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Distonic isomers of ionized benzaldehyde

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Dedicated to the memory of our colleague and friend Pierre Longevialle.

Abstract

Dissociative ionization of phthalaldehyde **1** and collisional deiodination of protonated isomeric iodobenzaldehydes **2**–**4** were attempted in searching for the possible production of distonic isomers (**b**–**d**) of ionized benzaldehyde **a**. These distonic species were initially produced in these experiments, but most of them readily isomerized to ionized benzaldehyde. Density functional theory B3LYP/6-31+G(d,p) calculations indicate that the distonic ions are surprisingly low energy species being 50–60 kJ mol^{-1} above **a**, but kinetically metastable with respect to **b** → **a** isomerization that has an energy barrier of only 70 kJ mol^{-1}. It is also suggested that low energy hydrogen migrations or a benzyl/tropylium isomerization likely precede collisional deiodination of protonated iodobenzaldehydes. (Int J Mass Spectrom 217 (2002) 65–73) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tandem mass spectrometry; Benzaldehyde; Distonic ions; Quantum mechanical calculations

1. Introduction

Radical cations of substituted benzenes have recently been shown to exist either in the classical aromatic structures or in their distonic isomeric forms [1] in which a hydrogen atom from the aromatic ring was transferred onto the substituent. The gas phase syntheses of such distonic ions relied on an initial selective protonation occurred at the substituent site, followed by an elimination of a suitable neutral leaving group from the benzene ring to create the radical center.

Evidence has been presented for a regioselective protonation of the substituent, instead of a ring protonation, of some monosubstituted benzenes including benzonitrile, benzaldehyde and nitrobenzene [2]. The proton affinities (PA) of these compounds were indeed found to be higher than the value predicted from a linear correlation between benzenic PAs with the σ^+ parameter. It is therefore expected that, given the presence of appropriate substituents, protonated disubstituted benzenic compounds could be valuable precursors for the preparation of new distonic radical cations. For example, isomers of ionized nitrobenzene [3] were prepared by collisional

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activation (loss of $NO_2^{\bullet}$) of protonated *meta*- and *para*-dinitrobenzenes. Protonated iodobenzonitriles behave similarly and the collision-induced loss of the iodine atom allowed the production of 2-, 3- and 4-dehydrobenzonitrilium ions [4].

In this work, we present the results obtained for protonated iodobenzaldehydes in an attempt to produce dehydrophenylhydroxycarbenium ions that are the formal and potentially stable isomers of benzaldehyde radical cation. MS experiments were also complemented by density functional theory computations to derive quantitatively some useful energetic information.

2. Experimental

Spectra were recorded on a large scale tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of $c_1E_1B_1c_2E_2c_3c_4E_3B_2c_5E_4$ geometry (E stands for electric sector, B for magnetic sector and c for collision cell) [5]. General conditions were 8 kV accelerating voltage, 200 μA trap current (in the electron ionization mode, EI), 1 mA (in the chemical ionization mode, CI), 70 eV ionizing electron energy and 200 °C ion source temperature. The solid samples were introduced with a direct insertion probe, while the liquid samples were injected in the ion source via a heated (180 °C) septum inlet.

Collision-induced dissociation (CID) with He of fast (8 keV kinetic energy) mass selected ions was performed in c_4 and the CID spectra were recorded by scanning the field of E_3 collecting the ions in the fifth field-free region with an off-axis photomultiplier detector.

The installation of an rf-only quadruple collision cell (Qcell) inside the instrument between E_2 and E_3 has also been reported elsewhere [6]. This modification allows not only the study of associative ion–molecule reactions but also the study of collisional activation of decelerated ions. Briefly, the experiments utilizing the Qcell consist of the selection of a beam of fast ions (8 keV) with the three first sectors ($E_1B_1E_2$), the deceleration of these ions to approximately 5 eV (to maximize ion–molecule reactions) or 20–30 eV (to maximize CID). The interaction between the ions and the reagent gas (the pressure of the gas is estimated to be about 10^{-3} Torr) is thereafter realized in the Qcell and, after re-acceleration at 8 keV, all the ions generated in the quadruple are separated and mass measured by scanning the field of the second magnet. The high energy CA spectra of mass selected (with B_2) ions generated in the Qcell can be recorded by a scanning of the field of E_4 after collisional excitation in c_5.

