International Journal of Mass Spectrometry 275 (2008) 110–116

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Unimolecular chemistry of metastable dimethyl isophthalate radical cations

Robert Flammang[a,*], Noémie Dechamps[a], Pascal Gerbaux[a],
Pham-Cam Nam[b,c], Minh Tho Nguyen[b]

[a] Laboratory of Organic Chemistry-Center of Mass Spectrometry, University of Mons-Hainaut, Avenue Maistriau 19, B-7000 Mons, Belgium
[b] Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium
[c] Department of Chemical Engineering, University of Danang, 54 Nguyen Luong Bang Street, Danang, Viet Nam

ARTICLE INFO

Article history:
Received 4 April 2008
Received in revised form 20 May 2008
Accepted 26 May 2008
Available online 30 June 2008

Keywords:
Dimethyl isophthalate
Mass spectrometry
Metastable ion
Proton transport catalysis

ABSTRACT

The MS/MS spectrum of the metastable molecular ions of dimethyl isophthalate **1** differs from that of the isomeric dimethyl terephthalate **2** by the observation of, *inter alia*, a quite intense loss of C,H_2,O ascribed to formaldehyde. Results obtained using a combination of mass spectrometry techniques suggest that this process could consist of an isomerization reaction of the molecular ion into an ion–neutral complex (INC) linking a benzoyl radical and neutral formaldehyde to a proton $[Ar{-}C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$. Within the complex, a proton transfer catalyzed by formaldehyde occurs resulting in the production of an ionized cyclohexadienylidene methanone (ketene) structure.

1. Introduction

Phthalates, or phthalate esters, are a group of chemical compounds that are mainly used as plasticizers, i.e., substances added to plastics to increase their flexibility. They are chiefly used to turn polyvinyl chloride from a hard plastic into a flexible plastic [1]. Since plasticizers are not chemically bound to polymer, significant migration into the environment is possible, and a large variety of mass spectrometric methods have been developed for their detection and characterization [2]. In particular and in closer relation with the present report, several papers have appeared using tandem mass spectrometric techniques concerning fragmentation mechanisms of ionized phthalates, isophthalates and terephthalates [3].

During a recent study related with the decarboxylation mechanism of metastable methyl benzoate ions [4], we had the opportunity to investigate the behavior of several metastable four-substituted methyl benzoate ions. In the particular case of dimethyl terephthalate **2**, we have noticed a peculiar behavior of the corresponding metastable molecular ions, which results in an intense and unexpected (for a methyl ester) loss of a methyl radical [5]. Such a reaction was also detected for metastable dimethyl isophthalate **1**, but to a quite lower extent. The behavior of the latter metastable ions constitutes the subject of the present report, in particular the competitive intense fragmentations expelling a hydrogen atom or formaldehyde.

2. Experimental

The spectra were recorded on a hybrid tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of $cE_1B_1cE_2ccE_3B_2cE_4$ geometry (E_i stands for electric sector, B_i for magnetic sector, and c for conventional collision cells). Typical conditions already reported elsewhere [6,7] 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 10 years ago [8]. The cell allows, *inter alia*, the study of associative ion/molecule reactions [5]. Briefly, the experiments utilizing the hexapole 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 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

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* Corresponding author. Tel.: +32 65 37 33 36; fax: +32 65 37 35 15.
E-mail address: Robert.Flammang@umh.ac.be (R. Flammang).

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doi:10.1016/j.ijms.2008.05.031

