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Metastable dimethyl phthalate molecular ions: Does the loss of a methoxyl radical proceed with or without anchimeric assistance?

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ABSTRACT

Using MS/MS/MS experiments and quantum chemical calculations, it is demonstrated that oxygen (carbonyl) methylated phthalic anhydride cations are produced when metastable dimethyl phthalate molecular ions expel a methoxyl radical. At higher internal energies, isomeric acyl ions are competitively generated.

1. Introduction

Phthalates, or phthalate esters, are esters of phthalic acid and are mainly used as plasticizers by plastics companies. Such substances are added to plastics to increase their flexibility, transparency, durability and longevity. They are primarily used to soften polyvinyl chloride. Phthalates are used in a large variety of products, from enteric coatings of pharmaceutical pills and nutritional supplements to viscosity control agents, gelling agents and binders. End applications include adhesives and glues, personal care products, medical devices, detergents and surfactants, paints, pharmaceuticals, food products and textiles. Phthalates are also used in a variety of household applications. Personal care items containing phthalates include perfume, and hair spray. They are also found in modern electronics and medical applications such as catheters and blood transfusion devices. The most widely used phthalates are the di-2-ethyl hexyl phthalate (DEHP), the diisodecyl phthalate (DIDP) and the diisononyl phthalate (DINP). DEHP is the dominant plasticizer used in PVC. Benzylbutylphthalate (BBzP) is used in the manufacture of foamed PVC, which is mostly used as a flooring material. Starting in 2004, manufacturers produced about 363 000 tons of phthalates each year [1]. Nowadays, phthalates are being phased out of many products in the United States and European Union over health concerns. Indeed, phthalates are easily released into the environment because they are not covalently bound to the plastic materials in which they are mixed and, as a consequence, people are exposed to phthalates on a regular basis. Several recent studies demonstrated the negative health effects played by phthalates. Suspected effects are, for example, endocrine disruption, abnormal obesity, insulin resistance and damages to the liver and testes eventually leading to male infertility [2].

Due to their chemical natures, such analytes are conveniently analyzed from complex mixtures by using GC–MS methodologies [3]. Given the fact that, in such analysis, the ion preparation is realized inside an electronic ionization (EI) source, we decided sometime ago to experimentally and theoretically approach the gas phase behaviors of phthalates and related molecules upon EI ionization [4]. In particular, the chemistry of long-lived, metastable, molecular ions of dimethyl terephthalate [5] and dimethyl isophthalate [6] was recently studied by using tandem mass spectrometry methodologies and quantum chemical calculations.

In the present report, we present the final part of this investigation by describing our experimental and theoretical results obtained for the third positional isomer, dimethyl phthalate **1**.

2. Experimental

The spectra were recorded on a hybrid tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors

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of $cE_1B_1cE_2hE_3B_2cE_4$ geometry (E_i stands for electric sector, B_i for magnetic sector, c for conventional collision cells and h for an rf-only hexapole collision/reaction cell). Typical conditions already reported elsewhere [7,8] 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. The hexapole cell allows, *inter alia*, the study of associative ion/molecule reactions [9], the specific preparation of ions by charge exchange [10] and the study of collision induced dissociations (CID, low kinetic energy regime) [11]. This cell can also be used as a particularly large field-free region in which metastable ions decompose [5,6]. The high-energy collisional activation (CA) spectra of such mass-selected products generated in the hexapole cell and retaining the full kinetic energy can be recorded by scanning the field of E_4 after selection of the ions with E_3 and B_2.

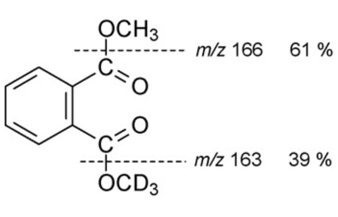
Calculations were performed using the Gaussian 03 suite of programs [12]. Optimization of the stationary point geometries (reactants, intermediates, products and transition structures) and calculation of their harmonic vibrational frequencies and zero-point energies were conducted using density functional theory (DFT) with the popular hybrid B3LYP functional [13], in conjunction with the 6-311++G(d,p) basis set. Zero-point energies (ZPE) were scaled by a scaling factor of 0.98. To confirm direct links from transition structures (TS) to the corresponding reactants and products, relevant intrinsic reaction coordinate (IRC) paths were computed at the same B3LYP/6-311++G(d,p) level. The unrestricted formalism (UHF, UB3LYP) was used for open-shell systems.

