

Internal energy effects on charge stripping spectra of $[C_7H_8]^{\cdot+}$ and $[C_5H_6]^{\cdot+}$ radical cations

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Abstract

MS/MS/MS experiments were carried out using a large-scale tandem mass spectrometer featuring a sector-quadrupole-sector geometry to probe the $C_7H_8^{\cdot+}$ and $C_5H_6^{\cdot+}$ radical cations. These ions (m/z 92 and 66) were produced from metastable ionized precursors or charge exchange reactions in the quadrupole cell; subsequent fragmentations and double ionization were performed after mass-selection and collisional activation with oxygen. Charge stripping spectra show significant variations in the relative intensities of the same doubly charged species generated in different ways. These variations are likely to be associated with the inherent differences in internal energy content. © 2005 Elsevier B.V. All rights reserved.

1. Introduction

Collisional ionization (or charge stripping, CS) and collisional activation (CA) spectra of molecular ions are usually recorded simultaneously in a single experiment, for instance during the scanning of an electric sector field of a reversed geometry mass spectrometer [1,2]. It has been shown that the CS spectra allow stable isomeric ions to be distinguished even in the cases where the CA technique fails [3–5]. Due to the almost generally lower intensity in the mass spectra of the doubly charged species, as compared to that of singly charged species, accidental superimposition tends to suppress the CS information, which can nevertheless be restored in making use of a special instrumentation [6,7].

The important factors, which affect the relative abundances of the peaks in a CS spectrum, have been analyzed elsewhere [8]. These include the nature of the collision gas [9], the slit settings [4] and the translational energy of the singly charged parent ions [10]. We wish to report in this

Letter an additional factor affecting these relative abundances, namely the average internal energy deposited in the singly charged precursors before collisional double ionization occurs. The ionic systems chosen, as for a case study, are the $C_7H_8^{\cdot+}$ and $C_5H_6^{\cdot+}$ radical cations, that have been generated by charge exchange reactions or by dissociation of metastable precursors.

2. Experimental

The mass spectra were recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of $cE_1B_1cE_2qcE_3B_2cE_4$ geometry (E_i stands for an electric sector, B_i for a magnetic sector, q for a quadrupole collision cell, and c for a ‘conventional’ collision cell). Typical conditions of the experiments have been reported elsewhere [11]. The installation of the RF-only quadrupole collision cell (Q cell) inside the instrument between E_2 and E_3 has also been described [12]. Briefly, this modification allows the associative ion-molecule reactions to be studied, along with the study of low energy (ca. 20–30 eV) collision induced dissociations of decelerated ions, and the study of metastably generated ions but retaining

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the full initial kinetic energy of the precursors. All the samples were commercially available and used without any further purification. Tables 1 and 2 collect all the samples used in the present study, together with the identity of the neutral molecule lost in the dissociative ionization experiments and the reagents employed in the charge exchange experiments.

All calculations are performed with the GAUSSIAN98 set of programs [13]. Geometrical parameters of the structures considered are initially optimized and subsequently characterized by harmonic vibrational analyses using the density functional theory with the popular hybrid B3LYP functionals [14,15], in conjunction with the d,p-polarized 6-311++G(d,p) basis set and the unrestricted formalism (UB3LYP) for open-shell systems. The zero point energy corrections (ZPE) to relative energies are also obtained at this level. To compute accurate relative energies, we have employed the higher-level theoretical G2 method and in particular the G2(MP2) modified version. This computational method is amply recognized as being able to reproduce or predict unknown thermochemical data of compounds containing first- and second-row atoms with a target accuracy of about 12 kJ mol⁻¹ [16–18].

3. Results and discussion

C₇H₈⁺ (*m/z* 92) ions are generated in high abundance during the unexpected decarboxylation of *metastable* methyl benzoate ions and this reaction was shown to start with a 1,4-hydrogen shift from the methyl group on the carbonyl oxygen atom [19]. In order to complete the overall reaction sequence, a determination of the actual struc-

ture(s) of the product ions is necessary and thus constitutes the driving force of the present study.

