

# On the loss of a methyl radical from metastable dimethyl terephthalate molecular ions

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## Abstract

The MS/MS spectrum of the metastable molecular ions of dimethyl terephthalate **1** features an unexpected, quite intense, loss of a methyl radical. Using a combination of mass spectrometry techniques, it is shown that this process consists of a pseudo simple cleavage reaction isomerizing, in the first step, one of the two methoxycarbonyl substituents into a distonic  $\text{ArC}^+(\text{-OH})\text{-OCH}_2\cdot$  ( $\text{Ar} = \text{CH}_3\text{O}_2\text{C}-\text{C}_6\text{H}_4-$ ) connectivity. The final product is established to be protonated 5-carboxyphthalide. The overall mechanism of the methyl loss includes a sequence of five steps as supported by quantum chemical (DFT) calculations.

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**Keywords:** Dimethyl terephthalate; Mass spectrometry; Metastable ions; Quantum chemical DFT calculations

## 1. Introduction

In the course of a study of the decarboxylation mechanism of metastable methyl benzoate ions [1], we had recently the opportunity to investigate the behavior of several metastable 4-substituted methyl benzoate ions. In the particular case of dimethyl terephthalate **1**, we have noticed a peculiar behavior of the corresponding metastable molecular ions, which results in an intense and unexpected loss of a methyl radical. Such reaction, which is indeed not significantly observed in the 70 eV electron ionization mass spectrum of dimethyl terephthalate **1** (the same for the isomeric isophthalate **2** and phthalate **3**) [2], constitutes the subject of the present report.

## 2. Experimental

The spectra were recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combin-

ing six sectors of  $\text{cE}_1\text{B}_1\text{cE}_2\text{qcE}_3\text{B}_2\text{cE}_4$  geometry ( $\text{E}_i$  stands for electric sector,  $\text{B}_i$  for magnetic sector, q for a quadrupole collision cell and c for conventional collision cells). Typical conditions have been reported elsewhere [3]. The installation of the RF-only quadrupole collision cell (Qcell) inside the instrument between  $\text{E}_2$  and  $\text{E}_3$  has also been reported [4]. This modification allows the study of associative ion-molecule reactions and the study of low energy (ca. 20–30 eV) collision induced dissociations of decelerated ions. Briefly, the experiments utilizing the quadrupole 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. The interaction between the ions and the reagent gas is thereafter realized in the Qcell and, after re-acceleration at 8 keV, all the ions generated in the quadrupole are separated and mass measured by scanning the field of the second magnet. Without the presence of a reagent (or collision) gas, the quadrupole could be considered as a particular field-free region. The products of dissociation of decelerated mass-selected metastable ions can then be recorded after re-acceleration by such a  $\text{B}_2$  magnet scanning. Such spectra will be referred as “resolved” MIKE spectra in the text. The high-energy collisional activation (CA) spectra of

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mass-selected ions generated in the Qcell can be recorded by a scanning of the field of  $E_4$  after selection of the ions with  $E_3$  and  $B_2$ .

All the samples were commercially available (Aldrich) and used without any further purification.

Quantum chemical calculations were carried out using the Gaussian 03 set of programs [5]. Geometry optimizations of the stationary points including methyl benzoate radical cation and its isomers and the corresponding transition structures (TS) connecting the relevant equilibrium structures were conducted at the UB3LYP/6-311++G(d,p) level of density functional theory. The identity of the local minima and TS's has been established by harmonic vibrational frequency calculations at this level. In several cases, intrinsic reaction coordinate (IRC) calculations were performed to ascertain the connection between a TS and two local minima. Unless otherwise noted, relative energies on the potential energy surfaces were obtained from UB3LYP/6-311++G(d,p) + ZPE calculation, and given in  $\text{kJ mol}^{-1}$ .

### 3. Results and discussion

#### 3.1. Experimental results

Fig. 1a shows the “resolved” MIKE spectra of the molecular ions of dimethyl terephthalate **1** (Scheme 1). Four reactions are seen to compete within the metastable energy window, namely the loss of a hydrogen atom ( $m/z$  193), the loss of a methyl group ( $m/z$  179), the loss of  $\text{C}_2\text{H}_3\text{O}$  ( $m/z$  163) and the loss of  $\text{C}_2\text{H}_3\text{O}_2$  ( $m/z$  135) (also to a very minor extent,  $\text{C}_8\text{H}_6\text{O}$  ion formation ( $m/z$  118)). If the two latter reactions are expected for an aromatic methyl ester, the direct loss of a hydrogen atom and especially the loss of a methyl group are rather new and unexpected.