3. Results and discussion

3.1. Mass spectrometry results

The 70 eV electron ionization (EI) mass spectrum of dimethyl phthalate (MW 194 g mol^{-1}) was reported on numerous occasions, usually under GC/EI/MS conditions required for an efficient detection, characterization and quantitation in samples of various origin (foods, drugs, etc.). A typical mass spectrum can be found in reference 14 which shows *m/z* 194, 163 (base peak), 135 and 133 as the principal ions in the high mass region. Replacement of the six methyl hydrogen atoms by six deuterium atoms indicates a quantitative displacement of these peaks at *m/z* 200, 166, 138 and 134 [14].

As far as *metastable* ions are concerned, *m/z* 194 molecular ions decompose specifically by loss of 31 u (C,H_3,O loss), while the so-obtained *m/z* 163 ions decompose by competitive losses of carbon monoxide or formaldehyde giving peaks at *m/z* 135 and 133 respectively as shown by ion kinetic energy spectrometry (IKE spectrometry) [14]. Compared to the unimolecular chemistry of its dimethyl terephthalate and isophthalate isomers, the dissociation of the molecular ions of dimethyl phthalate ($\mathbf{1}^{\bullet+}$) appears thus deceptively simple. This is actually the case not only for ion source reactions but also for metastable decompositions occurring during the flight and such a behavior contrasts with the extremely complex fragmentation of long-lived dimethyl terephthalate and isophthalate ions recently studied in our laboratory [5,6] using advanced tandem mass spectrometry methodologies.



1a

Scheme 1. Dissociation of the metastable *m/z* 197 ions of the partially deuterium labeled dimethyl-d$_3$ phthalate **1a** and relative abundance of the product ions.

Partial transesterification of dimethyl phthalate with perdeuterated methanol catalyzed by sulfuric acid generates the isotopologue **1a** (MW 197 g mol^{-1}) shown in Scheme 1. As expected, the *m/z* 194 → 163 reaction observed for the undeuterated compound is now replaced by two competitive reactions indicated by the dotted lines in Scheme 1. However, both processes reveal different efficiencies as exemplified by the different branching ratios (see Scheme 1). A small secondary kinetic isotope effect ($i = 1.56$) is thus