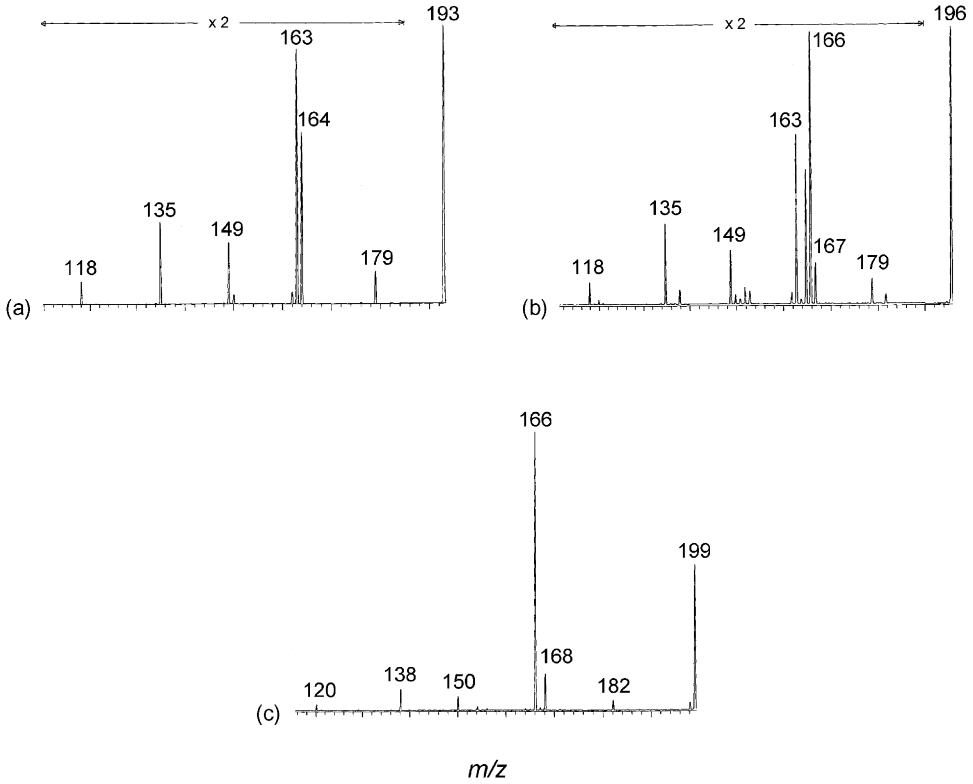


Fig. 1. "Resolved" MIKE spectra of the molecular ions of dimethyl isophthalate **1** (*m*/*z* 194, a) and deuterium labeled **1a** (*m*/*z* 197, b) and **1b** (*m*/*z* 200, c) isophthalates.

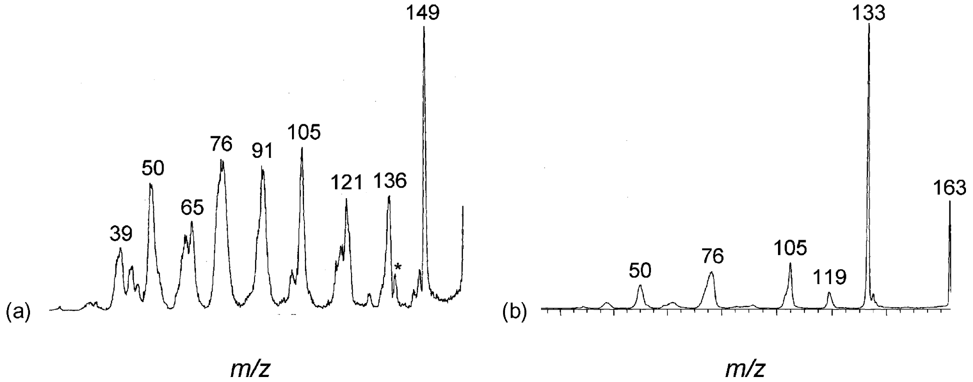


Fig. 2. CA (air collision gas) spectra of (a) metastably generated *m*/*z* 164 ions of dimethyl isophthalate and (b) the molecular ions of methyl 3-formylbenzoate. *Artifact peak.

B_2. Products of dissociation of metastable ions within the hexapole without collision gas or reagent gas can be recorded in the same way and will be referred to in the text as "resolved" MIKE spectra.

All the samples were commercially available and used without further purification.

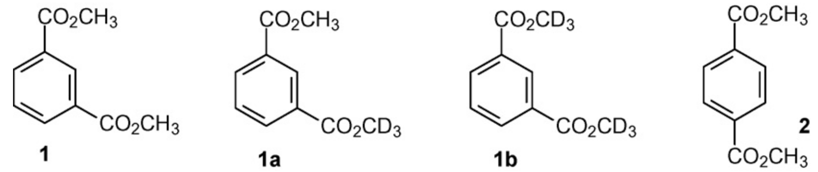
Quantum chemical calculations were carried out at the UB3LYP/6-311++G(d,p) (+ZPE) level of density functional theory using the Gaussian 98 set of programs [9].

3. Results and discussion

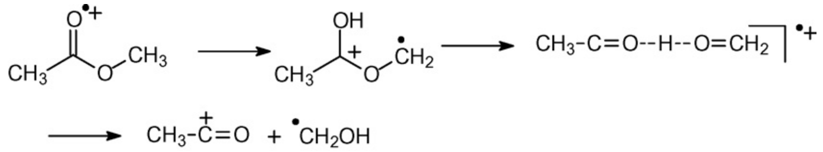
The "resolved" MIKE spectrum of the molecular ions of the title compound **1** (see Scheme 1, *m*/*z* 194) is depicted in Fig. 1a. This spectrum appears surprisingly quite complex and features a base peak for a hydrogen atom loss and other intense cleavages expelling a methoxyl radical (*m*/*z* 163) or formaldehyde (*m*/*z* 164). This latter reaction was not seen at all in the 70 eV mass spectrum, the detected signal at *m*/*z* 164 corresponding only to the ^{13}C isotopic peak of *m*/*z* 163.

