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Investigations of the fragmentation pathways of benzylpyridinium ions under ESI/MS conditions

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Benzylpyridinium ions are often used as 'thermometer ions' in order to evaluate the internal energy distribution of the ions formed in sources of mass spectrometers. However, the detailed fragmentation pathways of these parent ions were not well established. In particular, fragmentation involving a rearrangement (RR) process may be influencing the simulated distribution curves. In a previous study, we suggested that such RR actually occurred under electrospray ionization/mass spectrometry (ESI/MS) and fast atom bombardment/mass spectrometry (FAB/MS) experiments. Here, we present a systematic study of different substituted benzylpyridinium ions. Theoretical calculations showed that RR fragmentation leading to substituted tropylium ions could occur under 'soft ionization' conditions, such as ESI or FAB. Experimental results obtained under gas-phase reactivity conditions. Mass-analyzed kinetic experiments were also carried out to gain information on the reaction pathways that actually occur, and these experimental results are in agreement with the reaction pathways theoretically proposed. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: benzylpyridinium ions; ion/molecule reactions; mass spectrometry; tropylium ions; DFT calculations

Introduction

An important aspect in monitoring the properties of gaseous ions and understanding their reactivities is the internal energy content imposed to the species emerging from the ion source. The classical method of electron ionization, for example, is well known to generate 'hot' ions including excited electronic states several electron volts above the ground-state species.^[1,2] In the case of electrospray ionization/mass spectrometry (ESI/MS), the internal energy of the parent ions may depend on the instruments.^[3–7] In order to compare the mass spectra obtained using different mass spectrometers, some methods were proposed to calibrate the instruments with another.^[3–9]

In these earlier studies, substituted benzylpyridinium chloride salts ($R-C_6H_4CH_2-NC_5H_5^+X^-$) were used as molecular thermometers. To this end, De Pauw fitted the internal energy distribution of ions formed under fast atom bombardment (FAB) and electrospray ionization (ESI) source conditions^[3-6] using the Mass Kinetics software^[7-9] to determine the distribution of internal energies deposited in desolvated ions produced by ESI source conditions.^[3] For these studies, substituted benzylpyridinium compounds were used because it was considered that (1) their fragmentation occurred through a common direct bond cleavage (DC) between N and C to yield stable substituted benzyl cation and (2) this DC was not accompanied by a significant reverse activation energy process.^[3,4,6,10,11]

However, based on mass-analyzed kinetic energy release experiments of *para*-H-, *para*-CH₃-, and *para*-OCH₃-substituted benzylpyridinium ions,^[12] we previously proposed that tropylium ions can also be formed during the fragmentation of benzylpyridinium ions generated by FAB. Complementary calculations supported the existence of a reaction pathway for the rearrangement to tropylium. However, these first experimental results concerned only FAB ionization sources. Another preliminary study dealing with *para*-H, *para*-CH₃, and *para-t*-butyl benzylpyridinium ions suggested that the formation of tropylium ions could occur from some substituted benzylpyridinium ions even under ESI/MS conditions.^[13] However, the precise influence of the nature and the position of the substituent on the activation energies of the rearrangement (RR) processes *versus* DCs remained unclear. Owing to the frequently chosen benzylpyridinium ion for the calibration studies, the knowledge of those compounds which undergo RR prior to or in the course of fragmentation is thus of prime importance.

In this report, we present a systematic study of the fragmentation for a series of substituted benzylpyridinium ions, i.e. the parent compound (*p*-H) and the derivatives *o*-CH₃, *m*-CH₃, *p*-CH₃, *p*-F,

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p-Cl, *p*-CN, *p*-CF₃, *m*-OCH₃ and *p*-NO₂.^[3,4,6,11] In addition to these compounds, traditionally used as 'thermometer ions', studies of multiply methylated derivatives are likely to provide additional insights into the fragmentation pathways; *p*-(*t*-butyl), 3,5-dimethyl, 2,5-dimethyl, 2,4-dimethyl and pentametyl benzylpyridiniums were also included in both the experimental and theoretical studies in this present work.

