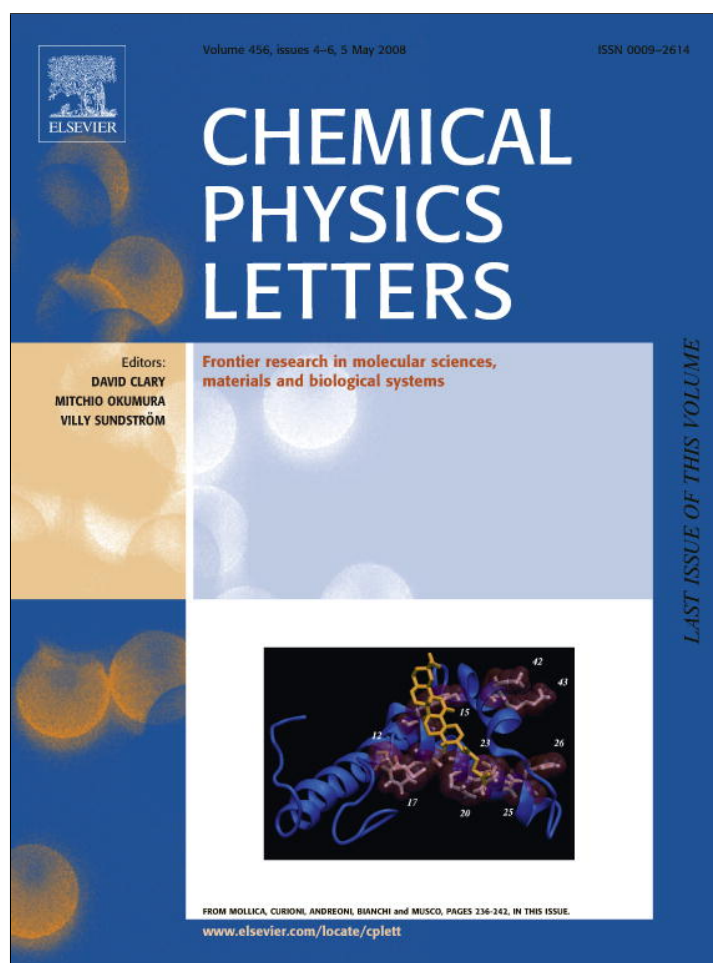


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The cyclohexadienyldenemethanone radical cation is a more stable distonic isomer of ionized benzaldehyde

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ABSTRACT

Quantum chemical calculations (G3B3 and B3LYP/6-311++G(d,p)) and tandem mass spectrometric experiments demonstrate the higher stability of 1,3-cyclohexadienyldenemethanone radical cation compared to ionized benzaldehyde. Characterized by a heat of formation of 833 kJ mol^{-1} (at 298 K), this ketene $\text{C}_7\text{H}_6\text{O}^+$ isomer is found 43 kJ mol^{-1} more stable. It has been generated by ion/molecule reaction between ionized benzaldehyde and neutral methanol, a new example of proton transport catalysis tautomerization. The greater stability of the ketene ion is due to the low IE of the neutral (7.49 eV).

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1. Introduction

Numerous recent experimental and theoretical studies have reported on the rearrangement of ionized carbonyl compounds into their more stable enol radical cations through bimolecular interaction with an appropriate base. The corresponding unimolecular hydrogen transfer is usually associated with a large energy barrier and does not occur in the gas phase. The bimolecular process, termed ‘proton transport catalysis’ [1,2], was shown to efficiently catalyze the enolization of acetaldehyde [3], acetone [4,5], acetophenone [6], and acetamide [7,8] molecular ions. In simple terms, the added base acts to capture the proton from the carbonyl ion and subsequently put it back but at another site to form the isomer. Therefore, a required condition for an efficient proton transport catalysis converting a $[\text{H-X-Y}]^+$ ion into its more stable isomeric form $[\text{X-Y-H}]^+$ [9], is that the proton affinity (PA) of the base should be situated between the PA's of the conjugate base $[\text{X-Y}]^-$ at both X and Y centers.