In the same vein, the structure of the C₇H₈⁺ ions formed from *metastable* phenylacetic acid ions (loss of CO₂), phenylacetaldehyde ions (loss of CO), phenylacetamide ions (loss of HNCO) and phenylacetone ions (loss of ketene) has also been investigated.

It has been reported [4] that the most stable C₇H₈⁺ isomers, namely the ionized toluene **1**⁺ and isotoluene **2**⁺, can be identified by collisional activation/ionization. Ionized isotoluene **2**⁺ was produced by metastable decomposition of ionized *n*-butylbenzene (loss of propene) and identified by an increased intensity of the *m/z* 78 peak corresponding to the loss of a methylene CH₂, and by a marked difference on the relative intensities in the doubly charged ion region.

In order to avoid possible instrumental influences (for instance different slits settings), we have recorded again all the MS³ spectra using the following procedure: (1) mass-selection and deceleration of the precursor ions in the quadrupole cell, (2) spontaneous decomposition within the cell and re-acceleration of the ionized products at 8 kV, (3) mass-selection of the *m/z* 92 ions using a combination of two (E, B) sectors, (4) collisional activation with oxygen and (5) recording of the products by scanning the field of the last electric sector. Moreover, toluene molecular ions **1**⁺ were also prepared directly in the quadrupole by use of a charge exchange reaction (CE) between ionized furan prepared in the ion source and neutral toluene injected in the quadrupole. Given the relative ionization energies between furan and toluene (IE(furan) = 8.88 eV and IE(toluene) = 8.82 eV) [20], it was expected that the reaction should be quasi-thermoneutral and it was indeed observed that *m/z* 92 ions were generated in high yield (about 3% of the un-reacted ion peak), whereas *m/z* 91 ions were completely absent. For the sake of comparison, ionized cycloheptatriene **3**⁺, another C₇H₈⁺ isomer, was also prepared by charge exchange, the reagent species being in this case ionized dimethyl sulfide (IE(dimethyl sulfide) = 8.69 eV and IE(cycloheptatriene) = 8.29 eV) [20]. This procedure thus presents an advantage over more ‘classical’ MS³ experiments involving collisional activation at the same high (8 keV) translational energy.

All the MS³ spectra were collected in Fig. 1. The spectra of the toluene **1**⁺ and presumed isotoluene **2**⁺ ions were found to be quasi identical but with a reduced intensity of the peaks in the *m/z* 70–80 region of the second case. In agreement with the earlier data of Burgers et al. [4], within this region, the peak at *m/z* 78 is found somewhat enhanced as compared to that at *m/z* 77 in the case of the *n*-butylbenzene precursor. Our results are, however, less consistent with the literature data as far as charge stripping is concerned (see Fig. 1). The following considerations can thus be derived from the obtained CA and CS data:

- (1) Spectra (a) and (b) are attributed to isotoluene **2**⁺ and toluene **1**⁺ ions, respectively.

Table 1
Precursors used for generating the [C₇H₈]⁺ radical cations

Precursors of [C ₇ H ₈] ⁺	Neutral lost	Charge exchange reagent
Toluene	–	Furan
Toluene	–	Carbon disulfide
Toluene	–	Methanol
		Dichloromethane
Cycloheptatriène	–	Dimethyl sulfide
<i>n</i> -Butyl benzene	Propene	–
Methyl benzoate	Carbon dioxide	–
Neopentyl benzoate ^a	Carbon dioxide	–
Phenylacetic acid	Carbon dioxide	–
Phenyl acetaldehyde	Carbon monoxide	–
Phenyl acetamide	Isocyanic acid	–
Phenyl acetone	Ketene	–

^a [neopentyl benzoate–isobutene]⁺ ions.