While carboxylate anions are stable species, carboxylate cations are not. This fragmentation must therefore be more complex than a single bond cleavage and unimolecular rearrangements certainly precede dissociation (pseudo simple bond cleavage).

One possible interpretation for the pathway consists of a loss of structural integrity after ionization. Isomerization of  $\mathbf{1}^{\bullet+}$  into  $\mathbf{3}^{\bullet+}$  could indeed bring the two carbomethoxy groups to a sufficiently close proximity to allow the occurrence of an *ortho* effect. For instance, the loss of a methyl radical from ionized methyl *o*-toluate has been demonstrated to start by hydrogen migration from the benzylic position to the oxygen of the carbonyl group before losing the methyl group of the initial ester function [6]. Such a behavior has been extended to other *ortho*-substituted methyl benzoates [7]. This hypothesis can however readily be discarded on the basis of the MIKE spectra of the molecular ions of dimethyl phthalate **3** and dimethyl isophthalate **2**. The former features only one fragmentation, the loss of  $\text{C}_2\text{H}_3\text{O}$  ( $m/z$  163) whereas the second shows a more complex dissociation pattern with mainly three intense peaks corresponding to the competitive losses of H ( $m/z$  193, 100%),  $\text{C}_2\text{H}_2\text{O}$  ( $m/z$  164, 61%) and  $\text{C}_2\text{H}_3\text{O}$  ( $m/z$  163, 91%). It is therefore clear that the metastable molecular ions of **1–3** are *not* isomerized to each other or to a common structure before fragmentation.

