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A metastable ion and collision-induced dissociation study of the $(M–C_2H_4)^{\bullet+}$ ion from 3-phenyl-1-bromopropane

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Abstract

The molecular ion of 3-phenyl-1-bromopropane is known to eliminate ethylene containing the methylene groups of positions 1 and 2 following an exchange between the hydrogen atoms from position 1 and the ortho positions of the phenyl ring. During this reaction migration of the bromine atom to some position in the molecular ion must take place. The eventual position to which the bromine atom has migrated has been probed by studying the metastable behaviour and collision-induced dissociation reactions of the $(M–C_2H_4)^{\bullet+}$ ion. From comparison with appropriate reference ions it is found that the $(M–C_2H_4)^{\bullet+}$ ion has the structure of ionized benzyl bromide. The mechanistic implication of this finding is briefly discussed. (Int J Mass Spectrom 188 (1999) 1–6) © 1999 Elsevier Science B.V.

Keywords: Metastable ions; Collision-induced dissociation; Kinetic energy release; Unimolecular dissociation reaction mechanism; 3-phenyl-1-bromopropane

1. Introduction

Three decades ago it was shown that the molecular ion of 3-phenyl-1-bromopropane eliminates ethylene following an extensive exchange between the hydrogen atoms from the carbon atom of position 1 and those from the ortho positions of the phenyl ring [1]. Since then the views on the chemistry of gas phase ions [2–6] and the experimental methods [7–12] to study this field have been broadened and expanded dramatically in mass spectrometry.

The aforementioned hydrogen atom exchange in the molecular ion of 3-phenyl-1-bromopropane [1] is one of the many observations made in mass spectrometry, which have provided evidence for the stepwise mechanism of a 1,5-hydrogen shift in gas phase ions [13–15]. However, following this exchange the bromine atom must migrate to enable the elimination of ethylene that in addition to the exchanged methylene group of position 1 contains the methylene group of position 2 according to the deuterium labelling applied [1]. A very plausible landing site for the migrating bromine atom would be the phenyl ring, in which not only one of the ortho positions, but, in principle, also the ipso position might be considered. Moreover, in view of the significantly lower ionization energy

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Dedicated to Brian Green on the occasion of his 65th birthday with thanks for his friendship and fun during experiments in the demo laboratory of VG Micromass in Manchester, UK.

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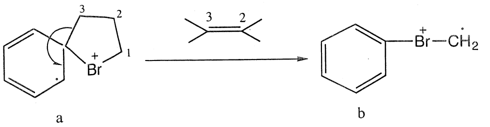
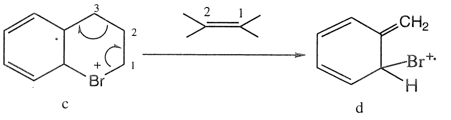
(IE) of *n*-propylbenzene (IE = 8.72 eV [16]) than of *n*-propyl bromide (IE = 10.19 eV [16]) it is quite likely that the neutral bromine atom attacks the charged phenyl ring in the molecular ion of 3-phenyl-1-bromopropane to form initially a bromonium type of ion. Upon ipso attack this would lead to ion **a**, which is expected to eliminate ethylene containing the methylene groups of positions 2 and 3 [see Eq. (1)] rather than those of positions 1 and 2 being observed experimentally (vide supra).



(1)

Ortho attack, however, would lead to ion **c**, which is expected to eliminate ethylene containing the methylene groups of positions 1 and 2 [see Eq. (2)] in agreement with the observations made [1].



(2)

Thus, the $(M–C_2H_4)^{\bullet+}$ ion generated upon electron ionization (EI) from 3-phenyl-1-bromopropane is expected to have the structure of ion **d**, that is, the tautomer of ionized ortho-bromotoluene. To confirm or disprove this expected ion structure we therefore have conducted a metastable ion and collision-induced dissociation (CID) [17,18] study of the $(M–C_2H_4)^{\bullet+}$ ion of interest and of isomeric reference ions.