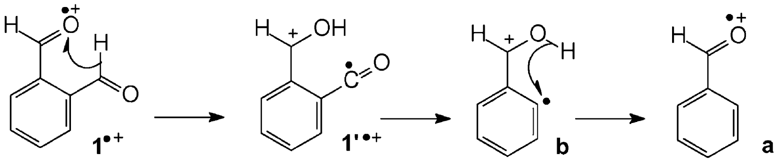
Phthalaldehyde **1**, the iodobenzaldehydes **2**–**4** and benzaldehyde **5** were commercially available (Aldrich) and used without any further purification.

3. Results and discussion

3.1. Dissociative ionization of phthalaldehyde 1

In contrast to its *meta*- and *para*-isomers, phthaldehyde where both formyl substituents are situated in *ortho*-positions with each other, shows an intense peak at *m/z* 106 (ca. 45% of the base peak) in its electron ionization mass spectrum (EIMS) [7]. This particularity suggests the occurrence of a strong *ortho*-effect resulting in a loss of carbon monoxide following hydrogen transfer (Scheme 1). The $[M–CO]^{\bullet+}$ ions formed initially should therefore present the distonic (carbenic) connectivity as in structure **b**, which is an isomer of conventional benzaldehyde radical cation structure **a**. However, the CID spectrum of these *m/z* 106 ions cannot be used directly for structure characterization because of severe interference with ^{13}C isotope satellites of the very abundant *m/z* 105 ion, which represents the base peak of the EIMS. Approximately 20% of the *m/z* 106 peak is indeed due to the contribution of $C_6{}^{13}CH_5O$ ions.

This interference can fortunately be avoided in metastably generated *m/z* 106 ions that are produced abundantly (ca. 30% of the *m/z* 134 peak corresponding to stable ions!) in the quadruple region (see Fig. 1a and Section 2) and this quite favorable situation has allowed us to obtain a good quality CID spectrum



Scheme 1.

of the re-accelerated (8 keV) m/z 106 ions. The CID spectrum thus obtained (Fig. 1b) resembles very closely that of the molecular ions of benzaldehyde.

Such a behavior is thus identical to the one observed in the nitrobenzene series where the initially generated *ortho*-distonic isomer readily isomerized via a 1,4-hydrogen shift to the more stable nitrobenzene radical cation [3]. As shown below, the corresponding energy barrier was theoretically estimated to be about 70 kJ mol^{-1} relative to the distonic ion **b** (114 kJ mol^{-1} with respect to the classical ion **a**).

3.2. Collisional deiodination of protonated iodobenzaldehydes 2–2

Iodobenzaldehydes with iodine in *ortho*-**2**, *meta*-**3** and *para*-**4** have been protonated in a chemical ionization ion source using methane as the reagent gas. The resulting metastable **2**–**4**H^+ ions decompose mainly by CO loss (*m/z* 205) and the second peak of importance seen at *m/z* 78 results most probably from a consecutive loss of iodine. Deiodination of the protonated molecules occurs only upon collisional excitation in the high energy or low kinetic energy regimes (see Table 1), but its yield rapidly decreases when iodine is displaced from the *para*- to *ortho*-position. Given the intensity of the collisionally generated *m/z* 106 ions, high quality CID spectra of re-accelerated $(C_7H_6O)^{\bullet+}$ radical cations can only be recorded for the **3**H^+ and **4**H^+ ions, not for **2**H^+.