In a previous study [10], we have characterized a distonic carbene isomer of ionized benzaldehyde $\mathbf{1}^+$ with the conventional ion remaining energetically more stable. We report in the present Letter experimental and theoretical evidence that ionized benzaldehyde $\mathbf{1}^+$ can be tautomerized into a more stable 1,3-cyclohexadi-

enyldenemethanone radical cation $\mathbf{2}^+$ (Scheme 1) by the catalytic action of an added base.

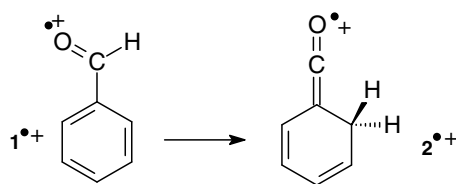
2. Methods

2.1. Experimental

The spectra were recorded on a hybrid tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six-sectors of $\text{cE}_1\text{B}_1\text{cE}_2\text{ccE}_3\text{B}_2\text{cE}_4$ geometry (E_i stands for electric sector, B_i for magnetic sector, and c for conventional collision cells). Typical conditions already reported elsewhere [11,12] were 70 eV electron energy, 200 μA trap current in the EI mode, 1 mA emission current in the CI mode and 8 kV accelerating voltage. Recently, an rf-only hexapole collision cell (H_{cell}) has been inserted inside the six-sector instrument between E_2 and E_3 , replacing an rf-only quadrupole collision cell installed about ten years ago. The cell allows, *inter alia*, the study of associative ion/molecule reactions [13]. Briefly, the experiments utilizing the hexapole consist of the selection of a beam of fast ions (8 keV) with the three first sectors ($\text{E}_1\text{B}_1\text{E}_2$), the deceleration of these ions to approximately 5 eV kinetic energy which is the voltage difference between the accelerating voltage and the floating voltage applied to the hexapole. The interaction between the ions and the reagent gas is thereafter realized in the H_{cell} and, after re-acceleration at 8 keV, all the ions generated in the hexapole are separated and mass measured by scanning the field of the second magnet. The high-energy collisional activation (CA) spectra of mass-selected ions generated in the H_{cell} can be recorded by scanning the field of E_4 after selection of the ions with E_3 and B_2 .

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Scheme 1.

Benzaldehyde and tropone were commercially available and used without further purification.

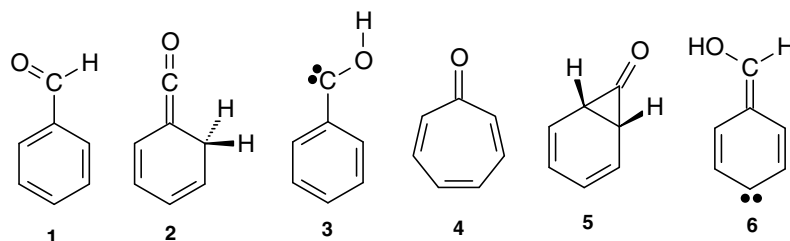
2.2. Computational

Quantum chemical calculations were carried out using the GAUSSIAN 03 set of programs [14]. Geometry optimizations of the $\text{C}_7\text{H}_6\text{O}^{\bullet+}$ stationary points including benzaldehyde radical cation and its isomers and the corresponding transition structures (TS) connecting the relevant equilibrium structures were conducted using density functional theory with the popular hybrid B3LYP functional and the 6-311++G(d,p) basis set. The identity of the local minima and TS's was established by harmonic vibrational frequency calculations at this level. The latter also provided the zero-point energy corrections to relative energies. Intrinsic reaction coordinate (IRC) calculations were performed to ascertain the connection between a TS and two local minima. To obtain more reliable heats of formation and thereby relative energies between isomeric forms, calculations were also carried out using the composite G3(B3) approach [15].

3. Results and discussion

Scheme 2 collects the structures of some neutral $\text{C}_7\text{H}_6\text{O}$ isomers which have been investigated in the present work. Among these compounds, **1** and **4** are conventional stable molecules, whereas the others can be considered as reactive molecules which cannot be prepared or handled under ordinary conditions.