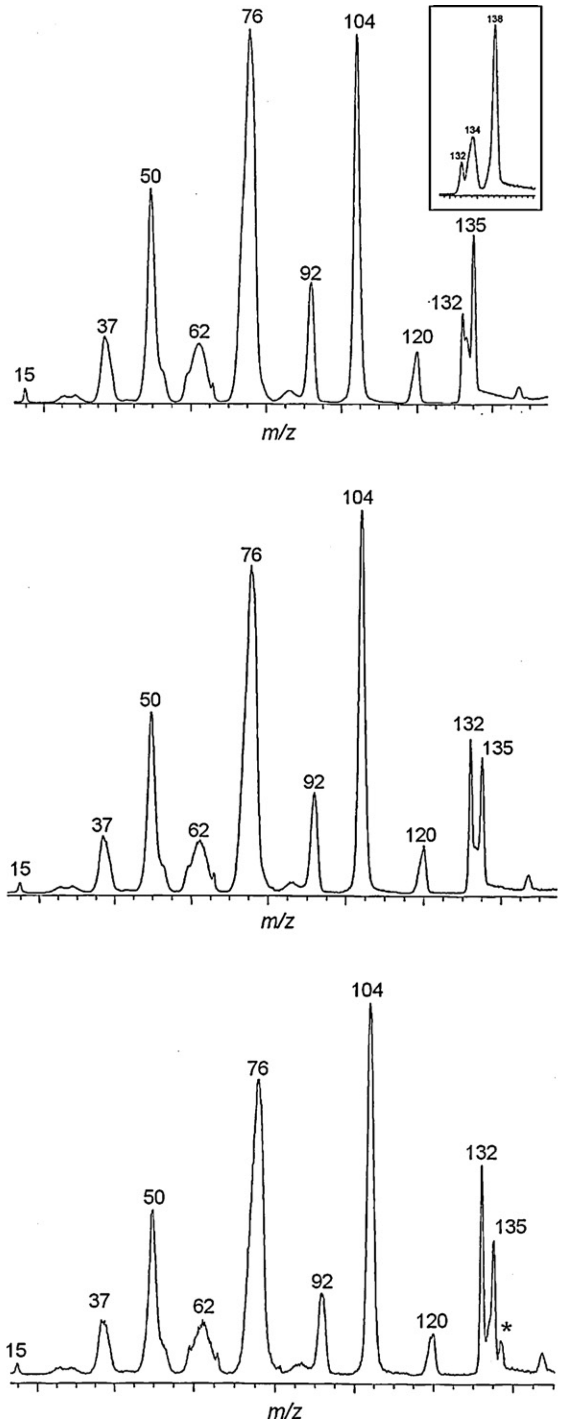
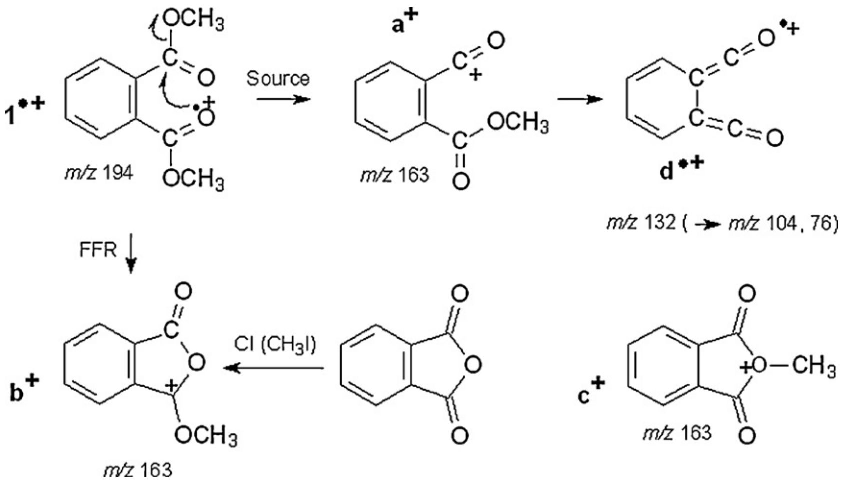


Fig. 1. Collisional activation spectra of the *m/z* 163 ions of dimethyl phthalate generated (a) within the EI ion source, (b) in the evacuated hexapole collision cell by fragmentation of the *metastable* molecular ions *m/z* 194 and (c) by chemical ionization (methylation) of phthalic anhydride using CI (CH_3I) conditions [8 keV kinetic energy of the ions and nitrogen collision gas in all cases]. *Artifact peak. Inset in (a): detail of the CA spectrum of the *m/z* 166 ions prepared from **1a**.



Scheme 2. Methoxyl radical losses from ionized dimethyl phthalate **1**$^{\bullet+}$ within the ion source or within a field-free region (third FFR) of the tandem mass spectrometer with the production of isomeric ions **a**$^+$ and **b**$^+$.

operating probably due to the modification of the reduced mass of the C–O bond upon deuteration.