The loss of formaldehyde was also not seen in the MIKE spectrum of the isomeric dimethyl terephthalate **2** molecular ions for which a methyl loss is in fact the most prominent process (*m*/*z* 179) [5]. Also, a carbon dioxide loss (*m*/*z* 150) which is the main reaction in the case of ionized methyl benzoate [4] is only scarcely observed (~4% of the *m*/*z* 193 base peak) in the present case.

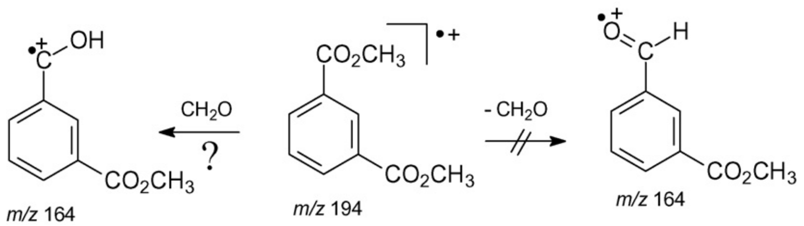
Treatment of isophthaloyl dichloride with a 1:1 mixture of methanol and perdeuterated methanol has allowed the preparation of the labeled phthalates **1a** and **1b** as evidenced by the appearance of peaks at *m*/*z* 197 and 200 in the 70 eV EI spectrum of the reaction mixture. The peak at *m*/*z* 197 is associated with the production of the labeled phthalate **1a** corresponding to the replacement in **1** of one CH_3 group by CD_3. The "resolved" MIKE spectrum of these partially labeled molecular ions is shown in Fig. 1b. The first conclusion derived from this spectrum is that the dominant loss of



Scheme 1.



Scheme 2. Mechanism proposed [7] for the loss of an hydroxymethyl radical from metastable ionized methyl acetate.



Scheme 3. Hypothetical production of an hydroxycarbene radical cation by formaldehyde loss from ionized dimethyl isophthalate.

hydrogen arises *exclusively* from the ring, not at all from the methyl groups. Secondly, the losses of a methoxyl radical and formaldehyde are subjected to kinetic isotope effects, but in opposite directions: CD_2O loss is preferred over CH_2O loss, while $CH_3O^\bullet$ loss is preferred over $CD_3O^\bullet$ loss. The isotope effect for the formaldehyde loss can be quantified as high as 3.2 by using the m/z 165:167 branching ratio in Fig. 1b. A similar isotope effect (about 4.0) was measured previously for the loss of a methyl group from metastable dimethyl terephthalate ions [5].

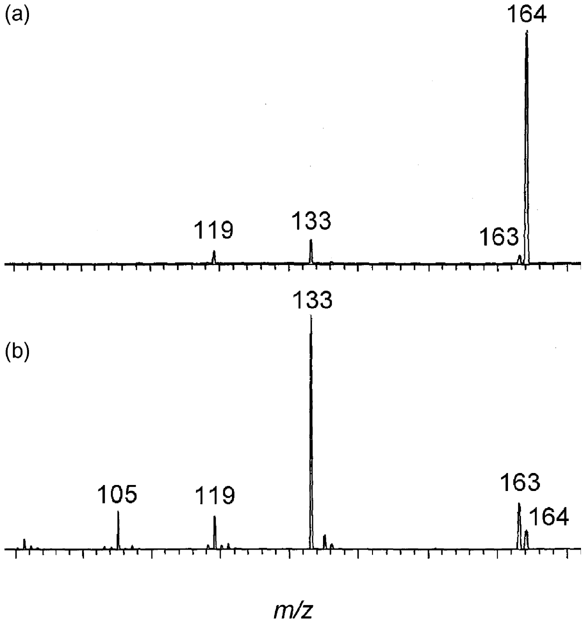


Fig. 3. Mass spectra (B scan) of the ions produced when methyl 3-formyl benzoate ions (m/z 164) are injected in the hexapole reaction cell without the presence of a reagent gas (a) and with a 10^{-3} Torr acetone pressure (b).

The “resolved” MIKE spectrum of the m/z 200 molecular ions (Fig. 1c) mainly indicates a significant decrease in intensity of the loss of a ring hydrogen atom.

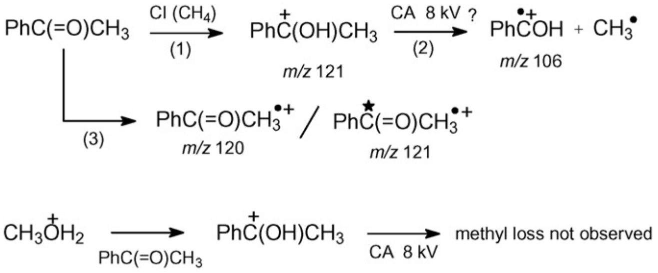
Compared to dimethyl terephthalate **2**, the major differences thus consist of (1) the more facile loss of an hydrogen atom (from the benzene ring) and (2) the occurrence of a formaldehyde loss. Several possible mechanisms for such a reactivity are considered hereafter.