In the low energy regime, the CID spectra are considerably simplified featuring peaks for loss of CO (*m/z* 205) and CO + $I^\bullet$ (*m/z* 78) (already observed without a target) together with *m/z* 106 and 105 ions. Just as in the case of the high energy regime, the direct loss of iodine is only scarcely seen for **2**H^+ ions. Given the fact that the *m/z* 106 ions can be produced in reasonable yield in the quadruple collision cell, better quality, in terms of sensitivity and resolution (compared to “conventional” MS/MS/MS spectra), CID spectra of *re-accelerated* ions generated from **3**H^+ and **4**H^+ become readily accessible.

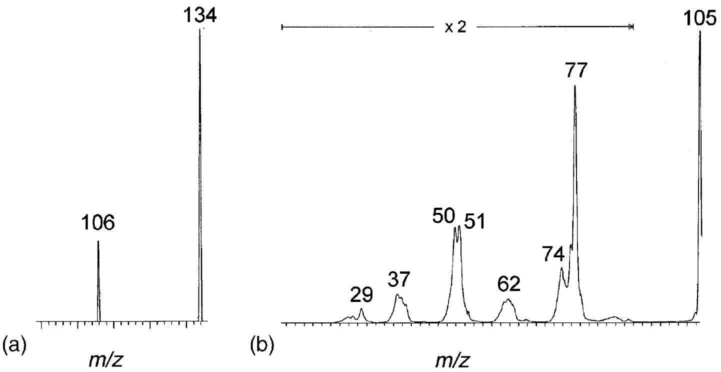


Fig. 1. (a) Metastable ion spectrum of the molecular ions (*m/z* 134) of phthalaldehyde **1** and (b) CID spectrum (nitrogen collision gas) of metastably-generated *m/z* 106 ions generated by dissociative ionization of phthalaldehyde **1**.

Table 1
Most significant peaks in the high energy CID spectra (He collision gas, 8 keV ions) and low energy CID spectra (argon collision gas, ca. 20–30 eV ions, corresponding to center of mass energies of maximum 2.9–4.4 eV) of the protonated 4-, 3- and 2-iodobenzaldehydes

R	Gas	m/z							
		205	203	127	116.5	106	105	78	77
4-I	He	20	100	4	<1	54	39	81	17
	Ar	14	–	–	–	16	17	100	6
3-I	He	52	60	3	<1	12	36	100	26
	Ar	10	–	–	–	16	30	100	5
2-I	He	13	94	9	1	3	86	100	47
	Ar	21	–	–	–	2	23	100	2

3.2.1. Protonated 4-iodobenzaldehyde

The MS/MS/MS spectrum (Fig. 2b) of the $[MH–I]^{\bullet +}$ ions from protonated 4-iodobenzaldehyde is very similar to the CID spectrum of the conventional benzaldehyde radical cation (Fig. 2a). In both spectra, the losses of $H^{\bullet}$ and $H^{\bullet} + CO$ represent the most intense fragmentations; their relative intensities appear nevertheless to be reversed whereas the peak at *m/z* 78 is slightly more intense for the ions generated by the protonation–deiodination sequence. Therefore, these data indicate that most of the *m/z* 106 ions generated following the protonation–deiodination sequence have the benzaldehyde connectivity, although the occurrence of a small proportion of not yet defined isomeric ions cannot be completely ruled out.

3.2.2. Protonated 3-iodobenzaldehyde

Similar results were also obtained for protonation–deiodination of 3-iodobenzaldehyde **3** (Fig. 2c). Again, benzaldehyde radical cation is mainly, if not uniquely, produced by collisional deiodination of $\mathbf{3H}^{+}$ ions. To track the identity of the protons involved in the protonation–deiodination reaction sequence, we used CD_3OD chemical ionization of **3**. The results were in agreement with the relative PA of methanol and benzaldehydes, pointing out that $\mathbf{3D}^{+}$ ions (*m/z* 234) ions were generated. The low energy CID spectrum of $\mathbf{3D}^{+}$ is shown in Fig. 3a. The loss of iodine is a prominent fragmentation upon CID and the spectrum of the *m/z* 107 ions (Fig. 3b) shows a very prominent loss of $H^{\bullet}$, not $D^{\bullet}$. This is in line with the formation of benzaldehyde ions bearing the introduced deuteron in the ring, not in the aldehyde group.

