, and the reaction provides a method for bracketing this PA.

However, these measurements are frequently complicated by rapid competing reactions such as ionised ethylene transfer (Eq. (4)) or electron transfer (Eq. (5)) which makes impossible the use of the "Thermokinetic method" [31]. Electron transfer is also a seriously complicating factor, since it can lead to further protonation of the neutral which may introduce errors in the evaluation of the PA of the $^{\bullet}CH_2CH_2X$ radicals.

$$^{\bullet}CH_2CH_2XH^+ + M \rightarrow {}^{\bullet}CH_2CH_2M^+ + XH \qquad (4)$$

$$^{\bullet}CH_2CH_2XH^+ + M \rightarrow CH_2CH_2 + XH + M^{\bullet +} \qquad (5)$$

In order to overcome these difficulties, the results were analysed accordingly as follows:

(i) to distinguish proton transfer according to Eq. (3) from electron transfer leading to self-chemical

Table 3
Differences between calculated and measured PA of α- and β-radicals in kcal/mol

	$PA_{molecule} - PA_{radical}$ (calculated)	$PA_{molecule} - PA_{radical}$ (measured)	$\Delta PA_{calculated} - \Delta PA_{measured}$
$^{\bullet}CH_2CH_2OH$[a]	−0.3	+0.4	−0.7
$^{\bullet}CH_2CH_2OCH_3$[a]	−1.0	+0.7	−1.7
$^{\bullet}CH_2CH_2NH_2$[a]	+1.9	+3.5	−1.6
$^{\bullet}CH_2OH$[b]	13.9	15.7	−1.8
$CH_3{}^{\bullet}CHOH$[b]	11.5	14.5	−3.0
$^{\bullet}CH_2OCH_3$[b]	12.0	10.1	+1.9
$^{\bullet}CH_2NH_2$[b]	15.8	17.2	−1.4

[a] This work.
[b] Ref. [10].

ionisation of the neutral molecule, the measurements were performed, when possible, with extensively deuterium labelled neutral reactants, and in some cases with deuterium labelled distonic ions, particularly with labelling on heteroatom;

(ii) when exothermic, proton transfer generally occurs at near the collision rate. Ionised ethylene transfer can also be strongly exothermic and rapid [32]. For instance, for the reaction of the ${}^{\bullet}CH_2CH_2OH_2{}^+$ ion (*m/z* 46) with acetonitrile; the product corresponding to the protonation of the neutral molecule (*m/z* 42) and that corresponding to ionised ethylene transfer (*m/z* 69) are in comparable abundancies. In consequence, PA of the neutral reactant was taken to be greater than PA (${}^{\bullet}CH_2CH_2X$) only when protonation accounted for 50% or more of the product ion yield (excepting charge exchange). Only the most significative measurements are detailed in the text.

The ${}^{\bullet}CH_2CH_2OH_2{}^+$ ion, generated from ionised 1,3-propanediol [1], protonates slowly ($k_{prot}/k_{coll} = 0.2$) CH_3CHO (PA = 184 kcal/mol [8]). In contrast, k_{prot}/k_{coll} for ethanol (PA = 185.4 kcal/mol [8]) is about 0.6. Therefore, PA[${}^{\bullet}CH_2CH_2OH$] is close to PA[CH_3CH_2OH] or may be slightly below (185 ± 0.5 kcal/mol).

The ${}^{\bullet}CH_2CH_2O(H)CH_3{}^+$ ion, generated from ionised 1,2-dimethoxy ethane [1], slowly protonates dimethyl ether (PA = 189.5 kcal/mol [8]) and isobutene (PA = 191.9 kcal/mol [8]), but the protonation of methylethyl ether (PA = 193.4 kcal/mol [8]) is rapid. This leads us to suggest that PA[${}^{\bullet}CH_2CH_2OCH_3$] lies between 191.9 and 193.4 kcal/mol (192.7 ± 0.7 kcal/mol) and therefore about 0.7 ± 0.5 kcal/mol below that of methylethyl ether.

The ${}^{\bullet}CH_2CH_2NH_3{}^+$ ion, generated from ionised decylamine [1], rapidly protonates 2-Cl-pyridine (PA = 215.5 kcal/mol [8]) and 2-Br-pyridine (PA = 216.5 kcal/mol [8]) but does not protonate dimethyl formamide (212.3 kcal/mol [8]). This leads us to propose that PA[${}^{\bullet}CH_2CH_2NH_2$] lies between 213.5 and 215.5 kcal/mol. PA[$CH_3CH_2NH_2$] is 218.2 kcal/mol.

As the neutral may catalyse the isomerisation of the ${}^{\bullet}CH_2CH_2O(H)CH_2CH_3{}^+$ ion, generated from ionised 1,2-diethoxy ethane [1], into an α-distonic species [33], the deprotonation method is not useful in this case, the identity of the reactant ion being not known with certainty.