3.1. Isomerization of one methoxycarbonyl substituent before fragmentation

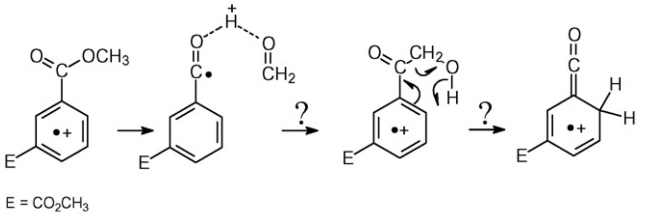
Metastable methyl acetate radical cations have been reported to lose 31 amu and this neutral species was not the methoxyl radical but rather it is more stable hydroxymethyl radical isomer (Scheme 2) [7].

That has been proposed previously in the literature for the decomposition of metastable methyl acetate ions on the basis of collisionaly induced dissociative ionization (CIDI) measurements [10]. The proposed mechanism was based on an ion–neutral complex (INC) intermediate as depicted in Scheme 2. In this Scheme, the conventional precursor ion is, in a first step, isomerized into a distonic species by a [1,4] hydrogen shift. Considering the structure of the INC intermediate, one can imagine several dissociation pathways, but on the basis of available heats of formation [11], the dissociation of ionized methyl acetate into an acetylium ion plus a hydroxymethyl radical is by far the lowest energy channel (627 kJ mol^{-1}). Heat of formation of ionized methyl hydroxycarbene plus formaldehyde or ionized acetaldehyde plus formaldehyde requires 757 and 713 kJ mol^{-1}, respectively. We have nevertheless considered similar mechanisms for the decomposition of metastable dimethyl isophthalate ions.

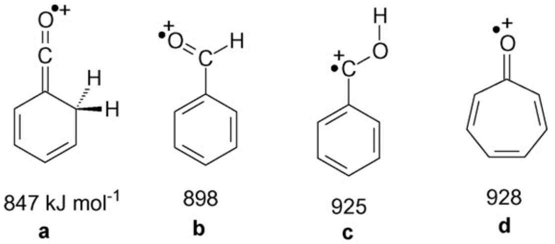
An MS/MS/MS experiment (Fig. 2a) performed on the metastably generated m/z 164 ions (loss of formaldehyde) indicates an intense loss of a methyl radical (m/z 149) and a quite complex dissociation pattern which will be investigated in more details in



Scheme 4. Methane chemical ionization of acetophenone (1), expected collisional demethylation of the MH+ ions (m/z 121) (2) and charge exchange reaction of acetophenone in the methane plasma (3).



Scheme 5. Suggested isomerization of a methoxycarbonyl into a hydroxyacetyl substituent.



Scheme 6. Heat of formation of some $C_7H_6O^{\bullet+}$ radical cations (m/z 106) calculated using a G3B3 approach [12]. (**a**) Cyclohexadienylidenemethanone ion; (**b**) benzaldehyde ion; (**c**) hydroxyphenyl carbene ion (*s-trans*); (**d**) tropone ion.

a following section. Methyl 3-formylbenzoate has also an appropriate composition for these fragment ions, but the CA spectrum of the corresponding molecular ions is found completely different featuring a quite intense peak for a C,H_3,O loss at m/z 133 (Fig. 2b). The product ion at m/z 164 could therefore be more likely an isomer of an aromatic aldehyde, for instance an hydroxy aryl carbene (see Scheme 3).

We have attempted to generate phenylhydroxycarbene radical cation by collisional demethylation of protonated acetophenone (Scheme 4).

Given the high proton affinity (PA) of acetophenone (859 kJ mol^{-1}) compared to benzene (759 kJ mol^{-1}) [11], it was assumed that oxygen protonation should mainly occur (step 1 in Scheme 4) under chemical ionization conditions and collisional demethylation of the protonated species was expected to produce the hydroxycarbene ion. Such a demethylation reaction was indeed observed, but the CA spectrum of the resulting m/z 106 ions (step 2 in Scheme 4) cannot be explained on the basis of a carbene connectivity. Actually, the $CH_3^{\bullet}$ loss observed in the CA spectrum of protonated acetophenone is an artifact due to an interference with the ^{13}C isotope peak of the small but present m/z 120 peak generated in a competitive charge exchange process. This is clearly indicated by an experiment where protonation of acetophenone occurs in the hexapole collision cell by using a beam of mass-selected protonated methanol (m/z 33). After proton transfer, the collisional loss of a methyl radical from the m/z 121 ions is only marginally detected under these experimental conditions which eliminate any possibility of charge exchange reaction.