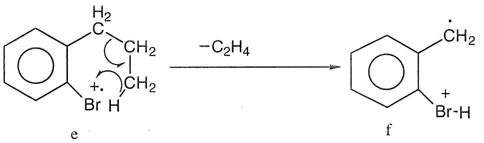
2. Results and discussion

2.1. Spontaneous dissociation

As reference ions have been studied the molecular ions of benzyl bromide and ortho-bromotoluene and the $(M–C_2H_4)^{\bullet+}$ ions from ortho-bromo *n*-propylbenzene. Their mass-analyzed ion kinetic energy (MIKE) spectra together with that of the $(M–C_2H_4)^{\bullet+}$ ion of 3-phenyl-1-bromopropane are presented in Fig. 1. The MIKE spectra of the molecular ions of benzyl bromide and ortho-bromotoluene are very simple and similar [see Fig. 1(a) and (b), respectively]. In addition to a minor $H^{\bullet}$ loss as shown by a small shoulder on the low mass side of both main ion beams, the base peak is found in both cases at *m/z* 91 because of expulsion of the bromine atom. However, the peak at *m/z* 91 generated from the benzyl bromide ion is considerably narrower than that from the ortho-bromotoluene ion as quantified by the measured kinetic energy release [19] $T_{0.5}$ values listed in Table 1.

The MIKE spectrum of the $(M–C_2H_4)^{\bullet+}$ ion from ortho-bromo *n*-propylbenzene shows peaks at *m/z* 169, 168, 157, 144, 91, and 90 [see Fig. 1(c)]. It should be noted in this case that the selected main ion beam of *m/z* 170 consists for about 90% of the natural ^{13}C isotopic ion of the $(M–C_2H_5)^+$ species. The MIKE spectrum of the latter ion (not shown) contains peaks at *m/z* 168, 167, 156, 143, and 90 corresponding with losses of $H^{\bullet}$, H_2, C_2H_3 [from metastably generated $(M–CH_3)^+$ = *m/z* 183 ions appearing at m* = 169.1], C_2H_2 and $Br^{\bullet}$, respectively.

Most of the peaks in the MIKE spectrum of the $(M–C_2H_4)^{\bullet+}$ ion from ortho-bromo *n*-propylbenzene are thus actually because of similar losses from the natural ^{13}C isotopic ion of the $(M–C_2H_5)^+$ species. However, the presence of the peak at *m/z* 90 in the MIKE spectrum under discussion must correspond to elimination of HBr from the $(M–C_2H_4)^{\bullet+}$ ion of ortho-bromo *n*-propylbenzene. This is further confirmed by the better mass resolved spectrum obtained with the use of a MIKES/Q scan [see inset in Fig. 1(c)]. This points at a transfer of a hydrogen atom to the bromine atom rather than to the phenyl ring during expulsion of ethylene from the molecular ion of ortho-bromo *n*-propylbenzene as visualized in Eq. (3):



(3)