In conclusion, FT-ICR measurements confirm calculations (Table 2). The difference between the PA of the neutral molecule and that of the β-radical is negligible for ${}^{\bullet}CH_2CH_2OH$ and for ${}^{\bullet}CH_2CH_2OCH_3$, but non-negligible for ${}^{\bullet}CH_2CH_2NH_2$.

However, starting from these results and from those of reference [10] dealing with α-radical studied by the same methods, a closer look indicates that the difference PA[CH_3X] − PA[${}^{\bullet}CH_2X$] is usually higher when measured than when calculated (Table 3). This gap has lead us to use a third method for PA determination.

3.3. Determination of $\Delta H_f[{}^{\bullet}CH_2CH_2XH^+]$ by AE measurements

Ionised 1,3-propanediol fragments to yield the ${}^{\bullet}CH_2CH_2OH_2{}^+$ distonic ion with formaldehyde elimination [1] (Eq. (5)). It will be assumed that the first step of this fragmentation is not rate determining since corresponding to 1,5-H transfer from a methylene group to oxygen, known to be easy [4–6].

$$HOCH_2CH_2CH_2OH^{\bullet +} \rightarrow {}^{\bullet}OCH_2CH_2CH_2OH_2{}^+ \rightarrow {}^{\bullet}CH_2CH_2OH_2{}^+ + CH_2O \quad (5)$$

IE and AE measurements performed on 1,3-propanediol radical cation (Fig. 1) give IE [1, 3-propanediol] = 9.7±0.05 eV and AE [${}^{\bullet}CH_2CH_2OH_2{}^+$] = 10.6±0.05 eV. Therefore, using ΔH_f [1, 3-propanediol] = −97.7 kcal/mol and $\Delta H_f[CH_2O]$ = −26 kcal/mol [7], we find $\Delta H_f[{}^{\bullet}CH_2CH_2OH_2{}^+]$ = 172.8 ± 1.2 kcal/mol. This value lies at least 2 kcal/mol under those previously measured [11,12] or calculated [16,17] (Table 4).

The ${}^{\bullet}CH_2CH_2OHCH_3{}^+$ distonic ion was generated by dissociative photoionisation of 1,2-dimethoxy ethane (Eq. (6)). Previous work [34] indicates that the kinetic energy release for this dissociation is small

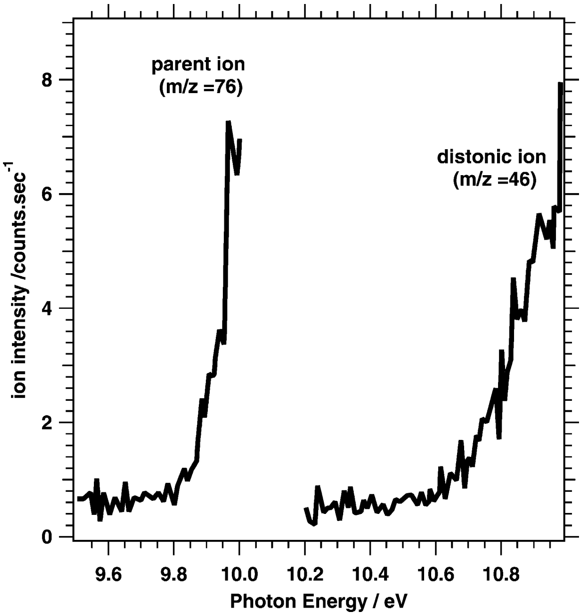

Fig. 1. IE [1,3-propanediol] and AE [$^{\bullet}CH_2CH_2OH_2{}^{+}$] measured by using VUV photoionisation.

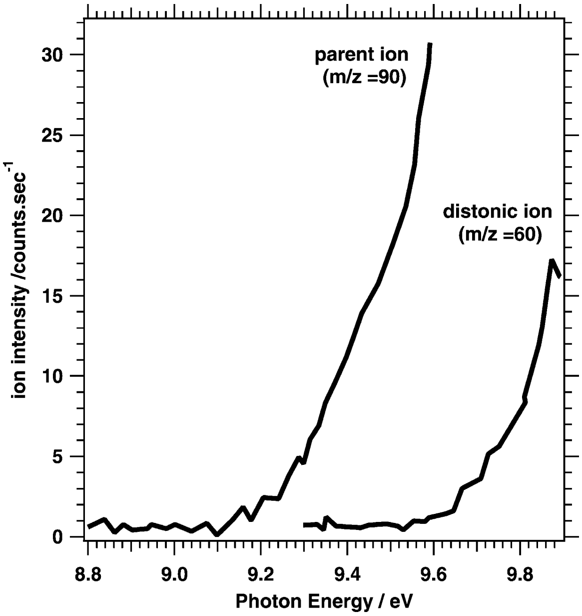

Fig. 2. IE [dimethoxy ethane] and AE [$^{\bullet}CH_2CH_2OHCH_3{}^{+}$] measured by using VUV photoionisation.