Table 2
Precursors used for generating the [C₅H₆]⁺ radical cations

Precursors of [C ₅ H ₆] ⁺	Neutral lost	Charge exchange reagent
Cyclopentadiene	–	Dimethylsulfide
Cyclopentadiene	–	Nitrobenzene
Cyclopentadiene	–	Dichloromethane
Phenol	Carbon monoxide	–
Thiophenol	Carbon monosulfide	–
Aniline	Isocyanhydric acid	–

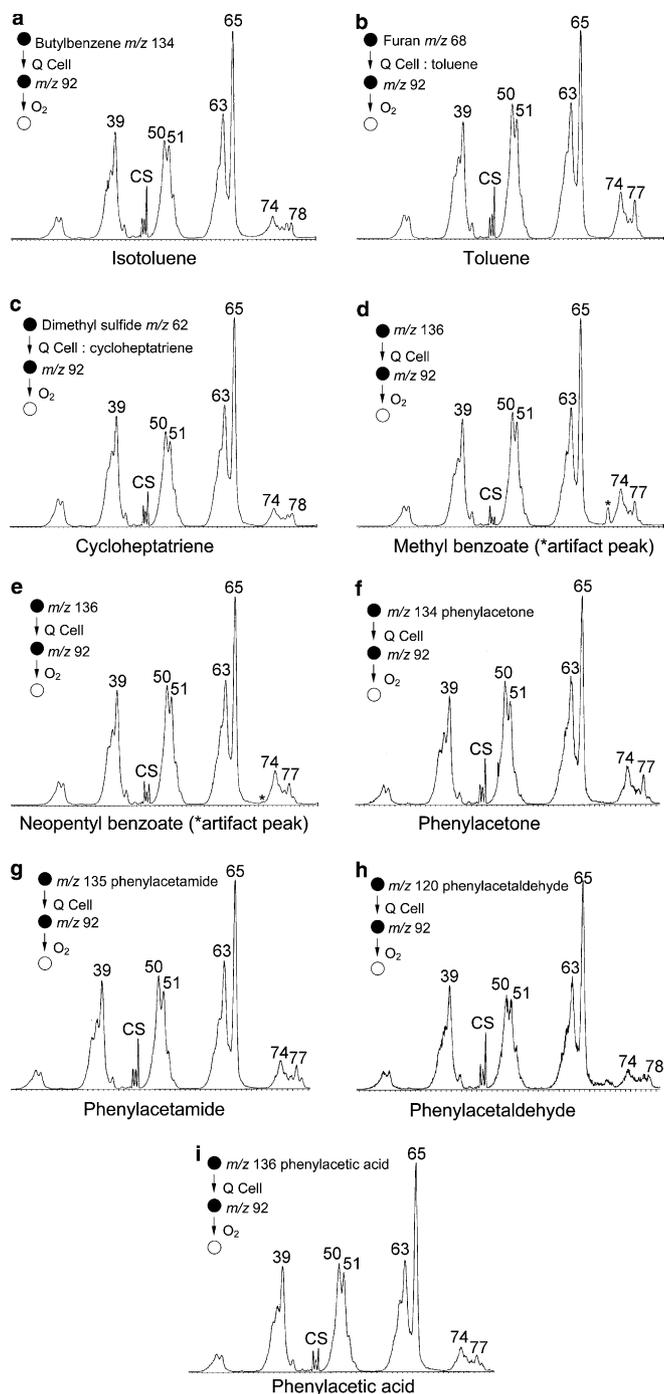


Fig. 1. MS/MS/MS spectra (O_2 collision gas) of m/z 92 ions prepared in the quadrupole cell by: (a) propene loss from ionized *n*-butylbenzene, (b) charge exchange between ionized furan and toluene, (c) charge exchange between ionized dimethylsulfide and cycloheptatriene, (d) CO_2 loss from ionized methyl benzoate, (e) CO_2 loss from (M-isobutene) $^{+}$ ions generated from neopentyl benzoate, (f) CH_2CO loss from ionized phenylacetone, (g) HNCO loss from ionized phenylacetamide, (h) CO loss from ionized phenylacetaldehyde and (i) CO_2 loss from ionized phenylacetic acid.