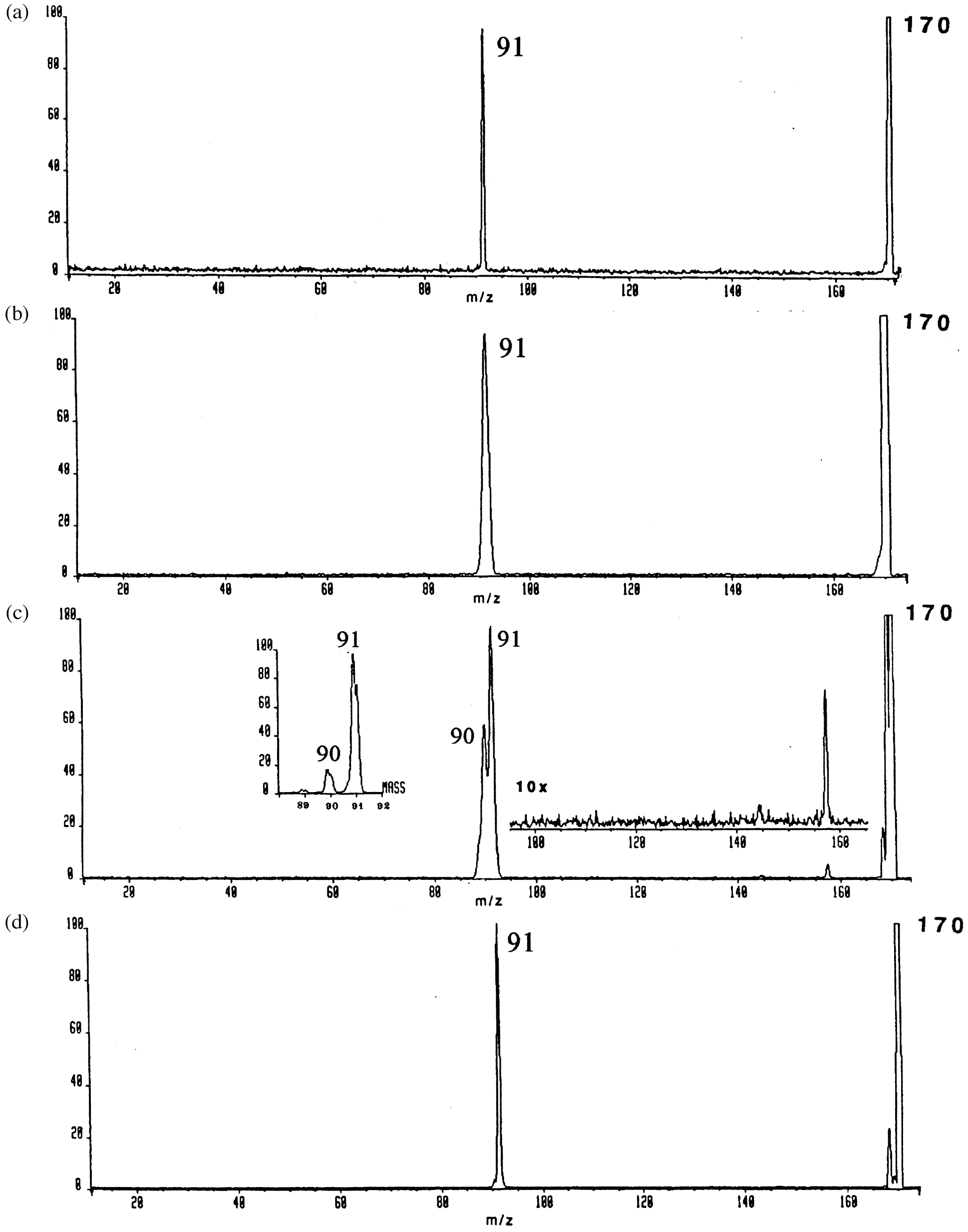
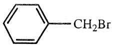
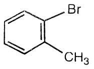
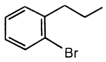
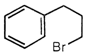


Fig. 1. MIKE spectra of the ^{79}Br containing molecular ions of (a) benzyl bromide and (b) ortho-bromotoluene and of the ^{79}Br containing $(M–C_2H_4)^{\bullet+}$ ions of (c) ortho-bromo *n*-propylbenzene and (d) 3-phenyl-1-bromopropane.

The MIKE spectrum of the $(M–C_2H_4)^{\bullet+}$ ion from 3-phenyl-1-bromopropane is different from those of ionized benzyl bromide and ortho-bromotoluene in the sense that it contains a relatively large peak at *m/z* 168 [see Fig. 1(d)]. Nevertheless, the $T_{0.5}$ kinetic energy release value measured for $Br^{\bullet}$ loss from this ion is identical to that measured for ionized benzyl bromide (see Table 1).

Table 1
Kinetic energy release $T_{0.5}$ values (in meV) for the bromine atom loss reaction *m/z* 170 → *m/z* 91 following electron ionization of some brominated aralkyl compounds (first two entries) and subsequent ethylene elimination (last two entries)

Compound	$T_{0.5}$ (meV)
	5
	96
	56
	5

2.2. Collision-induced dissociation

The CID spectra of the molecular ions of benzyl bromide, ortho-bromotoluene, and the $(M–C_2H_4)^{\bullet +}$ ion from 3-phenyl-1-bromopropane are displayed in Fig. 2. Those of ionized benzyl bromide and the $(M–C_2H_4)^{\bullet +}$ ion of interest appear to be very similar, if not identical [compare Fig. 2(a) and (c)]. No trace of a signal at *m/z* 156 is found in the CID spectrum of the $(M–C_2H_4)^{\bullet +}$ ion, not even upon amplification [see inset Fig. 2(c)], which might be expected if the ion would have the structure of ion **d**. The $(M–C_2H_4)^{\bullet +}$ ion certainly does not have the structure of ionized ortho-bromotoluene as the CID spectrum of the latter ion differs significantly both from that of the $(M–C_2H_4)^{\bullet +}$ ion and from that of ionized benzyl bromide with respect to the mass region between *m/z* 91 and *m/z* 170 [compare Fig. 2(b) with Fig. 2(a) and (c)]. Note, for example, the peak at *m/z* 155 in the CID spectrum given in Fig. 2(b) that indicates the presence of a methyl group in the corresponding precursor ion, which is in agreement with the ortho-bromotoluene structure.