3.2. Isomerization of one of the methoxycarbonyl substituents into an hydroxyl acetyl connectivity

Another mechanism which could also account for the formaldehyde loss is proposed in Scheme 5. One methoxy carbonyl function of the starting material could be isomerized into a 2-hydroxy acetophenone structure (bearing an ester function denoted by E) possibly *via* a hydrogen-bridged radical cation followed by hydrogen rearrangement toward the ring concerted with a loss of formaldehyde. If this mechanism applies, the final product should be a ketene radical cation.

Such hypothesis has found recently some theoretical and experimental support in this laboratory [12] demonstrating that the cyclohexadienylidenemethanone radical cation **a** is actually more stable than conventional ionized benzaldehyde **b** and other isomers as those shown in Scheme 6, namely ionized phenyl hydroxy carbene **c** and ionized tropone **d**.

The 70 eV EI mass spectrum of 2-hydroxyacetophenone has already been reported [13] and does not feature however any significant signal for a loss of formaldehyde, the major fragmentation being an intense loss of 31 u for a loss of C,H_3,O. We have nevertheless recorded the “resolved” MIKE spectrum of the molecular ions at m/z 136 because the unimolecular chemistry can be found drastically different for ion source reactions compared to field-free region reactions. However, the decomposition of the metastable m/z 136 ions is also a C,H_3,O radical loss without any significant evidence for a formaldehyde loss. This is in fact not unexpected as these two reactions require the same excess energy, about 109 kJ mol^{-1}, but probably quite different frequency factors (simple cleavage *viz.* rearrangement) resulting in the complete absence of competition over the whole domain of internal energies. *However, these findings do not prove that the mechanism depicted in Scheme 5 is not occurring at all for the metastable molecular ions of dimethyl isophthalate.*

3.3. Ion/molecule reactions within ion–neutral complexes

According to a proposed mechanism for the loss of ethene from the molecular ions of phenetole (phenyl ethyl ether) [14] passing through an ion–radical complex, mechanism nevertheless still subjected to a debate in the literature [15], we would like to suggest the

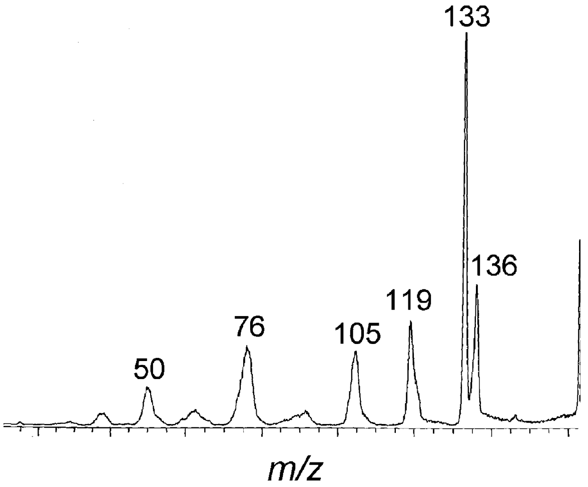
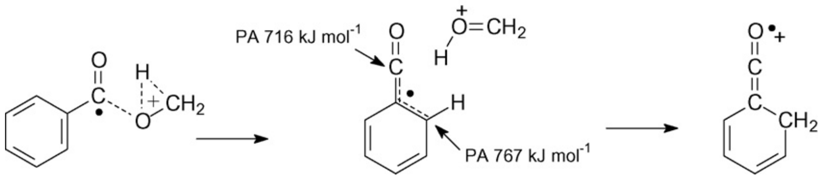
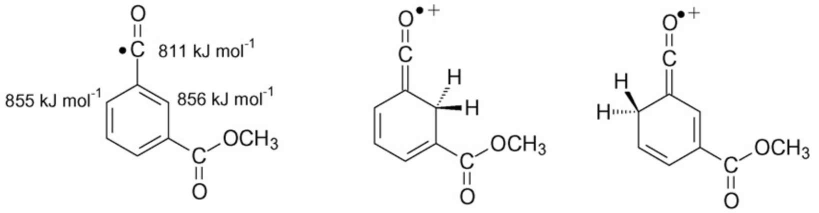


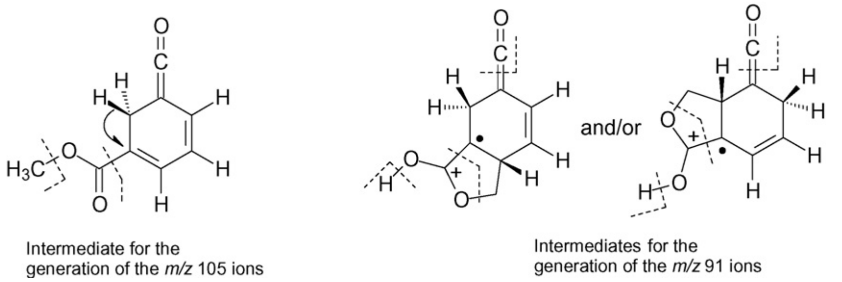
Fig. 4. High-energy CA spectrum of the residual m/z 164 ions to be compared with the spectrum shown in Fig. 2b.