Of particular importance with regard to the structures of the resulting fragment ions are earlier experiments of Dunbar, Ausloos and McLafferty, who showed that some $C_7H_7^+$ ions undergo consecutive reactions with neutral toluene.^[14–20] More precisely, these ion–molecule reactions proved that the tropylium ions are unreactive toward toluene, whereas the benzylium ions mediate a formal CH_2^+ .^[14–32] Accordingly, we employ this method to determine whether tropylium, benzylium or both isomers are formed during the fragmentation of benzylpyridinium compounds.

Experimental and Theoretical Methods

The details of the theoretical methodology have been described elsewhere.^[12] Briefly, *ab initio* and density functional theory (DFT) calculations were performed using the Gaussian 03 software.^[33] All optimizations and frequency calculations were carried out at the B3P86/6-31+G^{*} level, unless otherwise specified. First, the different structures considered for this study were built up using the results previously obtained from the intrinsic reaction coordinate (IRC) calculations in the case of the *p*-CH₃ and *p*-OCH₃ benzylium ions.^[12] Full optimizations were carried out to know the structures of the initial states, the final states and the intermediates. Transition structures were searched via partial optimizations followed by QST3 calculations. The energies reported below include zero point energy (ZPE).

The samples of substituted benzylpyridinium salts were prepared by treating the corresponding benzyl halides with excess anhydrous pyridine at 60 °C for 3 h. After the reaction, the excess of pyridine was evaporated to give a solid. The compounds were analyzed by mass spectrometry and used without further purification.^[4] Reagents for synthesis, toluene and 3-nitrobenzylalcohol (NBA), were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France).

For most mass-spectrometric experiments, we used a modified Finnigan LCQ Deca XP Plus (ThermoFinnigan, San Jose, CA, USA) ion-trap mass spectrometer equipped with an ESI source and operated in positive ion mode. Nitrogen was used as the nebulizer gas. The operating conditions were set as follows: spray voltage, 5.0 kV; capillary voltage, 40 V; heated capillary temperature, 75 °C; tube lens offset, 55 V and sheath gas flow rate, 10 arbitrary units. The samples were introduced into the ESI source via a needle at a flow rate of 5 μ l/min. Mass spectra were recorded from m/z 80 to 2000. Collision-induced dissociation (CID) of the mass-selected precursor ions was achieved by rf-excitation of the trapped ions using the helium buffer gas as the collision partner. The collision energy was optimized for each experiment and is expressed in terms of the manufacturer's normalized collision energy (%). The range from 0 to 100% corresponds to a resonance excitation a.c. signal of 0-2.5 V (zero-to-peak) at the secular frequency of the interest ion.^[34] This energy depends on the m/z value of the parent ion, but this value is not expressed directly in voltage units.

lon/molecule reactions in the trap were performed using the CID routine of the software while setting the activation amplitude

to 0%. For the introduction of toluene as a neutral reaction partner, the helium inlet of the ion-trap mass spectrometer was extended by a reservoir containing liquid toluene over which the helium gas was swept. The relative toluene content in the helium can be varied by cooling of the reservoir. In addition to toluene, $C_6H_5CH_3$, $C_6H_5CD_3$ and $C_6D_5CD_3$ were also employed in order to confirm the results obtained for the nondeuterated compound and to study the benzylpyridinium *o*-CH₃, *m*-CH₃ and *p*-CH₃ precursor ions (see below).

The kinetic energy releases (KERs) associated with the dissociation of metastable benzylpyridinium ions were determined with a reverse geometry sector-field mass spectrometer as described elsewhere.^[10] Ions were generated using FAB (Xe, 8 keV), the parent ions were mass-selected using a magnetic sector and the product ions evolving from unimolecular dissociations of the metastable parent ions in the field-free region following the magnet were monitored using an electrostatic analyzer (MIKE spectra). The average KERs and the resulting kinetic energy release distribution (KERD) curves were determined from the MIKE spectra obtained using Eqn (1), which employs sigmoid derivatives to reproduce the experimental data of Gaussian-shaped peaks.

$$I = \frac{d\left(\frac{a}{1+e^{-\frac{E_i - E_f}{b}}}\right)}{dE} = \frac{ae^{-\frac{E_i - E_f}{b}}}{b\left(1+e^{-\frac{E_i - E_f}{b}}\right)^2}$$
(1)