Table 1 lists the calculated heats of formation of some relevant isomers in both neutral $\text{C}_7\text{H}_6\text{O}$ and ionized $\text{C}_7\text{H}_6\text{O}^{\bullet+}$ forms. Each system contains a large number of isomers [16], and it is not our intention to explore in detail the potential energy surfaces. We rather consider a few structures closely related to benzaldehyde **1** and $1^{\bullet+}$, namely both states of 1,3-cyclohexadienylidenemethanone **2** and $2^{\bullet+}$, phenylhydroxy carbene **3** and $3^{\bullet+}$ (*s-trans* conformation), and tropone **4** and $4^{\bullet+}$. Norcaradienone **5** was expected to be the neutral precursor of the distonic acylium ion $7^{\bullet+}$ (see Fig. 1) by ring opening after electron ionization. The neutral counterpart of the distonic ion $6^{\bullet+}$ was of high-energy and consequently is not further considered, the same for other norcaradiene-like structures. Some of the $\text{C}_7\text{H}_6\text{O}^{\bullet+}$ isomers have been considered in a previous computational study [16] using the UB3LYP/6-31G(d) level of theory.



Scheme 2.

Table 1

Heats of formation calculated using the G3B3 approach

Species	ΔH_f (0 K)	ΔH_f (298 K)
Neutral $\text{C}_7\text{H}_6\text{O}$		
Benzaldehyde 1	-21.5	-36.2 (-37.2) ^a
1,3-Cyclohexadienylidenemethanone 2	124.4	109.0
Phenylhydroxycarbene 3	191.3	177.2
Tropone 4	78.5	64.0
Ionized $\text{C}_7\text{H}_6\text{O}^{\bullet+}$		
Benzaldehyde $1^{\bullet+}$	889.7	876.5 (879.3) ^a
1,3-Cyclohexadienylidenemethanone $2^{\bullet+}$	847.0	833.5
Phenylhydroxycarbene $3^{\bullet+}$	926.7	912.8
Tropone $4^{\bullet+}$	943.6	929.9

Values given in kJ mol^{-1} .

^a Experimental values taken from Ref. [17].

Using the G3B3 approach, the heat of formation of benzaldehyde amounts to $\Delta H_f(\mathbf{1}) = -21.5 \text{ kJ mol}^{-1}$ at 0 K and $-36.2 \text{ kJ mol}^{-1}$ at 298 K. The corresponding experimental values listed in the current NIST compilation are -36.8 ± 3 and $-37.2 \pm 0.9 \text{ kJ mol}^{-1}$ at 298 K [17]. The deviation is thus about 1 kJ mol^{-1} . For the ionization energy of **1**, the G3B3 value is $\text{IE}_a(\mathbf{1}) = 9.43 \text{ eV}$ (at 0 K). Although several experimental values were listed in the NIST data base for this quantity, a value of $9.50 \pm 0.08 \text{ eV}$ has been selected. As for a further calibration, we evaluated the proton affinity of benzaldehyde using the same approach and obtained $\text{PA}(\mathbf{1}) = 829 \text{ kJ mol}^{-1}$ at 298 K, which is close to the experimental value of 833 kJ mol^{-1} [17].

We noted in the recent literature a value of 77 kJ mol^{-1} (at 298 K) derived from CBS-QB3 calculations [16] for the heat of formation of tropone **4**. This value differs substantially from an earlier value of 44 kJ mol^{-1} [18] and the present G3B3 result of 64 kJ mol^{-1} . The G3B3 value of $\text{IE}_a(\mathbf{4}) = 8.96 \text{ eV}$ is slightly larger than the available experimental result of $8.88 \pm 0.05 \text{ eV}$ [17]. Due to the disparate results for tropone **4**, it seems reasonable to exclude the available values for **4** in a comparison between experimental and theoretical results. In this case, an average error bar of $\pm 6 \text{ kJ mol}^{-1}$ ($\pm 1.5 \text{ kcal/mol}$) could thus be assigned to the G3B3 heats of formation of this series of compounds.