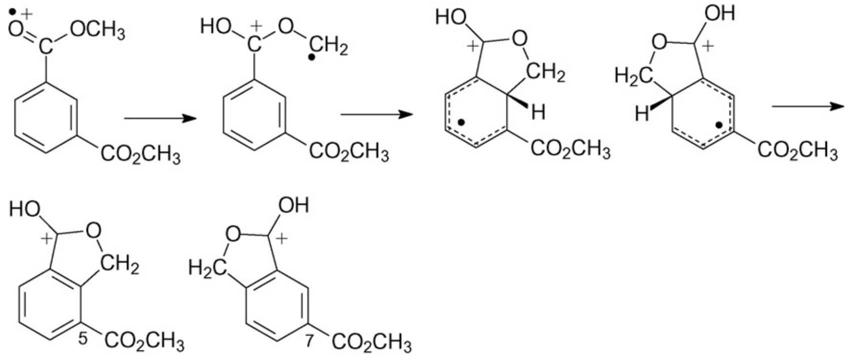
Scheme 7. Proton affinities of two sites of the benzoyl cation and production of the *m*/*z* 106 ketene ion within an ion–neutral complex.



Scheme 8. Calculated B3LYP/6-311++G(d,p) + ZPE proton affinities of three sites of the 3-methoxycarbonyl benzoyl radical and structure of the most favorable radical cations generated by proton transfer.



Scheme 9. Suggested structures for the intermediate ions involved in the formation of the *m*/*z* 105 and 91 fragment ions.



Scheme 10. Mechanism proposed for the loss of a hydrogen atom from the metastable molecular ions of dimethyl isophthalate.

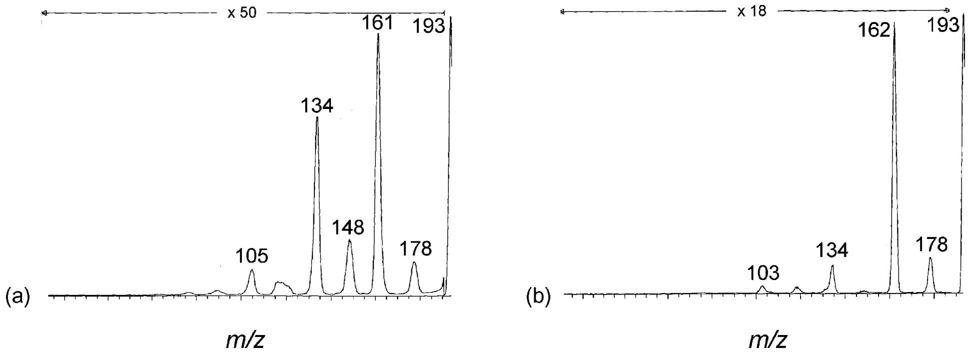


Fig. 5. CA spectra (oxygen collision gas) of the metastably generated $[M-H]^+$ (*m*/*z* 193) ions from ionized dimethyl isophthalate (a) and dimethyl terephthalate (b).

possible occurrence of a similar process for the present reaction as shown in Scheme 7.

When the C–O bond of ionized methyl benzoate starts to stretch, a [1,2] hydrogen shift could occur through a positively charged three-membered cyclic transition state generating an ion–neutral complex gathering the benzoyl radical and *O*-protonated formaldehyde. Starting with the proton affinity of formaldehyde (740 kJ mol^{-1} [11]) and the calculated proton affinities of two sites of the benzoyl radical, see Scheme 7, it is clear that ring protonation should be favored over carbonyl carbon protonation yielding the ketene radical cation, not ionized benzaldehyde. This loss of formaldehyde was nevertheless not observed in the methyl benzoate ion because another fragmentation channel, namely the loss of carbon dioxide [4], requires less critical energy.

The process depicted in Scheme 7 could in fact be considered as a proton transfer reaction catalyzed by formaldehyde [16]. Isomerization of ionized benzaldehyde into cyclohexadienylidenemethanone ion **a** by hydrogen shifts is prevented by high-energy barriers which may be very significantly reduced if a “catalyst” is introduced in the system and we have recently demonstrated that methanol, a base with a proton affinity of 744 kJ mol^{-1}, is particularly efficient for such a tautomerization [12].