The collisional activation (CA) spectrum of the source-generated m/z 163 ions is presented in Fig. 1a. Upon collisional activation, excited m/z 163 ions decompose by competitive losses of carbon monoxide (m/z 135), formaldehyde (m/z 133), [C,H_3,O]$^\bullet$ radical (m/z 132) and $CH_3OCO^\bullet$ radical (m/z 104). The base peak of the spectrum observed at m/z 76 for $C_6H_4^{\bullet+}$ radical cations is characteristic of a disubstituted benzene structure. It is important to emphasize that the m/z 132 signal is not observed in the MIKE spectrum of the precursor m/z 163 ions. Using the isotopologue **1a** (inset in Fig. 1a), the m/z 135, 133 and 132 peaks are now clearly resolved and shifted at the expected positions, namely m/z 138 for the CO loss, m/z 134 for the CH_2O loss whereas the m/z 132 signal remains at its original position, the labeling being lost in this fragmentation. This new, unreported [14], fragmentation is very significantly enhanced if the m/z 163 precursor ions are generated from the *metastable* m/z 194 molecular ions (Fig. 1b).

Consequently, we would like to suggest that the m/z 163 ions produced by decomposition of metastable molecular ions of dimethyl phthalate are isomers, **b**$^+$, of the acylium ions **a**$^+$ produced by fast decomposition within the ion source. The latter may be ascribed to substituted benzoyl ions (see Scheme 2) while the former are tentatively proposed to be generated by an anchimeric assistance of the carbonyl group for the methoxyl radical elimination. As an alternative pathway, it was previously proposed [15] that this elimination is assisted by the oxygen of the alkoxy group, but the resulting oxonium ion **c**$^+$ is probably strongly destabilized by the two remaining carbonyl groups.

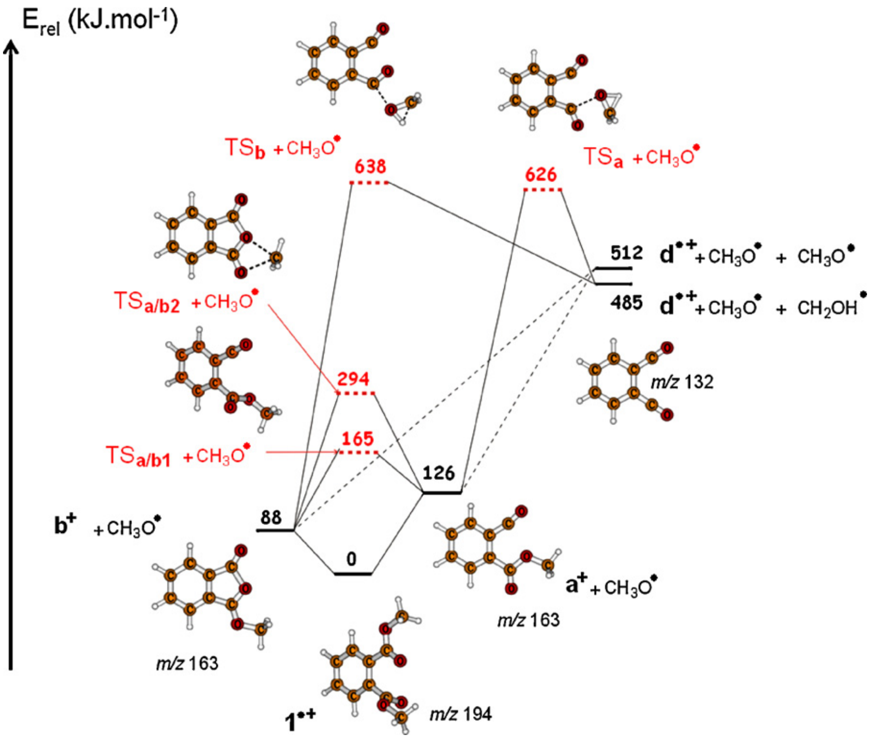


Fig. 2. Relative energy levels for ionized dimethyl phthalate **1**$^{\bullet+}$, its dissociation products **a**$^+$ and **b**$^+$ (plus a methoxyl radical) and the consecutive eliminations of C,H_3,O radical generating m/z 132 diketene ions **d**$^{\bullet+}$.