Amongst the neutral compounds considered, benzaldehyde **1** represents the lowest-energy isomer, with an increasing energy ordering (relative values in kJ mol^{-1} obtained from G3B3 calculations): **1** (0) > **4** (100) > **2** (146) > **3** (213). Upon ionization, the energy ordering of the radical cations is changed as follows: $2^{\bullet+}$ (-43) > $1^{\bullet+}$ (0) > $3^{\bullet+}$ (80) > $4^{\bullet+}$ (97) > $6^{\bullet+}$ (105). Accordingly, the ketene ion $2^{\bullet+}$ becomes the lowest-energy $\text{C}_7\text{H}_6\text{O}^{\bullet+}$ isomer, thanks to a stabilization of 43 kJ mol^{-1} relative to ionized benzaldehyde. Ionized carbene $3^{\bullet+}$ remains less stable than $1^{\bullet+}$ but slightly more stable than ionized tropone $4^{\bullet+}$. The relative energy between $3^{\bullet+}$ and $4^{\bullet+}$ has been calculated at the (U)B3LYP/6-31G* level of theory and the carbene was found to be less stable by a similar value of 15 kJ mol^{-1} [19].

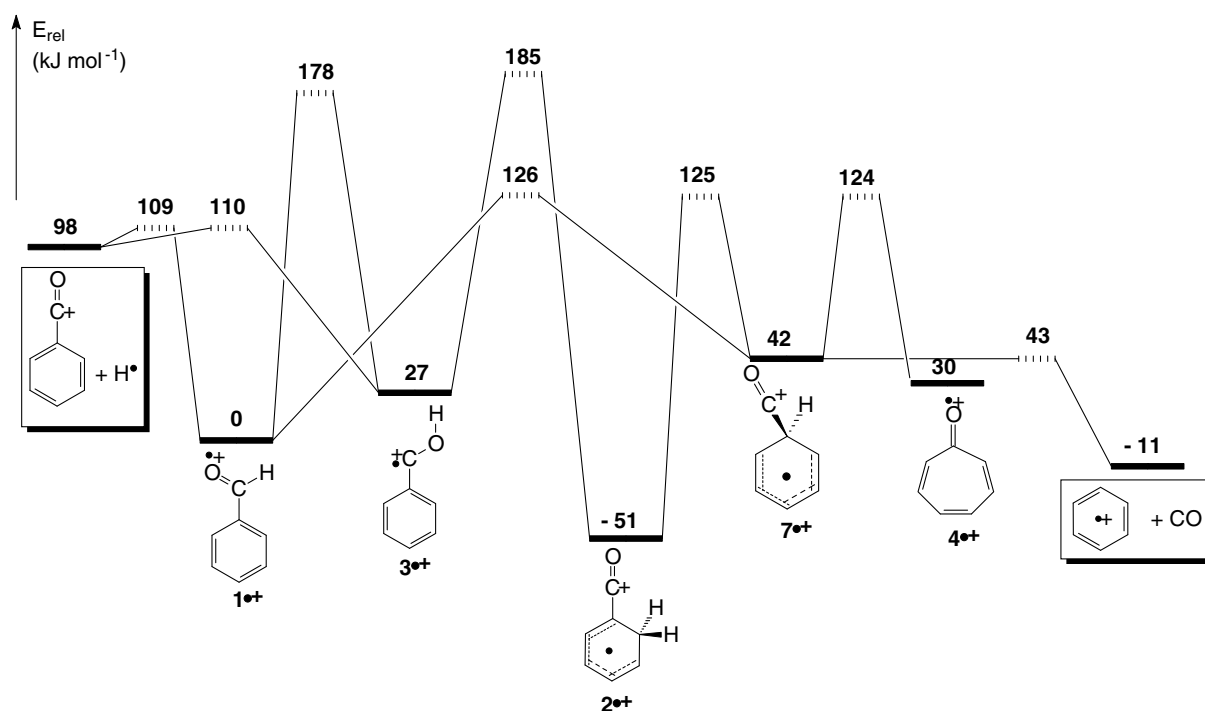


Fig. 1. Potential energy diagram connecting some $C_7H_6O^+$ radical cations. Relative energies given in kJ mol^{-1} were obtained from UB3LYP/6-311++G(d,p) + ZPE calculations.