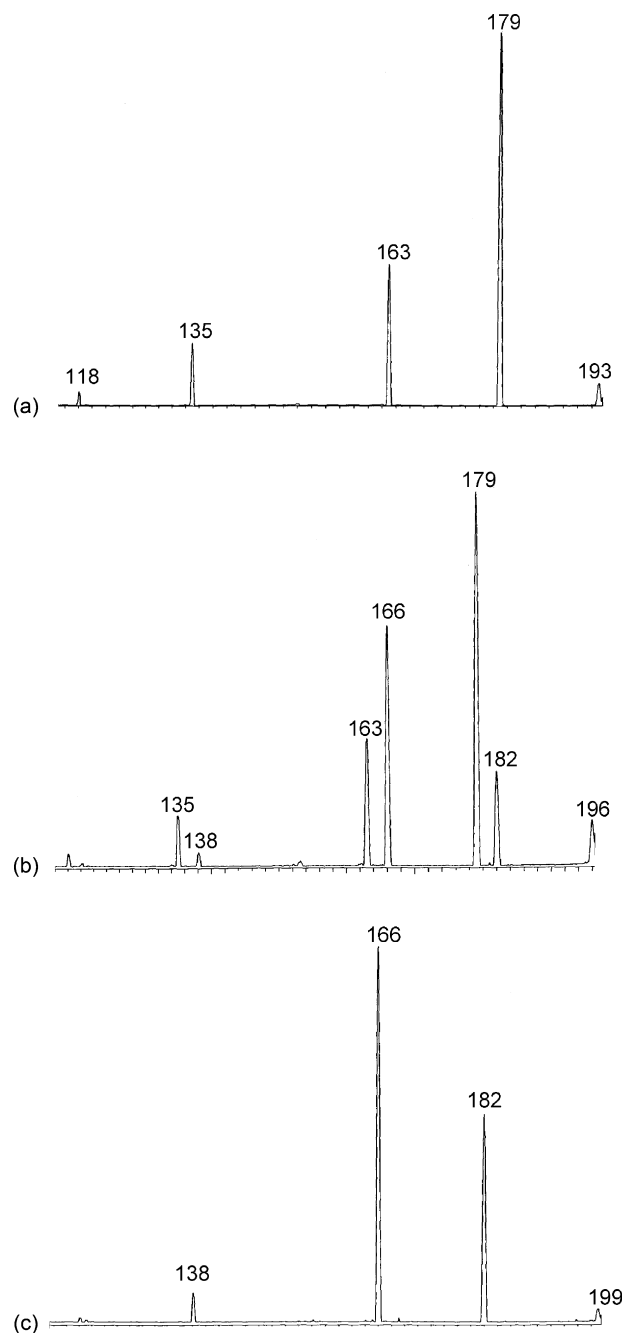
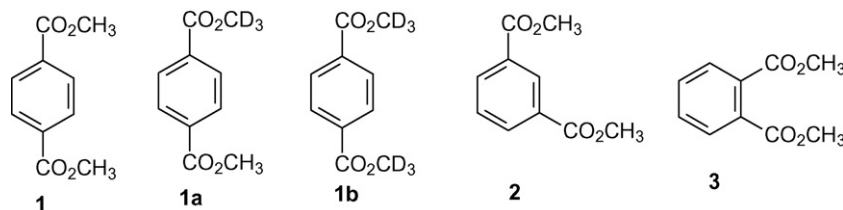
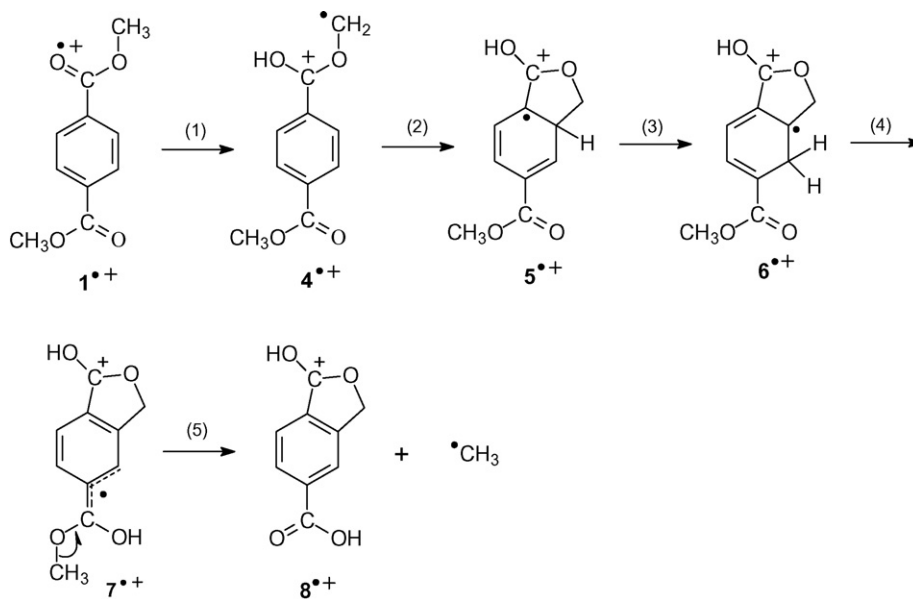


Fig. 1. (a–c) “Resolved” MIKE spectra of the molecular ions of dimethyl terephthalate **1** ( $m/z$  194) (a) and two isotopomers **1a** ( $m/z$  197) (b) and **1b** ( $m/z$  200) (c).

We have therefore considered another mechanism based on recent results proposed for the decomposition of metastable methyl benzoate molecular ions [1]. The first step in this mechanism, described by step (1) in Scheme 2, involves a [1,4] hydrogen migration from the methyl group towards the carbonyl group producing a distonic species  $\mathbf{4}^{\bullet+}$ . This distonic ion has in fact several different conformations generated by separate or subsequent rotations around the O–H and the other O–CH<sub>2</sub> single bonds. The energies of these conformations are rather close to each other. Once the radical site of one of the distonic species is situated in an appropriate position, it can then attack the *ortho* position of the benzene ring (step 2) producing a bicyclic inter-



Scheme 1.



Scheme 2. Intermediates likely involved in the loss of a methyl radical from metastable dimethyl terephthalate molecular ions.

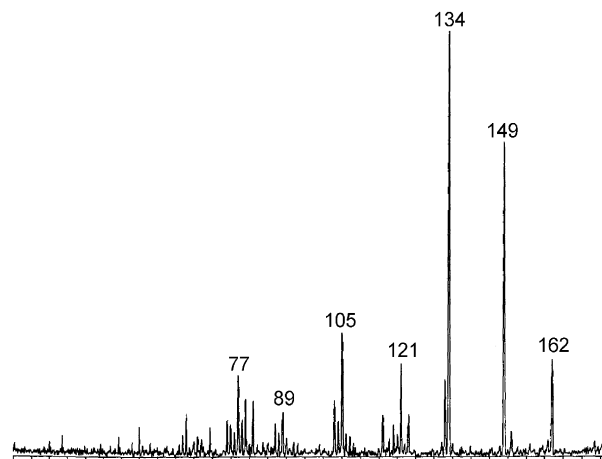
mediate ion. The original aromaticity is thus lost in this process, but the resulting species is nevertheless expected to be reasonably stable as the positive charge can be stabilized by the electron lone pairs of two oxygen atoms of the hemiacetal function and the radical site can be stabilized by conjugation (this point will be confirmed by quantum chemical calculations, *vide infra*).