As for an interpretation of this particular behavior, as compared with what previously observed in the nitrobenzene and benzonitrile series, we would suggest that the H/I atoms undergo intensive scrambling between carbon atoms of the ring during the protonation–deiodination sequence. This could be due to a proton migration (Scheme 2), or a carbon scrambling which could also arise from a rapid interconversion between hydroxybenzylic and hydroxytropylium ions before deiodination. Both mechanisms have precedents in the literature [8]. Note that rearrangements by ring-enlargements cannot occur in protonated nitrobenzenes or protonated benzonitriles. $[C_7H_7O]^{+}$ ions were previously studied with various mass spectrometric techniques [9,10].

3.3. Thermochemical data and quantum chemical calculations

Standard ab initio calculations were performed using the Gaussian'98 suite of programs [11]. Geometries were optimized by density functional calculations [12] that employ the hybrid functional (B3LYP) [13] and the 6-31+G(d,p) basis set. Selected geometrical parameters and relative energies of the points considered are summarized in the Fig. 4.

The distonic radical cations **b**–**d** are calculated to be less stable than ionized benzaldehyde **a** by ca. 50–65 kJ mol^{-1} (see Table 2). The ion structure shows

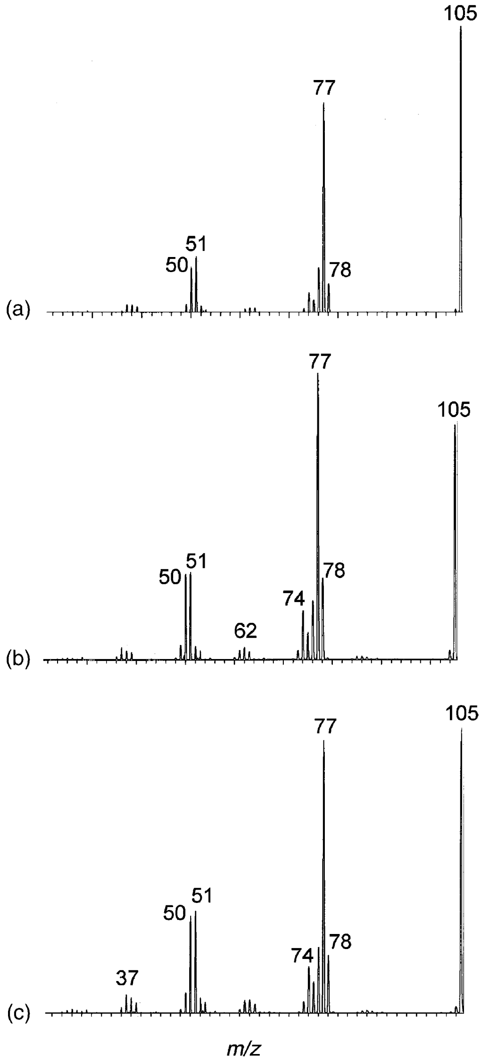


Fig. 2. CID spectra (oxygen collision gas, linked scan mode) of the molecular ions of benzaldehyde (a), $[MH–I]^{\bullet +}$ ions of 4-iodobenzaldehyde **4** (b), and $[MH–I]^{\bullet +}$ ions of 3-iodobenzaldehyde **3** (c).