Let us note the calculated ionization energies of the other isomers, $IE_a(2) = 7.49 \text{ eV}$ and $IE_a(3) = 7.62 \text{ eV}$. Thus, both the ketene **2** and carbene **3** species are characterized by relatively low IE 's. The $IE(3)$ is much smaller than the value for 1-hydroxyethylidene $IE_a(\text{CH}_3\text{COH}) = 8.20 \text{ eV}$ previously computed at the G3 level [20]; this points out the strong effect of the phenyl group on the carbene cation.

The high stability of 2^+ arises from the low IE of **2**. In 2^+ , the positive charge is found to be mainly located in the $(\text{C}=\text{O})^+$ group, whereas the excess electron is distributed within the two ring $\text{C}=\text{C}$ double bonds [21]. Accordingly, 2^+ features a separation of charge and radical centers and has thus a distonic [22] or a distonoid [23] character which is in part stabilized by its peculiar electronic structure. Both the troponium 4^+ and distonic carbene 6^+ radical cations are also low-energy species (the heat of formation of 6^+ amounts to 952 and 938 kJ mol^{-1} at 0 K and 298 K, respectively).

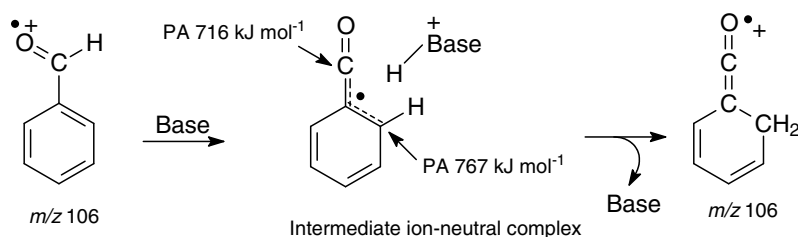
The minimum energy pathways connecting the isomers $C_7H_6O^+$ have also been constructed and the relevant energy profiles are schematically illustrated in Fig. 1, which also contains the competitive dissociation paths for the formation of the benzoyl cation plus the hydrogen atom, and the benzene radical cation plus carbon monoxide. Stability of the carbene ion 6^+ was analyzed in detail in our earlier paper [10].

Isomerization of the benzaldehyde ion 1^+ into the carbene ion 3^+ by a 1,2-H shift requires to overcome an energy barrier of

178 kJ mol^{-1} . Such a reaction is therefore not allowed as the lowest-energy dissociation channel of 1^+ , which is the loss of an hydrogen atom, requires 109 kJ mol^{-1} only. The same situation holds for the 1,2-H shift on the *ipso* position (126 kJ mol^{-1}) generating the distonic acylium ion 7^+ . A 1,3-H migration directly connecting ionized benzaldehyde 1^+ with the ketene 2^+ could not be located. In any case, such a process cannot compete either with the expected decarbonylation reaction yielding ionized benzene plus CO, or with the isomerization to ionized troponium 4^+ . We would conclude that the benzaldehyde ion 1^+ is protected against isomerization for such hydrogen shifts. In fact, the same situation holds for the other stable $C_7H_6O^+$ species. We also note that the radical cation 7^+ is not stable with respect to decarbonylation, due to the high stability of the benzene cation together with neutral carbon monoxide [17].

In summary, calculated results shown in Fig. 1 point out that the ionized $C_7H_6O^+$ species 1^+ , 2^+ , 3^+ and 4^+ are prevented from isomerization to each other by lower energy fragmentation channels. As a consequence, if prepared with appropriate precursors, they should present structurally distinct collisional activation spectra. This is actually the case for ionized benzaldehyde 1^+ and ionized troponium 4^+ , the former losing predominantly H^\bullet and the latter CO.