(2) The CA spectrum (d) indicates that the m/z 92 ions of methyl benzoate are actually toluene 1^{+} ions, but some variations in the relative abundance of the doubly-charged ions are nevertheless detected.

(3) Upon loss of CO_2 , ionized phenylacetic acid also produces toluene 1^{+} ions (spectrum i); the presence of some isotoluene 2^{+} ions cannot however completely be ruled out as a very slight increase of the m/z 78 peak was observed. Similar conclusions can also be drawn for the distonic ions [19] derived from neopentyl benzoate (spectrum e), *vide infra*.

(4) It is also apparent from the data that both toluene 1^{+} and cycloheptatriene 3^{+} ions, generated by a ‘soft’ charge exchange reaction, give rise to different CA spectra, at least in the m/z 70–80 region with a more intense m/z 78 peak in the cycloheptatriene case. It is worthy of note that the CA spectra of the corresponding ions generated in the ion source were found to be identical.

Charge exchange with neutral toluene in the quadrupole cell was also realized with two other compounds having each an IE larger than that of furan, namely carbon disulfide (IE = 10.1 eV) and dichloromethane (IE = 11.33 eV) [20]. Small but reproducible differences were observed in the relevant CS spectra (see Fig. 2). The intensity of the m/z 46 peak decreases with an increasing exothermicity of the charge transfer reaction. In the case of metastable methyl benzoate ions, the relative intensity of the CS peak (m/z 46) is even more reduced compared to the doubly-charged fragment m/z 45 (Fig. 2d). This trend may suggest that the loss of CO_2 is preceded by large energy barrier(s), and this is confirmed by theoretical calculations [21]. In this particular system at least, CS spectra should therefore be used with much caution for the attribution of ion structures.

The proposed decarboxylation mechanism of phenylacetic acid radical cation is, after the C– CO_2H cleavage, a hydrogen transport by protonated carbon dioxide to the basic sites of the benzyl radical, and the so-formed beam of m/z 92 ions seems to be a mixture of ionized toluene 1^{+} and isotoluene 2^{+} by comparison of the MS^3 spectra (Fig. 1). Three other analogous compounds have also been studied, including phenylacetaldehyde, phenylacetamide, and phenylacetone. The *metastable* molecular ions of these compounds lose neutral carbon monoxide (CO), isocyanic acid (HNCO) and ketene (CH_2CO), respectively, all generating m/z 92 ions. The resulting spectra of the MS^3 experiments performed on these m/z 92 ions are also shown in

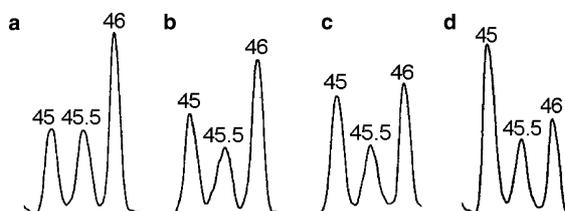


Fig. 2. Charge stripping spectra (m/z 46, 45.5, 45) in MS^3 spectra (O_2 collision gas) of m/z 92 ions prepared in the quadrupole cell by charge exchange of: (a) ionized furan, (b) carbon disulfide, (c) dichloromethane and neutral toluene and (d) metastable fragmentation of methyl benzoate molecular ions.