Taking all the observations together it seems that the nondecomposing $(M–C_2H_4)^{\bullet +}$ ion from 3-phenyl-1-bromopropane has the benzyl bromide structure. This conclusion is not inconsistent with the behaviour of the metastably decomposing $(M–C_2H_4)^{\bullet +}$ ion of interest, discussed above, which also is very similar to that of ionized benzyl bromide.

2.3. Mechanistic considerations and conclusion

Having obtained strong indications from the experimental results described above that the $(M–C_2H_4)^{\bullet +}$ ion from 3-phenyl-1-bromopropane has the benzyl bromide structure, it is appropriate to consider the mechanistic implications for the formation of this ion.

The formation of the $(M–C_2H_4)^{\bullet +}$ ion directly in the benzyl bromide structure would be possible via a formal 1,2-elimination, which in the present case could be viewed as an intramolecular S_N2 attack of the bromine atom on the benzylic carbon in the molecular ion of 3-phenyl-1-bromopropane under expulsion of ethylene. Such a reaction or, in general, S_N2 substitution in the gas phase is known to have a high energy barrier [20,21]. One might then expect a considerable kinetic energy release for the ethylene expulsion. However, this is not the case as indicated by the moderate $T_{0.5}$ value of 63 meV measured for this reaction.

Another possibility is that the Br atom migrates to one of the ortho positions of the phenyl ring as outlined in the introduction to give initially ion **d** that subsequently rearranges via a low energy barrier to the benzyl bromide ion. Considering that the ΔH_f^o of ionized toluene (901 kJ/mol [16]) and its ortho tautomer (934 kJ/mol [16]) differ by 33 kJ/mol, one may expect the ΔH_f^o of ion **d** to be around 925 kJ/mol on the basis of the ΔH_f^o value of 890 kJ/mol [16] for ionized ortho-bromotoluene. The ΔH_f^o value for ion **d** then is very close to that of ionized benzyl bromide, being 935 kJ/mol [16].

Of course, there may be a barrier between ion **d** and the ionized benzyl bromide structure. However, contrary to the relatively high energy demanding 1,3-hydrogen shift [22] to rearrange the ortho tautomeric toluene ion into its traditional structure, which have been shown to be distinct stable species [23,24], ion **d** may well isomerize easily via a smooth formation of a four-membered ring bromonium type ion **g**