We believe that all these experimental/theoretical results strongly support that cyclohexadienylidenemethanone ions could be considered as key-intermediates in the decomposition (formaldehyde loss) of metastable dimethyl isophthalate ions. Using B3LYP/6-311++G(d,p) + ZPE calculations, we have therefore evaluated the PAs at three sites of the 3-methoxycarbonyl benzoyl radical and found similar values for the two *ortho* positions (855–6 kJ mol^{-1}) which are slightly larger than the experimental PA proton affinity value for unsubstituted methyl benzoate. In other words, in the occurrence of an ion/molecule reaction similar to the reaction depicted in Scheme 7, one would obtain a mixture of two isomeric ketene ions bearing a methoxycarbonyl substituent as shown in Scheme 8.

Such a mixture could rationalize the CA spectrum of the m/z 164 ions (see Fig. 2a) featuring a base peak at m/z 149 for a methyl loss most probably preceded by hydrogen migration just as invoked in the case of dimethyl terephthalate [5]. Surprisingly, two reaction sequences involving respectively the m/z 105/77/51 and the m/z 91/65/39 fragment ions are also detected and we believe that the superimposition of these two sequences is strongly indicative of the fact that the m/z 164 ions actually consists of a mixture of isomeric species. The first sequence involves an hydrogen migration and loss of the ester group most probably in the form of carbon dioxide plus a methyl radical, a combination more stable than a methoxy acyl radical by 79 kJ mol^{-1} [17] (Scheme 9). The so-produced benzoyl cation (m/z 105) decomposes further by decarbonylation (m/z 77) and ethyne loss (m/z 51).

The second sequence is much more difficult to rationalize because the m/z 91 ions should correspond to $C_7H_7^+$ cations resulting from the losses of CO, CO_2 and $H^•$. All the carbon atoms of the $C_7H_7^+$ cations originate therefore from the ring and the methyl group; the same for all (except one) the hydrogen atoms. It is suggested that the methoxycarbonyl ketene ion, after isomerization of the ester group into a distonic species, cyclise into the species shown in Scheme 9 and undergo in sequence the fragmentations indicated by the dotted lines.

In order to experimentally support the intermediacy of ketene ions in the formaldehyde loss, we have tried to generate these radical cations by catalytic tautomerization of ionized 3-methoxycarbonyl benzaldehyde following procedures described recently for the benzaldehyde/cyclohexadienylidene methanone system [12]. Acetone has a proton affinity of 823 kJ mol^{-1} [11], a value lying between the PA’s given in Scheme 8 for the 3-methoxycarbonyl benzoyl radical. Its dipole moment is also quite high (2.88 D [18]). We have therefore applied chemical ionization conditions to a mixture of 3-methoxycarbonyl benzaldehyde and acetone, but here again no dimeric species was observed. We turned therefore to another kind of experiment allowed owing to the high vapor pressure of acetone which can be now easily introduced in the hexapole reaction cell. The results are presented in Fig. 3. In these experiments, a beam of mass-selected m/z 164 ions of 3-methoxycarbonyl benzaldehyde prepared by electron ionization is focused into the hexapole cell.

Fig. 3a shows the mass spectrum (B scan) of the ions contained in the hexapole in the absence of the reagent gas. These ions are mainly m/z 164 generated in the ion source with minute amount of m/z 163, 133 and 119 fragments. The high-energy CA spectrum of the m/z 164 ions is identical to the spectrum shown in Fig 2b. By increasing the pressure of acetone in the hexapole up to 10^{-3} Torr, the spectrum is strongly modified and the most intense peaks at m/z 163, 133 and 119 can be reasonably ascribed to collision-induced dissociation processes (Fig. 3b). Most of the m/z 164 have been decomposed, but it is quite interesting to note that the high-energy CA spectrum (Fig. 4) features important modifications: the appearance of an intense loss of carbon monoxide at m/z 136 and an intensity increase of the peak at m/z 119. It is thus clear that the “surviving” m/z 164 are probably the ketene ions rather than the aldehyde ions and that acetone has catalyzed the tautomerization process.

3.4. *Metastable hydrogen atom loss from ionized dimethyl isophthalate*

As explained earlier, the loss of a hydrogen atom is the most intense fragmentation of metastable dimethyl isophthalate molecular ions, see Fig. 1a. This reaction involves specifically the loss of one-ring hydrogen and is significantly slowed upon deuteration of the methyl groups. In agreement with the mechanisms proposed in the case of methyl benzoate and dimethyl terephthalate, we propose the reaction sequence depicted in Scheme 10.

In this sequence, one methoxycarbonyl substituent is isomerized into a distonic species which undergoes ring cyclisation and hydrogen loss into two isomeric protonated phthalides. The CA spectrum of the ions (m/z 193) depicted in Fig. 5a shows both (unresolved) losses of a methoxyl radical and methanol. The methanol loss could be due to the 5-methoxycarbonyl isomer by an *ortho* interaction with the methylene group. It is interesting to note that the CA spectrum of the m/z 193 ions of dimethyl terephthalate is mainly characterized by a methoxy loss (Fig. 5b), not a methanol loss. This observation is in agreement with positional integrity of the substituents during all the steps of the reaction process.