This model includes only three adjustable parameters, a, b, and E_f . In our case, it was possible to reproduce all the experimental data without any constraint on the values of these adjustable parameters because none of the experimental peaks was a composite one. The KERDs were accordingly derived using Eqn (2).

$$P(E) = \frac{a(E_i - E_f)}{2\gamma b^2} \left[\frac{e^{-\frac{E_i - E_f}{b}}}{\left(1 + e^{-\frac{E_i - E_f}{b}}\right)^2} - \frac{2\left(e^{-\frac{E_i - E_f}{b}}\right)^2}{\left(1 + e^{-\frac{E_i - E_f}{b}}\right)^3} \right]$$
(2)

Results and Discussion

Theoretical activation energies

As a starting point for the search of the relevant transition structures, we supposed that the general reaction pathway leading to the formation of tropylium ions is not affected by the substituents. Consequently, the reaction pathways obtained in the case of *p*-H, *p*-CH₃ and *p*-OCH₃ compounds^[12] were used to search for the most endothermic transition structures for the RR processes of all other benzylpyridinium ions. A previous study^[12] showed that the RR process should involve two intermediates and two transition states. As an example, Fig. 1 shows the reaction pathway proposed in the case of the fragmentation of the unsubstituted benzylpyridinium compound. In a first step, a triciclic structure is formed (TS₁^{RR}, Int₁^{RR}). Then, aring-opening results in the formation of a seven-member ring (TS₂^{RR}, Int₂^{RR}). A DC occurs from Int₂^{RR} to form a tropylium ion. On the basis of these calculations, the most endothermal transition state is the tricyclic sctructure TS₁^{RR}. But



Figure 1. Potential energy evolution during tropylium formation from the unsubstituted benzylpyridinium at the MP2/6-31+G* level of theory.^[12]

the final state is less stable than this transition state. Thus, unlike the general case, this RR process occurs without any reverse energy. The activation energies associated with the RR and direct cleavage processes were determined for all the substituents considered (Table 1). These results show that irrespective of the nature and the position of the substituent the formation of tropylium ions is systematically more favorable than that of direct bond processes. But do RR processes actually take place under ESI/MS conditions? This question is important because ESI sources are often considered as a soft ionization method that does not

promote RR processes.^[5] The characterization of the daughter ions experimentally formed is likely to shed some light on the fragmentation pathways of the parent ions. Therefore, gas-phase reactivity was carried out in combination with ESI/MS experiments.

Gas-phase reactivity studies

The reactivity difference between tropylium ions and benzylium ions allows to distinguish the isomeric ions by means of simple ion/molecule reactions.^[11-17] Accordingly, we were tempted to probe if the same concept can also be applied to the substituted benzylium and tropylium ions evolving upon CID of the corresponding benzylpyridinium precursors. In fact, the formal CH_2^+ transfer to neutral toluene to afford $C_8H_9^+$ (m/z 105) is not systematically favored thermochemically (see below). However, a preliminary study of the unsubstituted- and para-tbutyl-substituted benzylpyridinium ions showed the possibility of using such experiments to probe the structure of the fragment ions.^[13] Hence, we may use the subsequent reactivity of the primary fragments formed upon loss of neutral pyridine from the benzylpyridinium ions to assess the ratio of DC to afford the corresponding benzylium ions versus the RR to the respective tropylium isomers (Fig. 2).

It should be noted that these gas-phase reactions cannot be carried out from the o-CH₃, m-CH₃ and p-CH₃benzylpyridinium

Table 1. Influence of the substitution on the enthalpies of formation of the benzylium and tropylium ions from substituted benzylpyridinium ions and some relevant data of the associated transition structures (TS) as obtained using B3P86/6-31+G* calculations