(18 meV) which leads to postulate that the back energy is negligible.

$$\begin{aligned}&CH_3OCH_2CH_2OCH_3{}^{\bullet +}\\&\quad\rightarrow {}^{\bullet}CH_2OCH_2CH_2O(H)CH_3{}^{+}\\&\quad\rightarrow {}^{\bullet}CH_2CH_2OHCH_3{}^{+} + CH_2O \qquad (6)\end{aligned}$$

IE and AE measurements (Fig. 2) give IE [1,2- dimethoxy ethane] $= 9.2 \pm 0.05$ eV (kcal/mol) and AE [$^{\bullet}CH_2CH_2OCH_3{}^{+}$] $= 9.6 \pm 0.05$ eV. Therefore, using ΔH_f[1, 2-dimethoxy ethane] $= -81$ kcal/mol [7] and $\Delta H_f[CH_2O] = -26$ kcal/mol [7], we find $\Delta H_f[{}^{\bullet}CH_2CH_2OHCH_3{}^{+}] = 166.4 \pm 1$ kcal/mol. This value lies about 4 kcal/mol under that previously measured by Holmes and co-workers [13] but 4 kcal/mol above that previously evaluated by McAdoo et al. [14] (Table 1).

Table 4
$\Delta H_f[{}^{\bullet}CH_2CH_2XH^{+}]$ in kcal/mol

	X = OH	X = OCH_3
This work (experiment)	172.8	166.4
Literature (experiment)	181.2[a], 175.0[b]	170.3[c], 162.4[d]
Literature (calculation)	175.2[e], 178.1[f]	

[a] This work; Ref. [11].
[b] Ref. [12].
[c] Ref. [13].
[d] Ref. [14].
[e] Ref. [16].
[f] Ref. [17].

Starting from the measured value of $\Delta H_f[{}^{\bullet}CH_2CH_2XH^{+}]$, $PA_X[{}^{\bullet}CH_2CH_2X]$ was evaluated from Eq. (7):

$$PA_X[{}^{\bullet}CH_2CH_2X] = \Delta H_f[H^{+}] + \Delta H_f[{}^{\bullet}CH_2CH_2X] - \Delta H_f[{}^{\bullet}CH_2CH_2XH^{+}] \qquad (7)$$

$\Delta H_f[{}^{\bullet}CH_2CH_2X]$ are not known. They were evaluated by assuming that in β-radicals, the radical does not interact with the lone pair of the heteroatom. In other words, it has been considered that the difference ($\Delta H_f[{}^{\bullet}CH_2CH_2X] - \Delta H_f[CH_3CH_2X]$) is equal to the ($\Delta H_f[{}^{\bullet}CH_2CH_2CH_3] - \Delta H_f[CH_3CH_2CH_3]$). This approximation leads to the PA_X reported in Table 3.

Assuming that this hypothesis is good, the so determined PA are in very good agreement with calculation for the two systems studied even if calculations yield, as for the calculated neutral molecules, a slightly higher value.

4. Conclusion

1. This work confirms that PA of α-radicals lie far below those of the corresponding saturated molecules.
2. In contrast, as a first and rough evaluation, it can be considered that a radical in the β-position, has a negligible influence on the PA at heteroatom.
3. A good value for PA[$^{\bullet}CH_2CH_2OH$] is probably close to 185.8 ± 0.5 kcal/mol, which is higher than the values previously published [11,12,16,17]. PA[$^{\bullet}CH_2CH_2OCH_3$] was found to be 193.3 ± 0.5 kcal/mol which falls in the range of the previous measurements and evaluations [13,14].
4. The uncertainty is greater for PA[$^{\bullet}CH_2CH_2NH_2$]. From the results of this work and from those of literature [13,14], PA = 116 ± 1 kcal/mol can be adopted.
5. Finally, it is probable that, in the case of the deprotonation of distonic ions, for unexplained reasons, the kinetic method could underestimate the PA of radicals by about 1 kcal/mol.

Acknowledgements

We would like to thank the technical staff of LURE for operating the Super-ACO storage ring.