4. Conclusions

The unimolecular chemistry of long-lived, metastable, methyl benzoate molecular ions is particularly rich and quite difficult to rationalize. While metastable methyl benzoate ions predominantly lose carbon dioxide, metastable dimethyl terephthalate ions eliminate intensively a methyl radical. In the case of metastable dimethyl isophthalate ions, the subject of the present work, the chemistry is again strongly modified and the loss of formaldehyde is actually a preferred reaction channel beside an intense ring hydrogen loss. The conjugation of a methyl ester function with a benzene ring thus opens, after electron ionization, a series of new reaction pathways and the degree of competition in the metastable time-frame window appears highly dependent on electronic effects induced by this substitution. Various mechanisms for this loss of formaldehyde have been taken into account and the most consistent picture appears to involve carbonyl cyclohexa-1,3-diene (1,3-cyclohexadienylidenemethanone) radical cations as key intermediate. It is also suggested that the major loss of a ring hydrogen atom yields protonated phthalides *via* distonic intermediates.

Acknowledgements

The Mons laboratory thanks the FNRS, Fonds National de la Recherche Scientifique, for financial support in the acquisition of the AutoSpec 6F mass spectrometer. PG is a Research Associate of the FNRS. The Leuven group is indebted to the KUL Research Council (BOF) and the concerted Research Action Program (GOA) for continuing support.

References

[1] G. Wypych (Ed.), Handbook of Plasticizers, ChemTec Publishing, 2004.
[2] See for instance;
A.O. Earls, I.P. Axford, J.H. Braybrook, J. Chromatogr. A 983 (2003) 237.
[3] (a) Y. Yinon, Org. Mass Spectrom. 23 (1988) 755;
(b) S. Tajima, M. Mamada, S. Nakajima, Y. Takayashi, N.M.M. Nibbering, Aust. J. Chem. 56 (2003) 473;
(c) S. Tajima, A. Kojima, T. Sugimura, S. Nakajima, Y. Takahashi, N.M.M. Nibbering, Int. J. Mass Spectrom. 228 (2003) 89.
[4] N. Dechamps, R. Flammang, P. Gerbaux, P.C. Nam, M.T. Nguyen, J. Am. Soc. Mass Spectrom. 17 (2006) 807.
[5] R. Flammang, N. Dechamps, M. Boulvin, P. Gerbaux, P.C. Nam, M.T. Nguyen, Int. J. Mass Spectrom. 261 (2007) 134.
[6] R.H. Bateman, J. Brown, M. Lefevere, R. Flammang, Y. Van Haverbeke, Int. J. Mass Spectrom. Ion Processes 115 (1992) 205.
[7] R. Flammang, Y. Van Haverbeke, C. Braybrook, J. Brown, Rapid Commun. Mass Spectrom. 9 (1995) 795.
[8] V. Ramesh, P. Nagi Reddy, K. Bhanuphrakash, R. Srinivas, R. Flammang, N. Dechamps, P. Gerbaux, Int. J. Mass Spectrom. 263 (2007) 289.
[9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, F. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Repogle, J.A. Pople, Gaussian 98, Revision A.6, Gaussian Inc, Pittsburgh, PA, 1998.
[10] M.A. Trikoupis, J.K. Terlouw, in: N.M.M. Nibbering (Ed.), The Encyclopedia of Mass Spectrometry. Fundamentals of and Applications to Organic (and Organometallic) Compounds, vol. 4, Elsevier, 2005, p. 403.
[11] S.G. Lias, J.E. Bartmess, J.F. Liebmann, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988).
[12] R. Flammang, N. Dechamps, P. Gerbaux, P.C. Nam, M.T. Nguyen, Chem. Phys. Lett. 456 (2008) 141.
[13] NIST Library # 6459.
[14] E.L. Chronister, T.H. Morton, J. Am. Chem. Soc. 112 (1990) 133.
[15] J. Riley, T. Baer, J. Am. Soc. Mass Spectrom. 2 (1991) 464.
[16] P.C. Burgers, J.K. Terlouw, in: N.M.M. Nibbering (Ed.), The Encyclopedia of Mass Spectrometry. Fundamentals of and Applications to Organic (and Organometallic) Compounds, vol. 4, Elsevier, 2005, p. 173, and references therein.
[17] M.A. Trikoupis, J.K. Terlouw, P.C. Burgers, M. Peres, C. Lifshitz, J. Am. Soc. Mass Spectrom. 10 (1999) 869.
[18] R.C. Wheast (Ed.), Handbook of Chemistry and Physics, 57th ed., CRC Press, 1976–1977, p. E-64.