Table 3
Proton affinity values of neutrals lost from phenylacetic acid derivatives and *n*-butylbenzene during the formation of the *m/z* 92 ions

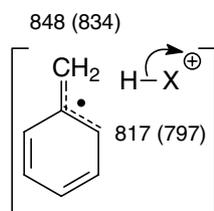
Neutrals	Proton affinities		
	Calculated (kJ mol ⁻¹)		Experimental [20] (kJ mol ⁻¹)
	B3LYP/6-311++G(d,p)	G2(MP2)	
Carbon dioxide	525	536	541
Carbon monoxide	582	587	594
Propene	762	739	752
Isocyanic acid	711	718	753
Ketene	802	820	825

Fig. 1. These reactions apparently follow a similar mechanism in which the key-intermediate is an ion–benzyl radical complex. A major difference is the proton affinity of the neutral lost (Table 3). The proton affinities follow the sequence: ketene > isocyanic acid > propene > carbon monoxide > carbon dioxide.

By calculations at the B3LYP/6-311++G(d,p) level of quantum chemical theory, we have determined the PA's of the benzyl radical whose predominant protonation sites correspond to the exocyclic methylene and its *ortho* position. In order to obtain PA's closer to the experimental values given in the literature (see Table 3), we have performed the same calculations using the G2(MP2) method. Table 3 shows indeed that the calculated PA values derived by the G2(MP2) method are situated in the range of expected error of ± 12 kJ mol⁻¹ with respect to values given in the literature (except for HNCO).

Two important conclusions can be derived from the comparison of the data of Table 3 and Scheme 1: the regioselectivity of the proton transfer and the overall exothermicity of the process. It is indeed expected that the *m/z* 92 ions formed by loss of ketene form ionized phenylacetone, if occurred as depicted in Scheme 1, should be pure toluene 1⁺ radical cations, with a small excess energy content as the ketene's PA lies between the two sites PA's of the benzyl radical. Protonated ketene will therefore transfer a proton to the benzylic site. On the contrary, both sites are prone to be protonated during the loss of isocyanic acid (from ionized phenylacetamide), carbon monoxide (from ionized phenylacetaldehyde) and carbon dioxide (from ionized phenylacetic acid), giving mixtures of both ionized toluene 1⁺ and isotoluene 2⁺.

Experimental results are thus supported by theoretical predictions: formation of ionized toluene 1⁺ by ketene



Scheme 1. Proton affinities at two sites of benzyl radical calculated at the B3LYP/6-311++G(d,p) and G2(MP2) (values in parenthesis) levels. Experimental value: PA = 831 kJ mol⁻¹ [20].

loss, and formation of a mixture of ionized toluene 1⁺ and isotoluene 2⁺ by HNCO or CO₂ losses. However, decarbonylation of phenylacetaldehyde does not afford a mixture of the two *m/z* 92 ion isomers (as predicted on the basis of the PA of CO), but exclusively ionized isotoluene 2⁺. This reaction does therefore not involve a hydrogen transport by carbon monoxide, but rather follows another mechanism. Metastable peak shape analysis (vide infra) supports this conclusion.

A *m/z* 92 peak shape analysis was performed from the MIKE spectra of the different molecular ions. In the case of phenylacetone and phenylacetamide, the metastable peaks are characterized by simple gaussian profiles and small kinetic energy releases, respectively, 12 and 22 meV as measured at half-height (*T*₅₀). This is in agreement with fragmentations involving ion-radical complexes [22]. Phenylacetaldehyde features however a flat-topped peak (*T*₅₀ = 284 meV) indicating the possible occurrence of a five-membered transition state which transfers the aldehydic hydrogen onto the ring. Such a concerted mechanism could certainly convert a substantial part of the internal energy of the transition state into translational energy [23,24]. The behavior of metastable phenylacetic acid ions is intermediate of the two previous cases (*T*₅₀ = 139 meV); the metastable peak presents a broad profile. Two different mechanisms may compete with each other in the metastable window, one involving an ion-radical complex and another involving a concerted six-member ring mechanism.

It is thus apparent that a clear-cut distinction between toluene 1⁺ and isotoluene 2⁺ ions can hardly be achieved when based on relative abundances of fragment ions in the *m/z* 70–80 region of the MS³ spectra. CS spectra also show some differences, but these differences could be associated with different internal energy contents. As for a support for this last statement, we have investigated another system, the C₅H₆⁺ radical cations.