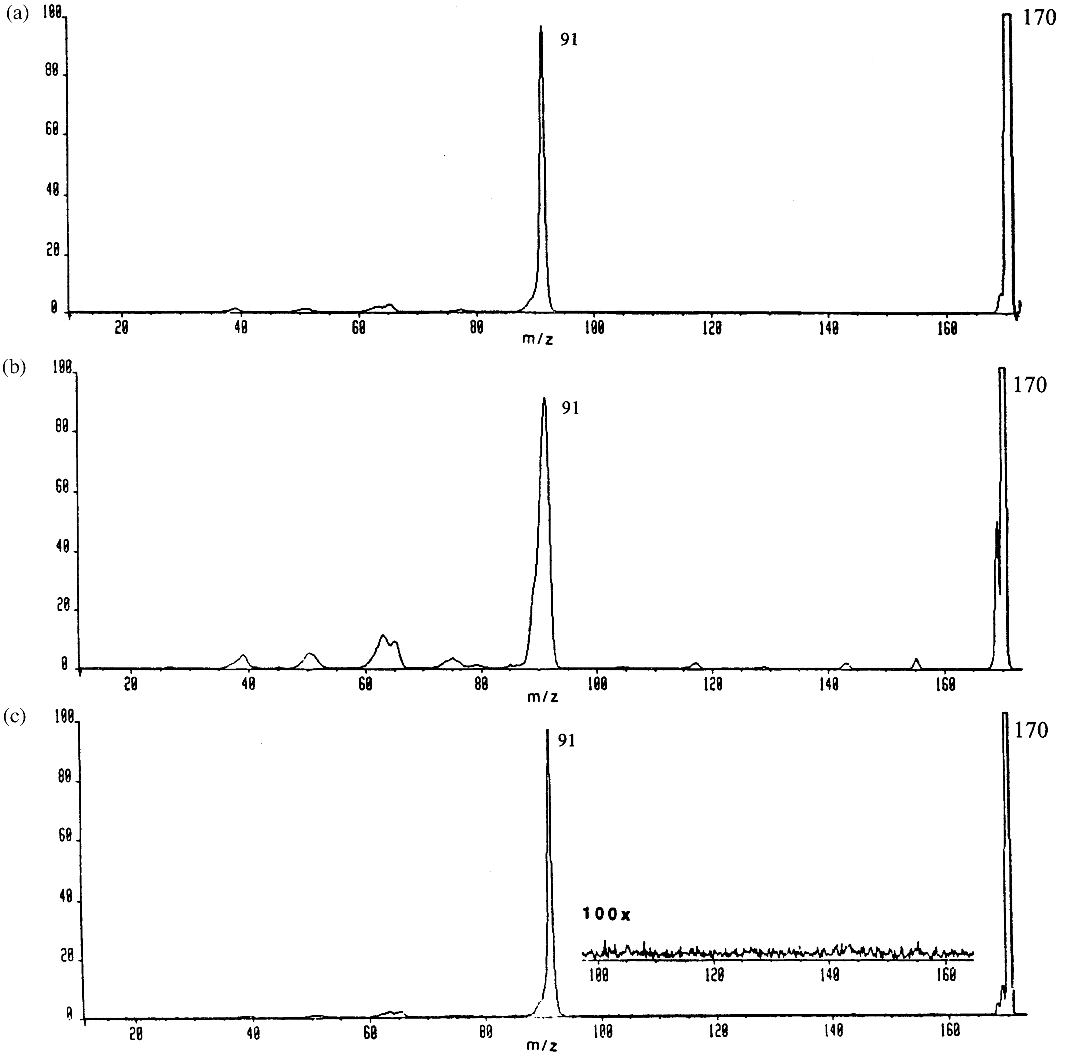
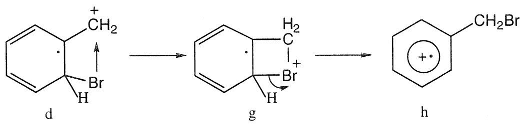


Fig. 2. CID spectra of the ^{79}Br containing molecular ions of (a) benzyl bromide and (b) ortho-bromotoluene and of the ^{79}Br containing $(M–C_2H_4)^{\bullet+}$ ions of (c) 3-phenyl-1-bromopropane.

(for another recently reported example of a four-membered ring bromonium ion, see [25]) and subsequent ring opening to the ionized benzyl bromide ion **h** as exemplified in Eq. (4):



(4)

The barrier for isomerization of ion **d** into ion **h** cannot exceed much the ΔH_f^o of ion **h** in view of the fact that the kinetic energy release $T_{0.5}$ value for $Br^\bullet$ loss from the $(M–C_2H_4)^{\bullet+}$ ion of 3-phenyl-1-bromopropane is identical to that for $Br^\bullet$ loss from ionized benzyl bromide (see Table 1).

It must then be concluded that the isomerization of ion **d** into ion **h** as the long-lived and metastably decomposing benzyl bromide ion structure of the

$(M–C_2H_4)^{\bullet +}$ ions of interest, is fueled apparently by part of the energy required for the elimination of ethylene from the molecular ions of 3-phenyl-1-bromopropane.

3. Experimental

The spectra were recorded by use of a VG micromass ZAB-HFqQ mass spectrometer with the configuration BEqQ (B = magnetic sector, E = electric sector, q = rf-only quadrupole, Q = quadrupole mass filter) that was coupled to a VG 11/250 data system. For the acquisition of the EI/MIKE [19] and EI/MIKE/CID [17,18] spectra, the brominated compounds were introduced into the ion source held at 150 °C through a septum inlet system heated to 150 °C and ionized by 70 eV electrons. The resolving power of the magnetic sector was set to 2000 (10% valley definition). The spectra were then obtained by scanning the electric sector voltage to transmit ions from 8 keV (main beam) to 500 eV; the total scan time was approximately 10 s. For the high energy MIKE/CID spectra, helium was used as the collision gas at such a pressure in the collision cell, that the intensity of the mass selected beam was reduced to 50% of its original value. Product ion signals were acquired with the data system in the “multichannel analyzer” (MCA) mode. Scans were generally of 10 s duration, and 5–10 scans were accumulated. The reported kinetic energy release values, $T_{0.5}$, were obtained from the width of the metastable peaks at half height as described earlier [26].

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