	Sum of electronic and thermal energy (Hartree)					Enthalpy of formation (kJ/mol)		
Substituent	Parent ions	Benzyl ion	Tropylium ion	TS	v_{imag} (cm ⁻¹)	Benzyl ion	Tropylium ion	TS
<i>p</i> -H	-520.43781	-271.39878	-271.4127	-520.4	-76	226	189	154
o-CH3	-559.87359	-310.84091	-310.85516	-559.8	-81	209	172	152.6
<i>m</i> -CH3	-559.87547	-310.8399	-310.85516	-559.8	-78	217	176	155.1
<i>p</i> -CH3	-559.87592	-310.84738	-310.85596	-559.9	-76	198	176	10.58
<i>p</i> -terbu		-429.14141	-429.14881	-678.2				
<i>p</i> -F	-619.82003	-370.78493	-370.79437	-619.8	-79	215	191	155.8
p-Cl	-980.34488	-731.31065	-731.316206	-980.3	-72	213	198	155.1
<i>p-</i> CN	-612.87841	-363.83149	-363.84054			246	223	
p-CF3	-858.03853	-608.99075	-609.00296	-858	-80	249	217	151.2
m-OCH3	-635.21715	-386.1823	-386.20614	-635.2	-78	215	152	147.7
p-NO2	-725.31791	-476.26462	-476.27828			263	227	
3,5 DiMe	-599.31289	-350.28087		-599.3	-86	207		149.9
2,5 DiMe	-599.31101	-350.28168		-599.2	-155	200		171.1
2,4 DiMe		-350.28869		-599.2	-147			
PentaMe	-717.60617	-468.59207	-468.59735			160	146	2E + 06

In this table, ν_{imag} is the imaginary frequency associated to the transition state.



Figure 2. Protocol for the distinction of RC₇H₆⁺ isomers by their reaction with toluene.





Figure 3. Effects of the activation time on the mass spectra obtained for the unsubstituted benzylpyridinium ion under gas-phase reaction conditions. Normalized collision energy: 20%.



Figure 4. Ion abundances in energy-dependent CID experiments of (a) mass-selected $[CIC_7H_6\bullet C_7H_8]^+$ generated by CID of mass-selected $[CIC_6H_4CH_2NC_5H_5]^+$ in the presence of toluene and (b) mass-selected $[(CH_3)_2C_7H_5\bullet C_7H_8]^+$ generated by CID of mass-selected $[(CH_3)_2C_6H_3CH_2-NC_5H_5]^+$ in the presence of toluene.

compounds. Indeed, for these cases, the daughter ions have the same m/z ratio as that of the species resulting from the gas-phase reactivity (m/z = 105).

In the analysis of the results, we may distinguish three scenarios: (1) Complete conversion of the daughter ion via CH_2^+ transfer indicates that the parent ions exclusively underwent DC of the C–N bond to yield the corresponding benzylium ions. (2) Partial reactivity of the daughter ions suggests that two populations of ions are formed with the reactive fraction due to the benzylium structure formed via DC and the nonreactive fraction due to the tropylium structure and thus rearrangment (RR). (3) Absence of reactivity indicates either that all ions follow the RR route to afford tropylium ions or CH_2^+ transfer.

Accordingly, MS/MS experiments were carried out in which the mass-selected benzylpyridinium precursor ions were subjected to CID in the presence of neutral toluene as a reagent, which means that fragmentation and the gas-phase reactions take place during the same MSⁿ step. As a variable, we employed the activation time (t_{act}) , i.e. the length of the rf-excitation pulse applied to the mass-selected benzylpyridinium precursor. For all benzylpyridinium ions studied here, suitable fragmentation periods for the parent ions were between 10 ms $\leq t_{act} \leq$ 500 ms. Figure 3 shows the evolution of the ion abundances with t_{act} in the case of the unsubstituted benzylpyridinium compound, using a normalized collision energy of 20%. In the first part of this graph, for 25 ms $\leq t_{act} \leq$ 75 ms, the parent ion (C₆H₅-CH₂-NC₅H₅⁺, *m/z* 170) disappears gradually and a proportional increase is observed in the daughter ion ($C_7H_7^+$, m/z 91), but a part of this ion already reacts to $C_8H_9^+$ (m/z 105), indicating the presence of benzylium ion. In the second part of the graph ($t_{act} > 75$ ms), the intensity of the parent ion continues decreasing and C₇H₇⁺ also gradually disappears. The intensity of the ion m/z 105 increases continuously and becomes the major product ion at extended activation times. At larger reaction times, some additional ions are observed (e.g. an ion at m/z 197 corresponding to an adduct of C₈H₉⁺ and toluene), which are due to consecutive ion/molecule reactions and are not further pursued.