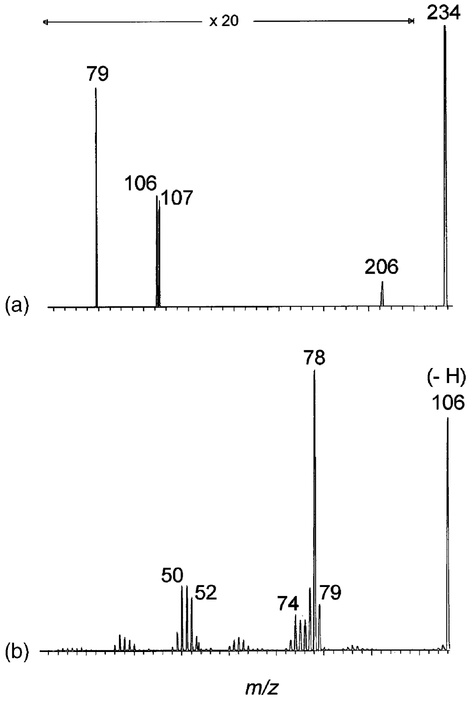
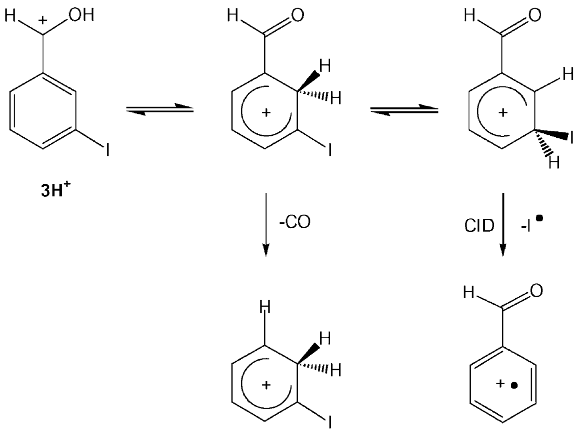


Fig. 3. Low energy CID spectrum (argon collision gas, 20–30 eV) of the $\mathbf{3D}^+$ ions (a) and CA spectrum (oxygen collision gas, 8 keV) of the *m/z* 107 ions (b).

rather unexceptional bond lengths and bond angles. The energy barriers for the isomerization connecting the distonic ion **b** with the more conventional ion **a** through a 1,4-hydrogen shift is calculated to be quite low, amounting to ca. 70 kJ mol^{-1} with respect to **b**, in agreement with the similarity of the observed CA spectra. Isomerization of ions **b**–**d** by 1,2-hydrogen shifts within the ring requires significantly large activation energies (ca. 310–330 kJ mol^{-1}). As suggested by a referee, transition states for 1,3-hydrogen shifts have also been taken into account, but cannot be found.



Scheme 2.