After the step (2) is passed, the chemistry of the metastable molecular ions of methyl benzoate and dimethyl terephthalate must diverge as the former compound loses carbon dioxide which is cleanly replaced by a methyl radical loss for the terephthalate ion.

Further isomerizations by hydrogen migrations (steps 3 and 4) can finally place the migrating hydrogen on the remaining carbonyl oxygen and trigger the homolysis of the H<sub>3</sub>C–O bond. The resulting cation is thus a protonated phthalide bearing a carboxylic group on the benzene ring, **8<sup>•+</sup>**. The CA spectrum of these *m/z* 179 ions depicted in Fig. 2 provides a strong support for this interpretation. Tell-tale peaks are indeed readily identified in the spectrum indicating the facile losses of HO• (*m/z* 162) and HO• + CO (*m/z* 134) in competition with the loss of CH<sub>2</sub>O (*m/z* 149). This last peak can readily be explained by fragmentation of the five-membered ring.

On standing with deuterated methanol, CD<sub>3</sub>OH, and a trace of concentrated sulfuric acid for several days at room temperature, dimethyl terephthalate **1** suffers *trans*-esterification as evidenced by the appearance of new peaks at *m/z* 197 and 200 in

the 70 eV EIMS spectrum. These peaks are evidently associated with the production of two isotopomers **1a** and **1b** (Scheme 1) that correspond to the replacement of one (or two) CH<sub>3</sub> group by CD<sub>3</sub>. The “resolved” MIKE spectra of these isotopomers are shown in Fig. 1b and c. The three peaks observed for **1** are now replaced, as expected, by six peaks (three “doublets”) for **1a**, but the components of each “doublet” have different intensities. This observation points towards the occurrence of kinetic iso-

Fig. 2. CA (B/E linked scan, oxygen collision gas) spectrum of the metastably generated *m/z* 179 ions from ionized dimethyl terephthalate **1**.

tope effects. For instance, the  $m/z$  179/ $m/z$  182 ratio is found to be  $\sim 3$ . In other words,  $\text{CD}_3^\bullet$  is lost preferably than  $\text{CH}_3^\bullet$ , due to the consequence of an easier migration of hydrogen as compared to deuterium. Overall, the step (1) described in Scheme 2 participates therefore in the rate-limiting step as it is also found in the case of methyl benzoate [2].

As far as the loss of a methoxyl radical is concerned, it is found that the loss of  $\text{CH}_3\text{O}^\bullet$  is now preferred over the loss of  $\text{CD}_3\text{O}^\bullet$ . The ratio  $m/z$  163/ $m/z$  166 is equal to  $\sim 0.5$ . As for a possible explanation, the neutral species from this elimination is not the methoxyl radical but rather its more stable hydroxymethyl radical isomer. That has been proposed previously in the literature for metastable methyl acetate ions on the basis of collisionally induced dissociative ionization (CIDI) experiments [8].

### 3.2. Quantum chemical calculations

In an attempt to support the mechanism proposed in Section 2, we have performed density functional theory (DFT) calculations using the UB3LYP functional in conjunction with

6-311++G(d,p) basis set. The portion of the potential energy surface including the relevant local minima and transition structures are illustrated in Fig. 3.

As in the case of metastable ionized methyl benzoate decomposition, it is found that the various conformations of the distonic species  $4^{\bullet+}$  (a–d) (Scheme 3) are less stable than the conventional species  $1^{\bullet+}$ , the stability difference ranging from 14 to 48  $\text{kJ mol}^{-1}$ .

