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Intermediate Ion Structures in the Fragmentation of Metastable 3-Methylbutan-2-ol Radical Cations

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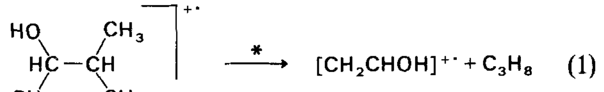
Ionized 3-methylbutan-2-ol displays four low-energy fragmentations, loss of $CH_3^\cdot$ and $C_3H_7^\cdot$ and loss of CH_4 and C_3H_8, the latter pair being produced by metastable ion decompositions. The electron-impact, metastable-ion and collision-induced dissociation mass spectra of ^{13}C and ^2H-labelled isotopomers have been recorded, together with appearance energy measurements. It was found that the fast (ion source) losses of $CH_3^\cdot$ and $C_3H_7^\cdot$ involved only simple bond cleavages between C(1) and C(2) and between C(2) and C(3), respectively, and without any positional interchange of isotopes. The loss of C_3H_8 produces ionized vinyl alcohol containing only C(1) and C(2). The H atoms involved are only those attached to C(1) and C(3). In deuterium-labelled analogues, the deuterium is preferentially located in the propane, e.g. metastable $CD_3CH(OH)CH(CH_3)_2$ yields predominantly $C_3H_6D_2$. On the basis of all the observations, it is proposed that low-energy molecular ions can form a stable proton-bridged molecule–radical complex, $[HOCHCH_2\cdots\overset{+}{H}\cdots\dot{C}H(CH_3)_2]$, and that this key intermediate is responsible for the isotope distribution in propane loss and also for the relatively low importance of the lowest energy dissociation, the simple C(1)—C(2) bond cleavage.

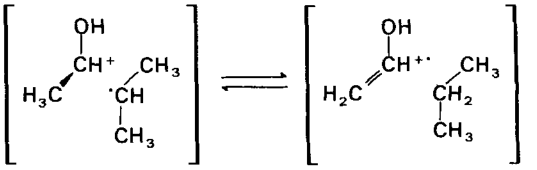
INTRODUCTION

The role of ion–neutral complexes as key intermediates and/or transition states in a large number of ionic fragmentation reactions has been thoroughly reviewed by McAdoo.[1] The present status of species such as ion-radical complexes[2] and proton-bound molecule–radical pairs[3] is far from clear, as theoretical calculations and experimental measurements compete to provide the most convincing explanation for processes which strain the concepts of conventional reaction mechanisms. Indeed, as stated by McAdoo,[1] 'further effort is needed to define experimental ways to distinguish (between) complex-mediated and conventional reactions.' A particularly challenging example of a reaction which *might* involve novel intermediates is the loss of propane from metastable ionized 3-methylbutan-2-ol, to produce ionized vinyl alcohol:



$$\xrightarrow{*} [CH_2CHOH]^{+\cdot} + C_3H_8 \quad (1)$$

This fragmentation could well be envisaged as a simple elimination, involving transfer of a hydrogen atom from the 1-methyl group to a departing *sec*-propyl radical, were it not for the report, by Hammerum and Audier,[4] that ionized $CD_3CH(OH)CH(CH_3)_2$ in its metastable ion (MI) mass spectrum produced a predominant ion of *m/z* 45, showing that *two* deuterium atoms were preferentially lost in the propane. They proposed that the key intermediates in this reaction were the complexes shown in Eqn (2).



(2)

On the face of it, this proposal is eminently reasonable, although, as will be discussed below, alternative mechanisms may be considered. In this work we employed the widest available range of mass spectrometric experimental methods in an endeavour to find sufficient evidence for the confident assignment of intermediate ion structures and fragmentation reaction mechanisms.

RESULTS AND DISCUSSION

Mass spectra

The normal electron-impact mass spectrum of this molecule is dominated by an ion of *m/z* 45, $CH_3\overset{+}{C}HOH$. The molecular ion is weak, ~2% of *m/z* 45, and *m/z* 55, $[C_4H_7]^+$ (13%), and *m/z* 73, $[C_4H_9O]^+$ (10%), are the only significant ions between *m/z* 45 and the molecular ion. The MI mass spectrum contains two intense peaks, *m/z* 44, $[CH_2CHOH]^{+\cdot}$ (37%), and *m/z* 72, $[C_4H_8O]^{+\cdot}$ (100%). Note that the latter process, CH_4 loss, was barely affected by collision-induced dissociation. The collisional-activation (CA) mass spectrum (see Experimental) of the molecular ion showed a large *m/z* 45 peak but *m/z* 44, the major MI peak, also increased with admission of collision gas, to become the base peak. The $[M - CH_3]^+$ ion, *m/z* 73, was only a minor peak in the CA mass spectrum (6%, relative to *m/z* 44).