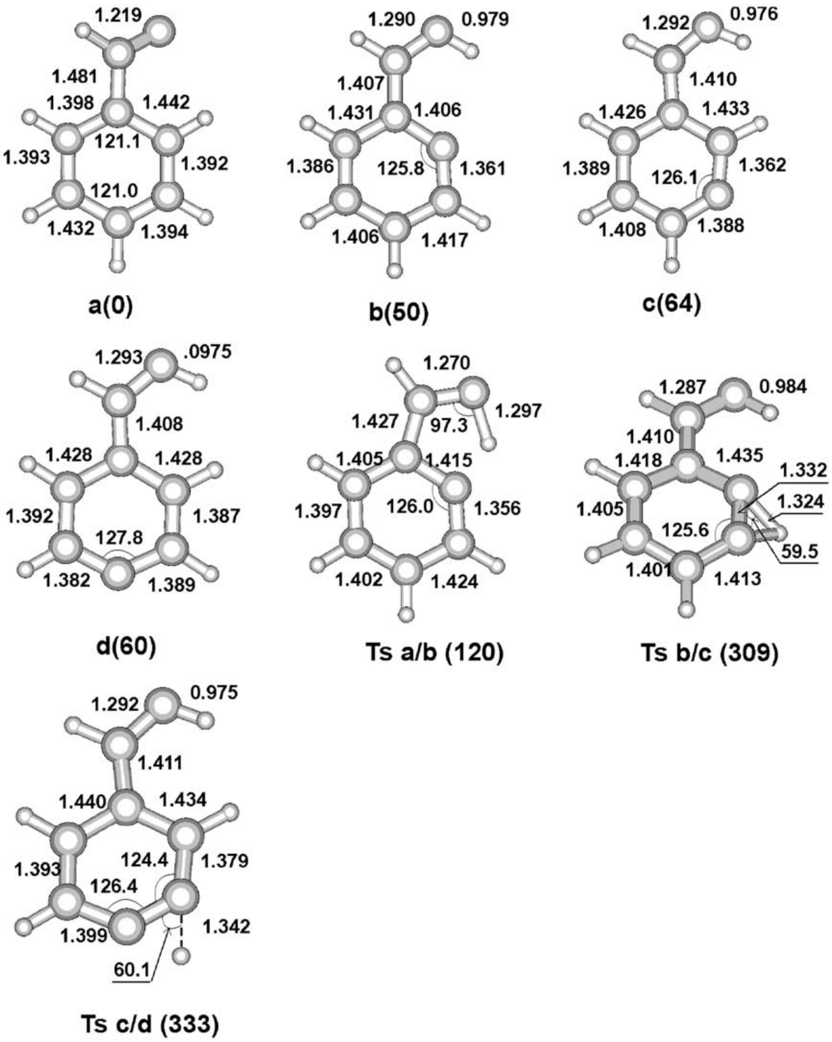


Fig. 4. Selected UB3LYP/6-31+G(d,p) optimized structures of $[C_7H_6O]^{\bullet+}$ radical cations. Bond lengths are given in angstroms and bond angles in degrees. Relative energies given in kJ mol^{-1} in parentheses were obtained from UB3LYP/6-31+G(d,p)+ZPE calculations. **Ts x/y** stands for a transition structure connecting two isomers **x** and **y**.

Table 2
Electronic energies, zero point energies, spin contamination and relative energies of the species **a**–**d** and transition states connecting them

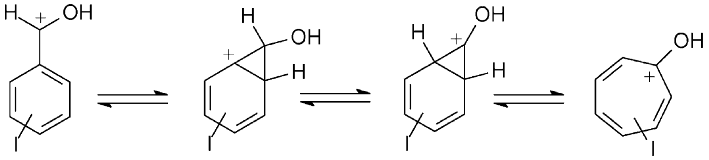
Species	Electronic energy (Hartree)	Zero point energy (kJ mol^{-1})	S^2	Relative energy (kJ mol^{-1})
a	−345.256395	282.2	0.7727	0
b	−345.239731	288.9	0.7597	50
c	−345.234156	288.0	0.7572	64
d	−345.235829	288.2	0.7596	60
Ts a/b	−345.205815	268.8	0.7580	120
Ts b/c	−345.134491	271.2	0.7661	309
Ts c/d	−345.125013	270.1	0.7657	333

The energetics of the hydroxybenzyl–hydroxytropylium rearrangement can be estimated by combining calculated and tabulated energy values. It follows from our calculations that *ortho*-protonated benzaldehyde and hydroxytropylium cation have very similar enthalpies of formation, e.g., $\Delta H_{\mathrm{f},298} = 2$ and $7\,\mathrm{kJ\,mol^{-1}}$ in favor of $C_6H_5CHOH^+$ by B3LYP/6-31+G(d,p) and MP2/6-311+G(3df,2p) calculations, respectively [14]. A similar difference in enthalpies could be assumed for the corresponding iodinated cations. The energy for the loss of the iodine atom from protonated iodobenzaldehyde (or hydroxyiodotropylium) can be estimated as follows. Based on the heat of formation difference between benzene and iodobenzene ($82\,\mathrm{kJ\,mol^{-1}}$) and the heat of formation of benzaldehyde ($-37\,\mathrm{kJ\,mol^{-1}}$) [15], the heat of formation (ΔH_f) of 2-iodobenzaldehyde is estimated to be $45 \pm 20\,\mathrm{kJ\,mol^{-1}}$. It seems moreover reasonable to assume that the PA of this compound is similar to that of benzaldehyde ($838\,\mathrm{kJ\,mol^{-1}}$); the heat of formation of *ortho*-protonated 2-iodobenzaldehyde can be derived as $737 \pm 20\,\mathrm{kJ\,mol^{-1}}$. A similar value, with a difference of 2–$7\,\mathrm{kJ\,mol^{-1}}$, could be ascribed to the isomeric hydroxyiodotropylium ion on the basis of the calculations discussed above. Using the computed relative energies and the available heats of formation of iodine atom ($107\,\mathrm{kJ\,mol^{-1}}$) and benzaldehyde radical cation ($879\,\mathrm{kJ\,mol^{-1}}$) [15], the elimination of the iodine atom from protonated iodobenzaldehyde is estimated to require $249\,\mathrm{kJ\,mol^{-1}}$ at the thermochemical threshold. This is largely in excess of the estimated barrier of $160\,\mathrm{kJ\,mol^{-1}}$ predicted for the benzylic/tropylium rearrangement (assumed to be analogous to the allylic cation—cyclopropyl cation rearrangement [16]). Such an equilibrium (Scheme 3) could explain the loss of positional identity of the distonic ions which could isomerize prior to iodine loss and eventually form ionized benzaldehyde. Note that an analogous isomerization was not observed for the *meta*- and *para*-distonic isomers of ionized nitrobenzene [3].