According to the previous literature results mentioned in the introduction, it is expected that tautomerization of the benzalde-



Scheme 3. Proton affinities of two sites of the benzoyl radical and production of the m/z 106 ketene ion within an ion-neutral complex.

hyde radical cation $1^{+\bullet}$ into the ketene ion $2^{+\bullet}$ could be catalyzed by the presence of an appropriate base, see Scheme 3. The base should present a proton affinity intermediate between the PA's of the two potential sites of the benzoyl radical. These PA's (0 K) have been estimated theoretically at 716 and 767 kJ mol^{-1} , respectively (B3LYP/6-311++G(d,p) + ZPE).

Experimentally, two different approaches could be envisaged with our large scale hybrid mass spectrometer (see experimental). In the first approach, benzaldehyde and the base are mixed within a chemical ionization ion source and submitted to electron ionization with the hope to detect an ion-neutral complex. Mass selection of this complex, deceleration and dissociation in the hexapole collision cell should regenerate m/z 106 radical cations, which, after re-acceleration, should be characterized by collisional activation. The second approach consists of the preparation of benzaldehyde ions by electron ionization (EI ion source), mass selection and deceleration into the hexapole collision cell pressurized with the base itself. Modification of the CA spectrum of the m/z 106 of benzaldehyde should be indicative of an isomerization process catalyzed by the base.

A proton affinity of 740 kJ mol^{-1} has been reported for formaldehyde [18], a value lying between the limits given in Scheme 3 suggesting that formaldehyde should be able to transport a proton from the carbonyl to the *ortho* position. Moreover, formaldehyde possesses a significant dipole moment of 2.3D [24] favoring strong electrostatic interaction with a radical cation. An experiment has therefore been performed in the chemical ionization source, the precursor of formaldehyde being paraformaldehyde introduced via a direct introduction probe and heated with a flash-vacuum pyrolysis unit [25] inserted between the probe and the ion source. In these conditions, we were nevertheless not able to detect any dimeric species at m/z 136. Most of the detected ions can be ascribed to self-chemical ionization of benzaldehyde.

Due to the fact that it is not an easy task to introduce formaldehyde within the hexapole collision cell, we have attempted to find another candidate presenting a proton affinity intermediate between the calculated PA's of the benzoyl radical. Methanol, with a proton affinity of 755 kJ mol^{-1} [18] appeared to be also a target of choice, but, just as in the case of formaldehyde, we were not able to detect any ion-neutral complex between ionized benzaldehyde and methanol under the CI conditions. We therefore turn to the second approach allowed by the appropriate vapor pressure of methanol. The results described below clearly prove that methanol can actually catalyse the isomerization of ionized benzaldehyde $1^{+\bullet}$ into a more stable ionized cyclohexadienylidene methanone $2^{+\bullet}$ structure.

As expected, the high-energy CA spectrum of the molecular ions of benzaldehyde, m/z 106, see Fig. 2a, features the sequential losses of H^{\bullet} (m/z 105), H^{\bullet} plus CO (m/z 77) and H^{\bullet} plus CO plus C_2H_2 (m/z 51). A small but significant peak is also noticed at m/z 29 corresponding to the formyl cation. This spectrum has been recorded after electron ionization of benzaldehyde in the EI source, mass selection of the m/z 106 ions with the first magnet (see experimental), deceleration from 8 keV to about 5 eV before entering the empty rf-only hexapole cell, re-acceleration to 8 keV, mass selection with the second magnet and finally collisional activation in front of the last electric sector (E scan).

The same experiment performed after pressurizing the rf-only hexapole cell with methanol (2×10^{-3} Torr) indicates some very significant differences, see Fig. 2b. Among these, the intensity increase of m/z 78, 52 (shoulder), 39 is particularly straightforward; these ions are produced by decarbonylation of an isomeric m/z 106 species giving m/z 78 ions followed by loss of ethyne (m/z 52) or a C_3H_3 radical (m/z 39). It is also worth noting that the production of doubly charged species is also increased (charge stripping peak at m/z 53) and that the peak at m/z 29 has almost disappeared.