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Energetics

The appearance energy (*AE*) values for the two metastable peaks were measured by the method described previously.[5] That for m/z 44 was found to be 10.1 ± 0.1 eV, close to that calculated (10.14 eV) for the production of ionized vinyl alcohol, $\Delta H_f = 757$ kJ mol^{-1},[6] and propane, $\Delta H_f = -104$ kJ mol^{-1};[6] ΔH_f[HOCH(CH$_3$)CH(CH$_3$)$_2$] = −325 kJ mol^{-1} (ionization energy (*IE*) = 9.75 ± 0.05 eV). The *AE* for m/z 72, 10.0 ± 0.1 eV, is well above that calculated for the products (see Fig. 1) The *AE* values for m/z 45 and m/z 73 were measured using energy-selected electrons; the results (10.1 ± 0.05 and 9.90 ± 0.05 eV, respectively) showed that, within experimental error, these reactions proceed at their thermochemical threshold. Note, however, that the fragmentation of *lower AE* contributes much less to the mass spectrum than the generation of m/z 45, which is 0.1–0.2 eV more energy demanding. The simple bond cleavages to m/z 45, [CH$_3\overset{+}{\text{C}}$HOH], and m/z 73, [HO$\overset{+}{\text{C}}$HCH(CH$_3$)$_2$], have energies close to those of the metastable fragmentations. That these metastable decompositions take place at an energy not far (30–37 kJ mol^{-1}) above the ionization energy of 3-methylbutan-2-ol makes it necessary for there to be other [C$_5$H$_{12}$O]$^{+\bullet}$ structures of lower ΔH_f, accessible to the molecular ion, in order to achieve a sufficient density of states for the fragmentations to take place in the microsecond time frame.

The kinetic energy releases ($T_{0.5}$) for the two metastable decompositions were 25.6 ± 1 meV for CH$_4$ loss and 1.4 ± 0.1 meV for C$_3$H$_8$ loss. The latter increased for the 3-d_1 and 1-d_3 molecules, to 2.1 ± 0.1 meV, whereas the methane loss for the same labelled compounds displayed lower $T_{0.5}$ values of 19.2 ± 1 meV. The $T_{0.5}$ values were unaffected by labelling in all other positions.

Labelling experiments

The results of ^{13}C and ^{2}H labelling experiments are shown in Table 1. Clearly *only* H atoms from positions 1 and 3 are involved in *both* metastable decompositions, *only* C-1 is lost in the methane and the *sec*-propyl C atoms *only* are lost in the propane. Not shown in Table 1 is the additional result that metastable [CH$_3$CH(OH)CH(CD$_3$)$_2$]$^{+\bullet}$ yields only [CH$_2$CHOH]$^{+\bullet}$ and [CH(OH)C(CD$_3$)$_2$]$^{+\bullet}$. The most surprising feature is that reported earlier by Hammerum and Audier,[4] namely that the dominant labelled propanes lost from the first three labelled compounds (Table 1) contain one or two deuterium atoms. Thus a statistical selection of H and D from the C(1) and C(3) H(D) atoms can be ruled out.

We propose, on the basis of the *AE* values and collision behaviour described above, that different intermediate, stable, [C$_5$H$_{12}$O]$^{+\bullet}$ ion structures are involved in the two metastable reaction channels, propane and methane loss.

What intermediate, potentially stable, species can be considered for these two fragmentations? In view of the exceptionally limited involvement of H atoms only at C(1) and C(3), and the fact that the carbon skeleton is not disrupted prior to loss of either *alkane*, *all* mechanisms involving distonic ions, which necessarily would involve the OH group (the only proton acceptor), can be ruled out. Ion–molecule complexes between the enol-ion products and the alkanes are possibly significant, but it should be borne in mind that a very large isotope effect has to be accommodated (see Table 1) in addition to the extraordinary specificity of H atom involvement.

Ion–radical complexes have been clearly identified in phenylalkyl ether ions,[7] but their behaviour provides no easy precedent for this study. The phenoxy radical and alkyl cation are believed to separate sufficiently for the