The chemistry of **a**$^+$ ions can be understood in terms of loss of the methoxyl radical ($CH_3O^\bullet$) into a diketene radical cation **d**$^{\bullet+}$, detected at m/z 132. This could appear in contradiction with the so-called even–even rule [16], but exceptions are nowadays legion [16,17]. Subsequent decarbonylation yields m/z 104 ions which decarbonylate again into $C_6H_4{}^{\bullet+}$ radical cations (m/z 76). These m/z 104 and 76 peaks are prominent processes seen in the CA spectrum of the m/z 163 ions whatever their origin.

Methylation of phthalic anhydride under chemical ionization conditions using methyl iodide as the reagent gas is expected to generate the isomeric structure **b**$^+$. The carbonyl oxygen site is indeed expected to present the highest methyl cation affinity compared to the dicoordinated oxygen or the ring carbons. The introduction in a chemical ionization source of methyl iodide as the reagent gas [18] together with phthalic anhydride leads to the production of a high concentration of m/z 163 ions whose CA spectrum (Fig. 1c) is almost identical to the spectrum of the metastably generated m/z 163 ions from dimethyl phthalate. In particular, the modification of the relative abundances of the m/z 135 and 132 ions is worthy of note.

3.2. Quantum chemical calculations

Dimethyl phthalate radical cation (**1**$^{\bullet+}$, m/z 194) has been chosen as the reference energy point in the schematic energy profile given in Fig. 2. As shown in Fig. 3, this ion structure has one methoxycarbonyl group nearly perpendicular to the planar ring of the molecule. The dihedral angle OCCC of ~94° is smaller in the radical cation than in the neutral precursor (~125°). The adiabatic ionization energy of dimethyl phthalate is calculated to amount to 9.41 eV (908 kJ mol^{-1}). As expected, this adiabatic value is lower than the experimental vertical value, 9.64 eV [19].

The cation **a**$^+$ (m/z 163) can be formed by direct bond cleavage without a significant energy barrier. In its planar conformation shown in Fig. 3, cation **a**$^+$ plus a methoxyl radical is calculated to be 126 kJ mol^{-1} higher in energy than the starting ionized dimethyl phthalate (Fig. 2).

Due to the proximity of the two methoxycarbonyl groups, however, the formation of a cyclized m/z 163 ion **b**$^+$ may be expected if a closure of the five-membered ring brings an over-stabilization. This is indeed found to be the case and the *O*-methylated phthalic anhydride ion **b**$^+$, resulting from an anchimerically assisted methoxyl radical loss, is calculated to be more stable than the acylium ion **a**$^+$ by 38 kJ mol^{-1}. Structure **b**$^+$ is also formed from ionized dimethyl phthalate without a significant energy barrier. The characteristics of these two reactions (relative energies and frequency factors) strongly support the fact that the cyclisation process may be more prominent at low internal energy (metastable ions) than under high internal energy conditions (ion source reactions).