3.4. Ion–molecule reactions with nitric oxide or tert-butyl nitrite

Nitric oxide has been described in several instances as an efficient trapping reagent of distonic radical cations. Representative examples of ion–molecule reactions are attachment of $NO^\bullet$, trapping of small radical cations by $NO^\bullet$, or displacement of neutral molecules by $NO^\bullet$ [17]. The benzaldehyde radical cation reacts with nitric oxide by charge exchange to form NO^+ (*m/z* 30), in agreement with the relative ionization energies (9.49 eV for benzaldehyde, viz. 9.26 eV for $NO^\bullet$) [15]. The same charge exchange reaction is also observed for the $[M–CO]^{\bullet+}$ ions of phthalaldehyde **1**, but other peaks are observed at *m/z* 90, 80 and 65. These peaks are ascribed to the fragmentation of isomeric ions complexed with nitric oxide. Benzoyl cations were indeed found inert toward nitric oxide excluding a possible interference caused by the corresponding ^{13}C-labeled ions (vide supra).

Recently, we observed that *tert*-butyl nitrite was a valuable reagent for the characterization of various isomeric ionized species in the gas phase [18]. Mass analysis of the ions produced in the reactions between ionized benzaldehyde and neutral *tert*-butyl nitrite gave the spectrum depicted in Fig. 5a. Beside protonation (60%, identified by peaks at *m/z* 104, 86 and 57) and formation of *m/z* 136 ions (40%, $NO^\bullet$ attachment), an intense peak at *m/z* 152 was also



Scheme 3.

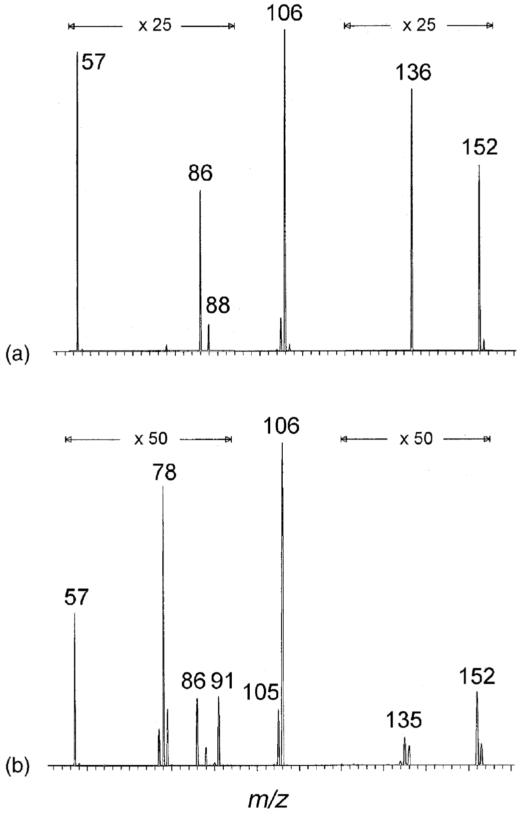
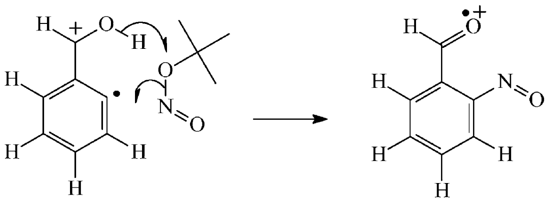