References

[1] S. Hammerum, Mass Spectrom. Rev. 7 (1988) 123.
[2] (a) K.M. Stirk, L.K.M. Kiminkinen, H.I. Kenttämaa, Chem. Rev. 92 (1992) 1649;
(b) R.L. Smith, P.K. Chou, H.I. Kenttämaa, Structure and reactivity of selected distonic radical cations, in: T. Baer, C.-Y. Ng, I. Powis (Eds.), The Structure, Energetics and Dynamics of Organic Ions, Wiley, Chichester, 1996, p. 197.
[3] H.E. Audier, J. Fossey, D. Leblanc, P. Mourgues, V. Troude, in: K.R. Jennings (Ed.), Intermediate in Ionic Gas Phase Chemistry. II. Distonic Ions in Fundamental and Applications of Gas Phase Ion Chemistry, 1999, p. 1.
[4] (a) G. Sozzi, H.E. Audier, A. Milliet, Bull. Soc. Chim. II (1984) 292;
(b) G. Bouchoux, N. Choret. Int. J. Mass Spectrom. 201 (2000) 161.
[5] H.E. Audier, G. Bouchoux, Y. Hoppilliard, A. Milliet, Org. Mass Spectrom. 57 (1982) 381.
[6] H.E. Audier, G. Sozzi, J.P. Denhez, Tetrahedron 42 (1986) 1179.
[7] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data, 17 (Suppl. 1) (1988).
[8] S.G. Lias, J.F. Liebman, R.D. Levin, J. Phys. Chem. Ref. Data 13 (1984) 695.
[9] J.L. Holmes, F.P. Lossing, Int. J. Mass Spectrom. Ion Process. 92 (1989) 111.
[10] H.E. Audier, J. Fossey, P. Mourgues, D. Leblanc, S. Hammerum, Int. J. Mass Spectrom. Ion Process. 157 (1996) 275.
[11] J.L. Holmes, F.P. Lossing, J.K. Terlouw, P.C. Burgers, J. Am. Chem. Soc. 104 (1982) 2931.
[12] P.C. Burgers, J.L. Holmes, J.K. Terlouw, B. van Baar, Org. Mass Spectom. 20 (1985) 202.
[13] J.R. Cao, M. George, J.L. Holmes, Org. Mass Spectrom. 2 (1991) 481.
[14] D.J. McAdoo, C. Hudson, V.M.S. Ramanujaman, M. George, Org. Mass Spectrum. 28 (1993) 1210.
[15] C. Wesdemiotis, P.O. Danis, R. Feng, J. Tso, F.W. McLafferty, J. Am. Chem. Soc. 107 (1985) 8059.
[16] W.J. Bouma, R.H. Nobes, L. Radom, J. Am. Chem. Soc. 105 (1983) 1743.
[17] R. Postma, P.J.A. Ruttink, J.K. Terlouw, J.L. Holmes, P.C. Burgers, Chem. Phys. Lett. 123 (1986) 409.
[18] B.F. Yates, L. Radom, J. Am. Chem. Soc. 109 (1987) 2910.
[19] P. Kofel, M. Allemann, H.P. Kellerhals, K.P. Wanczek, Int. J. Mass Spectrom. Ion Process. 65 (1985) 97.
[20] P. Caravatti, M. Allemann, Org. Mass Spectrom. 26 (1991) 514.
[21] E. Rolli, Thèse de doctorat, Ecole Polytechnique Fédérale de Lausanne, 1987.
[22] H.-H. Büker, H.F. Grützmacher, Int. J. Mass Spectrom. Ion Process. 109 (1991) 95.
[23] G.S. Gorman, J. Amster, Org. Mass Spectrom. 28 (1993) 1602.
[24] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[25] O. Dutuit, C. Alcaraz, D. Gerlich, P.M. Guyon, J.W. Hepburn, C. Metayer-Zeitoun, J.B. Ozenne, M. Schweizer, T. Weng, Chem. Phys. 109 (1996) 177.
[26] B.J. Smith, L. Radom, J. Am. Chem. Soc. 115 (1993) 4885.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Gaussian Inc., Pittsburgh, PA, 1998.
[28] (a) C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618;
(b) R. Krishnan, J.A. Pople, Int. J. Quantum Chem. Symp. 14 (1980) 91.

[29] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

[30] L.A. Curtiss, K. Raghavachari, J.A. Pople, J. Chem. Phys. 98 (1993) 1293.

[31] G. Bouchoux, J.-Y. Salpin, D. Leblanc, Int. J. Mass Spectrom. Ion Process. 153 (1996) 37.

[32] H.E. Audier, J. Fossey, D. Leblanc, P. Mourgues, Bull. Soc. Chim. Fr. 133 (1996) 59.

[33] V. Brenner, A. Milliet, P. Mourgues, G. Ohanessian, H.E. Audier, J. Phys. Chem. 99 (1995) 10837.

[34] A. Milliet, G. Sozzi, H.E. Audier, Org. Mass Spectrom. 27 (1992) 787.