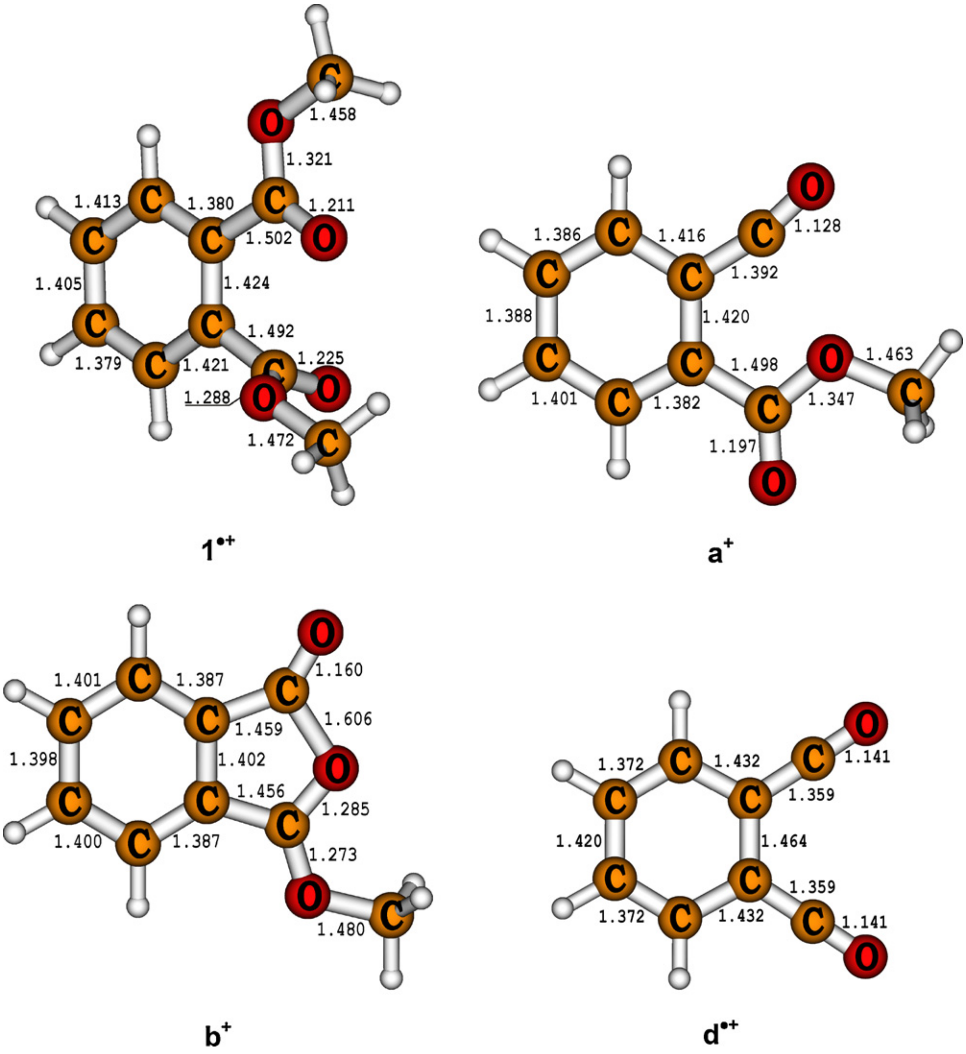


Fig. 3. Calculated bond lengths (in angstroms) for ionized dimethyl phthalate **1**$^{\bullet+}$, the isomeric ions **a**$^+$ and **b**$^+$ and the m/z 132 diketene fragment ion **d**$^{\bullet+}$.

For the sake of comparison, we also tried to calculate the relative energy of structure **c**, but such an oxonium connectivity was not found to be a minimum on the potential energy surface and the calculation optimized to the acylium structure $\mathbf{a}^+$ by stretching of the O—C(=O) single bond.

Two transition structures (TSs) have been found for the interconversion between both cations $\mathbf{a}^+$ and $\mathbf{b}^+$ (m/z 163). The first transition structure $\mathbf{TS_{a/b1}}$ corresponds to the rotation of the ester group around the planar of acylium group. $\mathbf{TS_{a/b1}}$ is located 165 kJ mol^{-1} higher in energy than ionized dimethyl phthalate. As a consequence, cations $\mathbf{a}^+$ and $\mathbf{b}^+$ are only protected against isomerization in each other by a really weak transition state, located 39 and 77 kJ mol^{-1} higher in energy than cations $\mathbf{a}^+$ and $\mathbf{b}^+$, respectively. The optimized geometrical parameters are showed in Fig. 4. It is worth mentioning that the optimized structure for $\mathbf{TS_{a/b1}}$ presents an ester group perpendicular to the plan of the benzene ring. All attempts to optimize a conformation of ion $\mathbf{a}^+$ in which the oxygen carbonyl atom of the ester group would point to the carbon atom of the acylium moiety invariably led to ion $\mathbf{b}^+$. We also found out a second transition state $\mathbf{TS_{a/b2}}$ that is situated 294 kJ mol^{-1} above the reference point, which is thus at 168 and 206 kJ mol^{-1} higher in energy than $\mathbf{a}^+$ and $\mathbf{b}^+$, respectively. This TS ($\mathbf{TS_{a/b2}}$) is related to a 1,3-methyl shift from O(1) to O(10) atoms, in which the elongation of the C–O bond distances (2.375 and 2.254 Å) clearly shows the process (Fig. 4). The weakness of both the calculated transition barriers explains the great similarity between the CA spectra of both isomers (Fig. 1). In such a case, the distinction between isomer ions is only achieved by running collisional activation experiments in the high kinetic energy regime (keV).