The transition structure connecting  $1^{\bullet+}$  to  $4b^{\bullet+}$  by a 1,4-hydrogen shift is calculated to be at 104  $\text{kJ mol}^{-1}$ , that is substantially higher in energy than the TS's for rotation connecting the various conformations of the radical cation. Once in an appropriate *trans-cis* conformation  $4c^{\bullet+}$  (see Scheme 3), a cyclisation into the intermediate ion  $5^{\bullet+}$  occurs with an energy barrier of 94  $\text{kJ mol}^{-1}$  relative to  $1^{\bullet+}$ . The ion  $5^{\bullet+}$  is thereafter expected to be able to follow mainly three distinct reaction channels including (1) a  $\text{CH}_2\text{--O}$  single bond cleavage as previously proposed in the case of the decarboxylation of ionized methyl benzoate, and (2) a loss of a hydrogen atom to yield a protonated phthalide bearing a methoxycarbonyl group or (3) a hydrogen ring-walk transforming initially  $5^{\bullet+}$  into  $6^{\bullet+}$ .

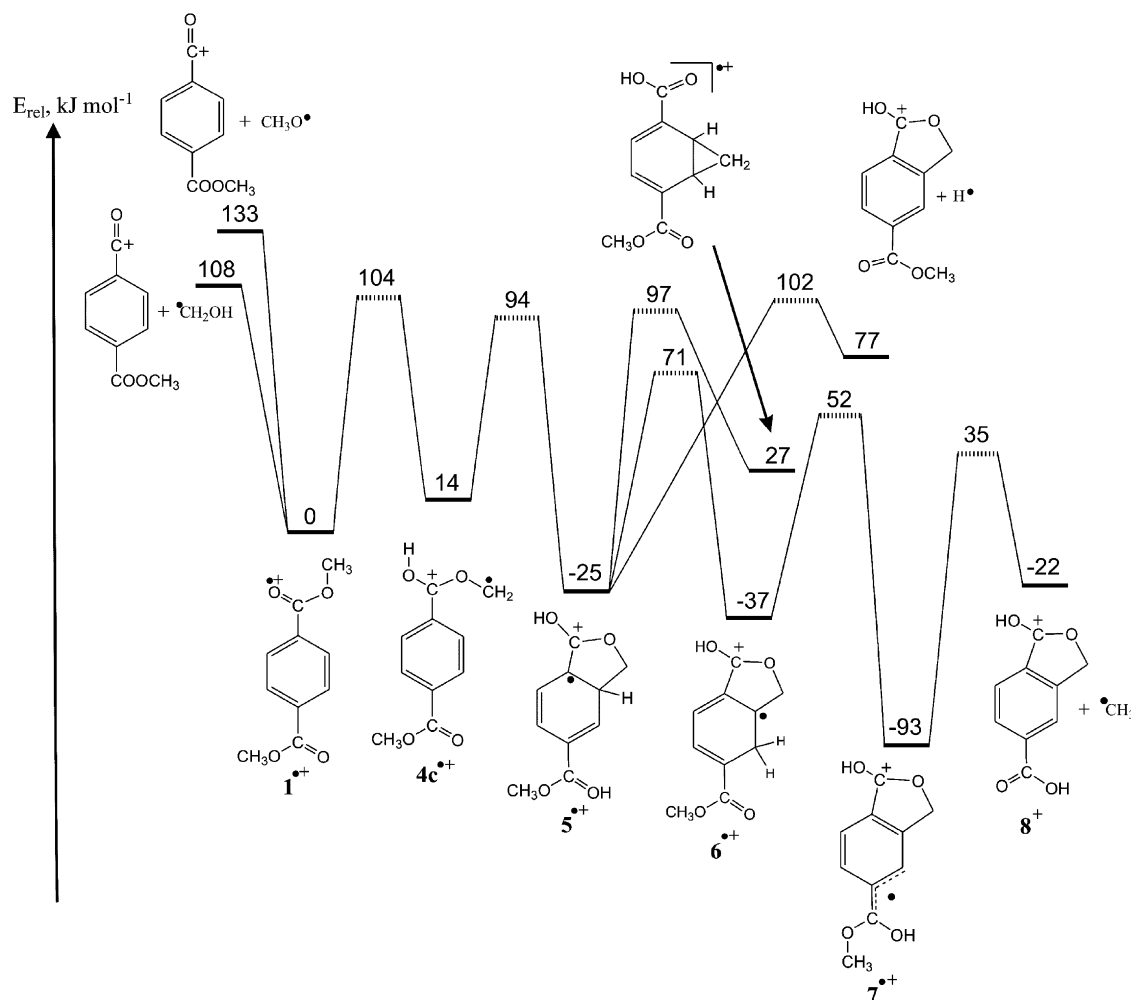
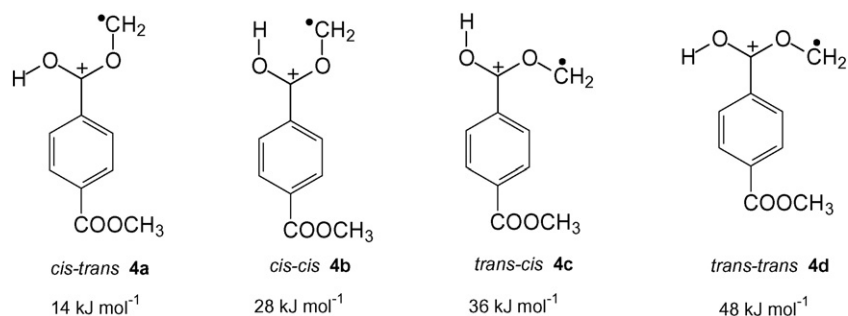