Ionized cyclopentadiene and acyclic isomers have been differentiated by their charge stripping spectra [8]. Surprisingly, the C₅H₆⁺ radical cations derived from dissociative ionization of phenol (loss of CO) and thiophenol (loss of CS), that are apparently closely related fragmentations, largely differ from each other. It was thus expected that, as in the previous C₇H₈⁺ case, internal energy effects also occurred. To probe further, we have prepared the cyclopentadiene ions by charge exchange with various ionized targets and the resulting MS³ spectra were compared to those of C₅H₆⁺ ions generated by metastable dissociation of phenol, thiophenol and aniline molecular ions. The CS data are collected in Table 4.

In Table 4, the entries A–C refer to the relative intensities of doubly charged species. It is apparent from these data that an increased exothermicity of the charge exchange reaction favors the abundance of the doubly charged fragments, relative to the *m/z* 33 ions. Such an evolution is even more pronounced in the case of the metastable phenol molecular ions (entry D), where the energy

Table 4
Charge stripping spectra of $C_5H_6^+$ radical cations

m/z	33	32.5	32	31.5	31	m/z 33/ $\sum m/z$ 32.5–31 ^b
A ^a	100	26	19	11	28	1.04
B	100	32	27	12	29	1.00
C	100	39	58	30	69	0.51
D	69	24	83	66	100	0.25
E	100	35	47	24	63	0.59
F	100	30	28	14	32	0.96

^a A: charge exchange between ionized dimethyl sulfide (IE = 8.69 eV) and cyclopentadiene (IE = 8.56 eV); B: charge exchange between ionized nitrobenzene (IE = 9.86 eV) and cyclopentadiene; C: charge exchange between ionized dichloromethane (IE = 11.32 eV) and cyclopentadiene; D: metastable carbon monoxide loss from the molecular ions of phenol; E: metastable hydrogen isocyanide loss from the molecular ions of aniline; F: metastable carbon monosulfide loss from the molecular ions of thiophenol. Ionization energies from Ref. [20].

^b Intensity ratios between the charge stripping peak and the sum of the doubly charged fragments.

barrier for tautomerization by 1,3-hydrogen shift was estimated theoretically to be about 276 kJ mol⁻¹ and 160 kJ mol⁻¹ higher in energy than ionized cyclopentadiene plus CO (see [21] and references therein). Closely related reactions eliminating a vinylidene-type fragment have also been found from metastable molecular ions of thiophenol and aniline. Actually, the neutral :C=S is found to be eliminated from ionized thiophenol, and neutral :C=NH eliminated from ionized aniline. The barrier height for tautomerization of thiophenol ions amounts to 214 kJ mol⁻¹, that is 104 kJ mol⁻¹ lower in energy than the final products (ionized cyclopentadiene plus CS), while the corresponding barrier in the case of aniline amounts to 322 kJ mol⁻¹, that is 11 kJ mol⁻¹ higher in energy than ionized cyclopentadiene plus :CNH. The loss of isocyanhydric acid, preferred to the more stable cyanhydric acid, has been proved experimentally [25]. It is thus clear, *at least qualitatively*, that the internal energy deposited in the products will follow the order phenol > aniline > thiophenol and this is reflected in the relative abundance of the m/z 33 ions compared to the doubly charged fragment ions (m/z 32.5–31). In other words, it appeared that the internal energy excess deposited in the $C_5H_6^+$ ($C_7H_8^+$) radical cations during their formation (metastable decompositions or charge exchange processes) leads to a partial isomerization by ring opening of the initially obtained cyclopentadiene ions. This is not straightforward on the basis of CA experiments but readily demonstrated by analysis of the CS data.

In summary, we have demonstrated in this Letter that internal energy deposited in molecular ion generated during MS experiments induces a marked effect on its charge stripping spectrum. This effect should be taken into

account when analyzing the relative abundances of CS peaks.

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