Among the consecutive decomposition processes of the m/z 163 ions, we have theoretically investigated the second [CH_3O] radical loss yielding m/z 132 radical cations, since the isomer distinction relies on the different relative intensities of the m/z 132 signal in the CA spectra (Fig. 1). Starting with the acylium ions $\mathbf{a}^+$, one pathway was found for the formation of m/z 132 radical cations plus a C,H_3,O radical (Fig. 2). This radical loss occurs via a transition state which is located at 626 kJ mol^{-1} above the reference point. In the relevant TS ($\mathbf{TS_a}$ in Fig. 4), the C—O bond distance is increased up to 2.246 Å which is about 0.909 Å longer than the C—O bond length (1.347 Å) in the minimum potential well of ion $\mathbf{a}^+$ (Fig. 3). The transition state structure for the fragmentation of ion $\mathbf{a}^+$ into m/z 132 fragment ion clearly indicates that the corresponding products are ionized diketene $\mathbf{d}^{\bullet+}$ (m/z 132) plus a hydroxymethyl radical. The shortening of the C—H and O—H distances to 1.312 and 1.224 Å, respectively, indicates indeed the expulsion of the more stable $^\bullet CH_2OH$ isomer (Fig. 4). The produced diketene ion $\mathbf{d}^{\bullet+}$ (m/z 132) has a planar structure and could then undergo consecutive decarbonylation processes yielding in sequence m/z 104 and m/z 76. Starting with the isomeric ions $\mathbf{b}^+$, a similar pathway was found for the formation of the same diketene m/z 132 radical cations (Fig. 2). This radical loss occurs via a transition state which is now located at 638 kJ mol^{-1} above the reference point. In the relevant TS ($\mathbf{TS_b}$ in Fig. 4), the C—O bond distance is increased up to 2.045 Å which is about 0.772 Å longer than the C—O bond length (1.273 Å) in the minimum potential well of ion $\mathbf{b}^+$ (Fig. 3). The structure of the transition state for the fragmentation of ion $\mathbf{b}^+$ into m/z 132 again indicates that the products are ionized diketene $\mathbf{d}^{\bullet+}$ (m/z 132) plus a hydroxymethyl radical. The shortening of the C—H and O—H distances to 1.416 and 1.124 Å, respectively, again indicates the loss of the more stable $^\bullet CH_2OH$ isomer.

As for an alternative for the consecutive loss of 31 u from ions $\mathbf{a}^+$ and $\mathbf{b}^+$, we also explored the possibility that the expelled neutral molecule was $CH_3O^\bullet$ instead of the more stable isomer $^\bullet CH_2OH$. Indeed, $CH_3O^\bullet$ is only 40 kJ mol^{-1} less than $^\bullet CH_2OH$ [19], whereas the calculated reverse barrier for $^\bullet CH_2OH$ loss amounts to 141 and 153 kJ mol^{-1} for ions $\mathbf{a}^+$ and $\mathbf{b}^+$, respectively (Fig. 2). Since it is