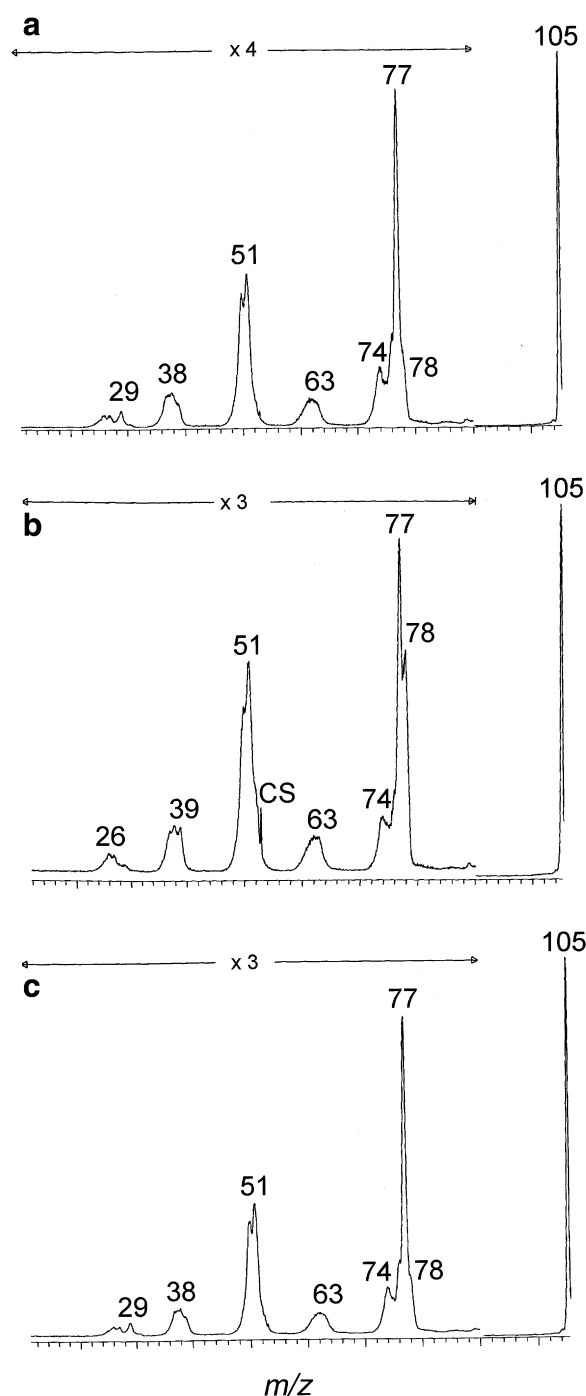


Fig. 2. High-energy CA spectra of m/z 106 $\text{C}_7\text{H}_6\text{O}^{+\bullet}$ radical cations generated by (a) electron ionization of benzaldehyde, (b) electron ionization of benzaldehyde followed by ion/molecule interaction with methanol in the rf-only hexapole cell, and (c) electron ionization of benzaldehyde followed by ion/molecule interaction with argon in the rf-only hexapole cell.

If methanol is now replaced by argon at an indicated 10^{-3} Torr pressure, the CA spectrum of the molecular ions of benzaldehyde shown in Fig. 2a is *not at all affected* (see Fig. 2c). This important result shows that collisional excitation of the m/z 106 ions is not responsible for the occurrence of an isomerization process (into $7^{+\bullet}$ for instance) rather to a pure chemical process. Various catalysis models have been proposed for the tautomerization of carbonylated radical cations [26], but we feel out of the scope of the present work to analyze theoretically the details of the actual mechanism.

4. Conclusion

In this combined experimental and theoretical study, we had the opportunity to explore theoretically the relative energies of some $C_7H_6O^+$ isomeric radical cations and found that the 1,3-cyclohexadienylidenemethanone radical cation 2^+ is actually more stable than the conventional ionized benzaldehyde 1^+ by about 43 kJ mol^{-1} . The ketene ion was produced from its benzaldehyde isomer by a catalytic action of methanol, which formally underwent a capture-release of a proton.

Hydroxyphenylcarbene ion 3^+ and tropone ion 4^+ are found to be higher in energy by about $35\text{--}55 \text{ kJ mol}^{-1}$. These species however appear to be protected against interconversion by hydrogen shifts. Accordingly, 3^+ could be observed if generated from an appropriate precursor.

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