Likewise, the ion/molecule reactions of all other benzylpyridinium compounds were studied under these experimental conditions. In many cases, the formation of adducts between the daughter ions and one molecule of toluene was observed, which formally correspond to the initial intermediates of CH_2^+ transfer. Different MS³ experiments were carried out in order to gain additional insight in this aspect. As an example, Fig. 4 shows the CID breakdown curves of the adduct ions $[CIC_7H_6 \bullet C_7H_8]^+$ and $[(CH_3)_2C_7H_5 \bullet C_7H_8]^+$ of the primary fragments derived from *p*-Cl-benzylpyridinium and 3,5-dimethyl-benzylpyridinium, respectively, as a function of the normalized collision energy. These examples show that upon CID the adduct ions can either decompose into the components, e.g. $CIC_7H_6^+$ (m/z 125) and $C_7H_7^+$ (m/z 91), respectively, or afford the ion at *m/z* 105, which is characteristic for the CH_2^+ transfer to toluene.

Similar results were obtained in the case of the use of deuteriated gas reactants such as $C_6H_5CD_3$ and $C_6D_5CD_3$. Indeed, unreactive, partially or totally reactive daughter ions, leading to the formation of a peak at m/z 108, were observed (Table 2). In addition, these experiments showed that the daughter ions obtained from m-CH₃ and p-CH₃ benzylpyridinium compounds reacted partially with toluene to give the ion m/z 108. Furthermore, the fragment ion formed using o-CH₃ benzylpyridinium precursor ion reacted totally with toluene to give the ion m/z 108. These results are summarized in Table 2.

In summary, the gas-phase reactivity study showed that some substituted benzylpyridinium reacted with toluene, others were unreactive and some showed partial reactivity, suggesting that both tropylium and benzylium daughter ions coexist. Figure 5 illustrates the influence of the substitution of the parent ions on the MS/MS spectra obtained in the case of a collision energy of 40% and an activation time of 10 ms. The results permit to categorize the benzylpyridinium ions into three families.

• The benzylpyridinium ions with *p*-H, *p*-Cl, *p*-l, *m*-OCH₃ and *p*-NO₂ yield daughter ions that react totally with toluene to give the ion *m*/*z* 105.

- The daughter ions obtained from 2,4-dimethyl, 2,5-dimethyl, 3,5-dimethyl and *p*-*t*-butyl benzylpyridinium ions partially react with the toluene to give the ion *m*/*z* 105.
- In the case of the pentamethyl- and *p*-OCH₃ derivatives, and benzylpyridinium compounds, the daughter ions do not react with toluene to form an ion at *m*/*z* 105.

According to Fig. 2, we assigned the first group to ions that only correspond to the benzylium structure (i.e. exclusive DC pathway), the second group points to a mixture of the DC and RR route, while the third group of unreactive ions can be explained by either exclusive RR or nonreactive benzylium ions. Considering the donor character of the substituents involved in the last group, nonreactive benzylium ions appear as the most likely explanation.

In a complementary manner, MS³ experiments were performed in order to separate the fragmentation step and the gas-phase reactivity process. Note that we did not observe strong changes in the mass spectra obtained with the fragmentation conditions of the parent ions. Furthermore, the experimental results obtained under these conditions are very similar to those obtained in the case of MS/MS experiments.

Kinetic energy release studies

For all the benzylpyridinium compounds studied, Eqns (1) and (2) were used to estimate the kinetic energy releases associated with the fragmentation of the metastable ions. For instance, Fig. 6 shows the experimental and the fitted peak, the residue obtained and the KERDs calculated in the case of the *para*-methoxy parent ion. The KERs that were determined using this method showed no significant influence of the substituents. As an example, Table 3 shows the values obtained from different parent ions.

Furthermore, the weak values obtained suggested that no kinetic energy release was associated with these fragmentation processes. Thus, two hypotheses are compatible with these experimental results:

• the metastable ions underwent only DC fragmentations or

Gas-phase reactivity: formation of an ion at							
R	m/z 105 with C ₆ H ₅ CH ₃	m/z 108 with C ₆ H ₅ CD ₃	m/z 108 with C ₆ D ₅ CD ₃	Conclusion			
<i>р</i> -Н	Total reaction	Total reaction	Total reaction	DC			
o-CH₃	*	Partial reaction	Partial reaction	RR + DC			
<i>m</i> -CH ₃	*	Total reaction	Total reaction	DC			
p-CH₃	*	Partial reaction	Partial reaction	RR + DC			
<i>p</i> -terbutyl	Partial reaction	Partial reaction	Partial reaction	RR + DC			
<i>p</i> -F	Partial reaction	Partial reaction	Partial reaction	RR + DC			
p-Cl	Total reaction	Total reaction	Total reaction	DC			
<i>p-</i> CN	Total reaction	Total reaction	Total reaction	DC			
p-CF ₃	Total reaction	Total reaction	Total reaction	DC			
<i>m</i> -OCH₃	Partial reaction	Partial reaction	Partial reaction	RR + DC			
p-NO ₂	Total reaction	Total reaction	Total reaction	DC			
3,5 Dimethyl	Partial reaction	Partial reaction	Partial reaction	RR + DC			
2,5 Dimethyl	Partial reaction	Partial reaction	Partial reaction	RR + DC			
2,4 Dimethyl	No reaction	No reaction	No reaction				
Pentamethyl	No reaction	No reaction	No reaction				

DC, direct bond cleavage; RR, rearrangement process. Star indicates that these reactions cannot be achieved due to the fact that daughter ions have a *m/z* ration of 105.





Figure 5. Influence of the substituent of the benzylpyridinium ions on the gas-phase reactivity between daughter ions and toluene. Collision energy of 40% was deposited on the parent ions selected in the ion-trap, and the activation time was 10 ms.



Figure 6. MIKE study of the *para-methoxy* benzylpyridinium ion fragmentation. A: experimental and theoretical peaks, B: residue in the fitted peak and C: kinetic energy release distribution calculated.

Table 3. Results of the MIKE study								
	Adjustable parameters			~KED>	KER at the maximum			
Substituent	а	b	Ei	(meV)	distribution (meV)			
<i>р-</i> Н	0.005	0.001	0.536	8.9	3.6			
m-CH ₃	0.005	0.001	0.569	20.1	8.5			
p-CH ₃	0.004	0.001	0.571	13.1	5.4			
<i>p</i> -terbutyl	0.005	0.001	0.649	15.2	6.2			
p-Cl	0.005	0.001	0.613	24.3	10.0			
m-OCH ₃	0.005	0.001	0.606	18.9	7.6			
p-NO ₂	0.005	0.001	0.633	40.8	17.0			
Pentamethyl	0.004	0.001	0.671	12.9	5.2			

• RR processes, without any reverse energy, occurred under the experimental conditions.

Note that this second hypothesis is in total accordance with our theoretical study. Indeed, we proposed that the formation of the tropylium ions from the benzylpyridinium compounds can occur without any reverse energy.^[10]

Conclusions

Formation of benzyl and tropylium ions from substituted benzylpyridinium compounds has been extensively studied by experimental methods and theoretical calculations.

On the basis of a previous study, we have considered different reaction pathways. The activation energy associated with the DC and with the RR processes was calculated. Results show that, in different cases, RR processes are thermodynamically more favorable than DCs.

These reaction pathways were further studied under ESI conditions using gas-phase reactions. Our results were used to sort out the benzylpyridinium compounds into different families:

- benzylpyridiniums for which daughter ions react totally with toluene to form the $C_8H_9^+$ ion,
- benzylpyridiniums for which daughter ions do not react with toluene,
- benzylpyridiniums for which daughter ions react partially with toluene to form the $C_8H_9^+$ ion.

Experiments on a commercial tropylium ion showed that the tropylium isomer reacts with toluene to form the $C_8H_9^+$ ion. Then, assuming that the formation of $C_8H_9^+$ ion during the gasphase reaction is the proof of the formation of tropylium ions, we determined which benzylpyridinium compounds underwent RR processes. It should be noted that these conclusions are in accordance with the theoretically estimated activation energies.

All these experimental and theoretical results showed that RR process might have occurred during the fragmentation of several benzylpyridinium ions, under ESI/MS or FAB/MIKE conditions: according to the gas-phase reactivity study, the tropylium ions can be formed during the fragmentation of several benzylpyridinium ions, even under these soft ionization processes.

These theoretical results will be further used to study the internal energy deposited on the parent ions under ESI conditions. Indeed, these new results show that the RR processes must be taken into account for several substituents.

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