Fig. 5. Ion–molecule reactions of ionized benzaldehyde (a) and [M–CO]$^{\bullet+}$ ions of phthalaldehyde **1** (b) with *tert*-butyl nitrite in the quadruple collision cell (B scan, see Section 2).



Scheme 4.

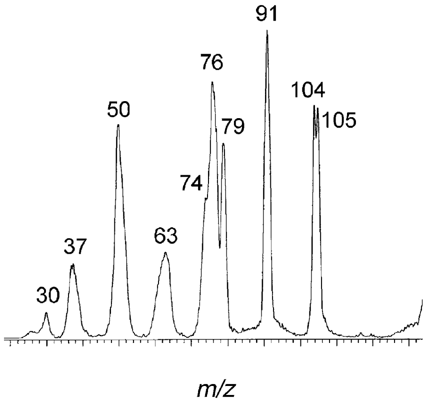


Fig. 6. CID spectrum (nitrogen collision gas) of the *m/z* 135 ions produced by ion–molecule reaction of [M–CO]$^{\bullet+}$ ions of phthalaldehyde **1** with *tert*-butyl nitrite.

observed, but it turned out that these ions arise from the ion–molecule reactions of the abundant *m/z* 105 fragments (collision-induced H$^{\bullet}$ loss) with *tert*-butyl nitrite.

The behavior of the [M–CO]$^{\bullet+}$ ions of phthalaldehyde **1** (contaminated with ^{13}C-labeled ions) appeared much more complex (Fig. 5b). Among the new generated signals, peaks at *m/z* 135, 91 and 79 ions are worthy of note. The *m/z* 135 ions are formally generated by NO$^{\bullet}$ attachment and loss of *tert*-butanol from the initially formed [**b**+*tert*-butylnitrite] complex (see Scheme 4). A closely related reaction was described for protonated benzonitrile [4]. The CA spectrum of these ions (Fig. 6) is closely related to the mass spectrum of 2-nitrosobenzaldehyde [19] and to the CA spectrum of the [M–O]$^{\bullet+}$ of 2-nitrobenzaldehyde.[4] In particular, peculiar rearrangement fragmentations yielding intense peaks at *m/z* 91 and 79 are also observed in Fig. 5b (losses of CO_2 and 2CO, respectively).

4. Conclusion

In summary, tandem mass spectrometric methodologies (CA and MS^3) demonstrate that the distonic carbenic isomers of the benzaldehyde radical cation are low energy and stable species within the time frame of microsecond. Density functional

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[4] The mass spectrum of 2-nitrobenzaldehyde has been presented elsewhere [F. Benoit, J.L. Holmes, Org. Mass Spectrom. 3 (1970) 993]; the molecular ion peak is less than 1% and the [M–O]$^{\bullet+}$ were not observed. We have nevertheless found that these ions are of significant abundance when the partial pressure of this compound in the ion source was very high.

theory B3LYP/6-31+G(d,p) calculations indicated that the distonic isomers lie about 50–60 kJ mol^{-1} above ionized benzaldehyde but readily undergo unimolecular rearrangement to the latter. Nevertheless, ion–molecule reactions with nitric oxide, or better *tert*-butyl nitrite, unambiguously indicated that distonic $[C_7H_6O]^{\bullet +}$ radical cations are also generated in the dissociative ionization experiments and in the protonation–deiodination processes.

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