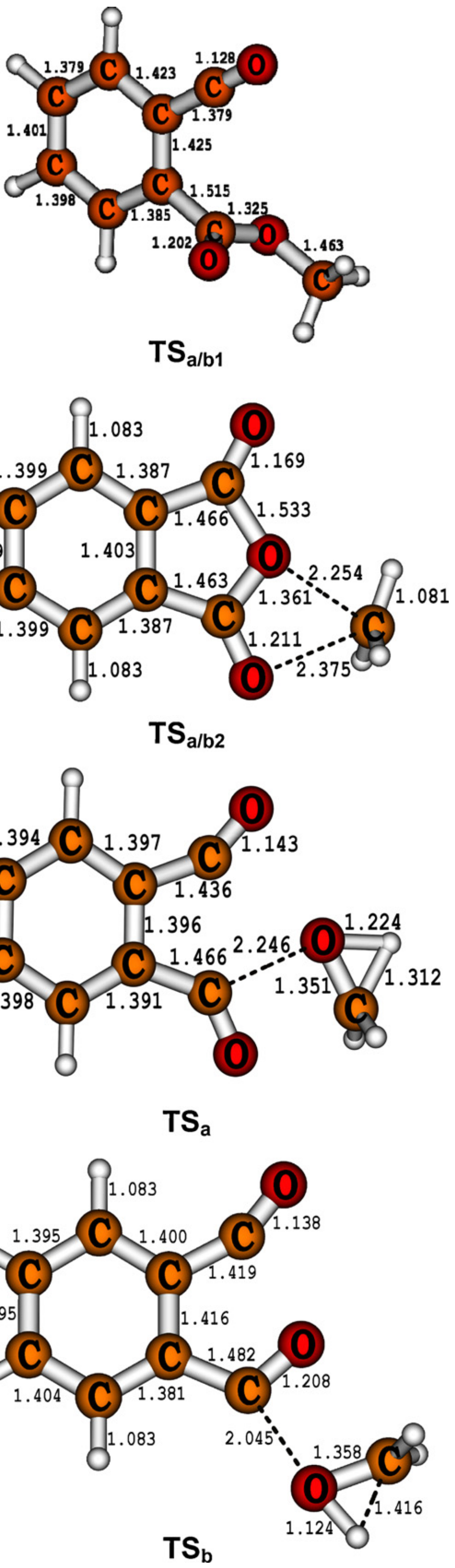


Fig. 4. Transition state structures for the isomerization of ions $\mathbf{a}^+$ and $\mathbf{b}^+$ by a (1,3) methyl shift and transition state structures for the C,H_3,O radical losses from isomeric ions $\mathbf{a}^+$ and $\mathbf{b}^+$.

expected that the $CH_3O^\bullet$ loss does not involve any reverse barrier to occur, the loss of the less stable $CH_3O^\bullet$ neutral could be associated with an energy requirement that is more than 100 kJ mol^{-1} lower than the dissociation threshold for the $^\bullet CH_2OH$ loss. From both ions **a**$^+$ and **b**$^+$, the losses of $CH_3O^\bullet$ were then considered. All attempts to locate transition structures for this $CH_3O^\bullet$ loss failed and it appeared that the losses of the $CH_3O^\bullet$ radical from both ions **a**$^+$ and **b**$^+$ are continuously endothermic processes (occurring without TS) leading to ions **d**$^{\bullet+}$ (*m*/*z* 132). As presented in Fig. 2, those processes require 386 and 424 kJ mol^{-1} for respectively ions **a**$^+$ and **b**$^+$. Those energy requirements being by far lower than the dissociation thresholds leading to the $^\bullet CH_2OH$ loss, it is expected than the 31 u loss from ions **a**$^+$ and **b**$^+$ corresponds to a $CH_3O^\bullet$ neutral loss.

4. Conclusions

Compared to the unimolecular chemistry of its positional isomers, tere- and isophthalates, the behavior of metastable dimethyl phthalate molecular ions appears at first sight deceptively simple. Experiments indicate however that *O*-methylated phthalic anhydride ions are competitively produced starting with long-living metastable molecular ions while acylium ions are produced for unstable ions quickly decomposing within the ion source. Structures for ions **a**$^+$ and **b**$^+$ supported by theoretical calculations are presented. A putative oxonium ion **c**$^+$ is not calculated as a minimum on the potential energy surface.

Acknowledgements

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