Fig. 3. Portion of the potential energy surface illustrating the unimolecular processes underwent by metastable  $1^{\bullet+}$  radical cations. Relative energies given in  $\text{kJ mol}^{-1}$  were determined from UB3LYP/6-311++G(d,p) + ZPE calculation.



Scheme 3. Relative energies of four rotamers of **4\*\*** (energies relative to ionized dimethyl terephthalate **1\*\*+**).

Given the fact that metastable carbon dioxide loss is actually *not* detected for the ion **1\*\*+** and that metastable hydrogen loss is only a minor process in the “resolved” MIKE spectrum, see Fig. 1, it is expected that the third reaction should be present with a lower energy barrier. Transition structure energies for reactions (1) to (3) are calculated to be 97, 102 and 71 kJ mol<sup>-1</sup>, respectively, in agreement with the experimental predictions shown in Scheme 4.

A hydrogen ring-walk around a benzene ring usually concerns successively all the carbon atoms [9]. In the present case however, the methoxycarbonyl function can act as a trap for the migrating hydrogen and, once attached on the carbonyl oxygen, ion **7\*\*+** presents an appropriate configuration to lose a methyl radical. The expected products are therefore protonated 5-carboxyphthalide and a methyl radical.

Finally, the potential energy surface shown in Fig. 3 indicates a critical reverse energy of 126 kJ mol<sup>-1</sup>. A significant part, being 48 kJ mol<sup>-1</sup>, of this energy is transformed into translational energy of the separating species as measured from the width at half-height of the metastable peak ( $T_{50} = 518$  meV, conventional E scan). Flat-topped or even dish-topped metastable peaks are usually seen for the loss of CH<sub>3</sub><sup>•</sup> from *ortho*-

substituted methyl benzoates after hydrogen transfer on the carbonyl oxygen [7].

#### 4. Conclusions

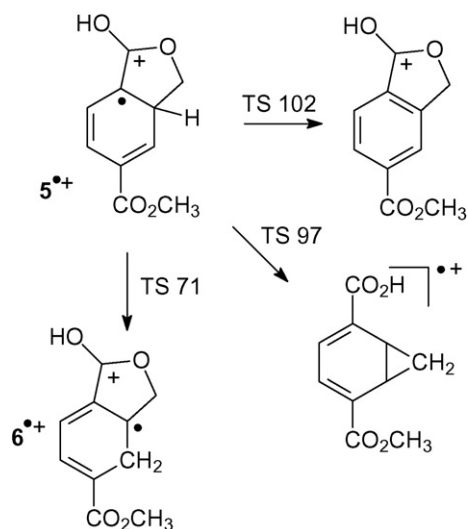
The peculiar loss of a methyl radical from the metastable molecular ions of dimethyl terephthalate ions has been investigated both experimentally and theoretically. It is proposed that the overall multi-step process is initiated by a rate-determining isomerization of one methoxycarbonyl function into a distonic connectivity as already proposed for metastable methyl benzoate ions. Protonated 5-carboxy phthalide plus a methyl radical are the ultimate products of this metastable fragmentation.

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Scheme 4. Possible reaction channels for the decomposition of **5\*\*+** ions. TS energies in kJ mol<sup>-1</sup>.

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