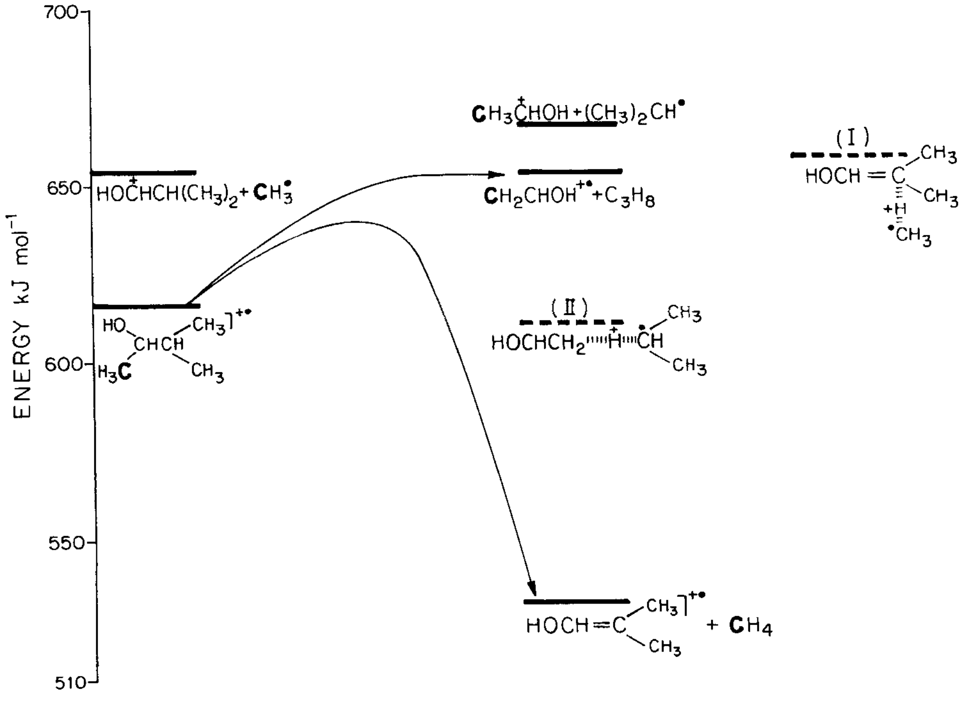
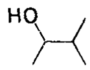
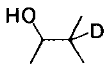
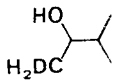
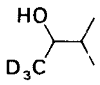
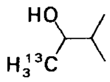
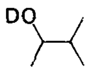


Figure 1. Energy diagram. Ionization energy of 3-methylbutan-2-ol = 9.75 eV. Appearance energies (*AE*) for the metastable peaks: *AE*(m/z 44) = 10.1 ± 0.1 eV, *AE*(m/z)72 = 10.0 ± 0.1 eV. All other energies from Ref. 6.

Table 1. Metastable peak abundances, relative to that of the main ion beam (=1000), for the losses of C_3H_8 and CH_4 from labelled 3-methylbutan-2-ol radical cations[a]

Compound	Fragment ion (*m/z*) 44	45	46	72	73
	4.4	—	—	12	—
	4.6 (100)	0.13 (17)	—	4.4	—
	5.7 (100)	0.3 (17)	—	4.4	—
	—	7.3 (100)	0.7 (33)	3.9	—
	—	3.3	—	7.7	—
	—	4.9	—	—	12

[a] Values in parentheses refer to relative metastable peak abundances measured in the first field-free region.

latter independently to isomerize to a thermodynamically more stable form, i.g. from an *n*-propyl to a *sec*-propyl cation. However, H/D scrambling is generally not observed to precede the specific β-proton transfer from a secondary (or tertiary) ion to the radical, which thereby generates ionized phenol and an alkene. In addition, this overall reaction involves a large reverse activation energy.

In any case, the ion–radical pair in Eqn (2) already involves the thermodynamically most stable forms of $[C_2H_5O]^+$ and $[C_3H_7]^{\bullet}$ and so no isomerization of the components is likely to yield a more stable ion. For ion–molecule and ion–radical complexes, only *ab initio* molecular orbital calculations are likely to provide information as to the relative energies of such species.

Proton-bridged ion–radical pairs have been identified in a number of systems, again largely dependent on theoretical calculations for their confident assignment.[3]

The energetics of proton-bridged ion–radical pairs can be estimated with reasonable certainty when the proton lies between heteroatoms, e.g. as described by Larson and McMahon for $A\overset{+}{H}B$ species,[8] where A and B are oxygen-containing molecules. Their equation, $D[AH—B] = 0.46[PA(B) - PA(A)] + 130 \pm 8$ kJ mol^{-1}, reflects the effect of the different proton affinities (*PA*) of A and B on the strong $A\overset{+}{H}—B$ bond, it having been shown that the dissociation energy, $D[A\overset{+}{H}—A] = 130 \pm 8$ kJ mol^{-1}, is essentially independent of A. Application of this expression to other systems is attractive because many *PA* values are available (or can be calculated from ion enthalpy data), but the basic $D[A\overset{+}{H}—A]$ information for carbon-centred systems is lacking. A comparison can be made, however, between potentially competing proton-bridged molecule–radical pairs. The *PA* values for $\mathit{C}H_2CHOH$ and $(CH_3)_2CH^{\bullet}$, $(CH_3)_2\mathit{C}CHOH$ and $CH_3^{\bullet}$ are 824, 674 and 833, 544 kJ mol^{-1}, respectively.[6] For the vinyl alcohols, H^+ attachment to the italicized C atom is thermochemically favoured. If the $A\overset{+}{H}—B$ binding in these species were as strong as in oxygen-containing species, then CH_2CHOH and $(CH_3)_2\dot{C}H$ would indeed be bound by a proton, with a dissociation energy to $[CH_2CHOH]^{+\bullet} + C_3H_8$ of about 60 kJ mol^{-1}; the other pair, however, would *not* be bound by a proton (see Fig. 1, where their estimated relative energies are shown). On this basis, only the vinyl alcohol–proton–*sec*-propyl radical species, II, may merit further consideration. Species I seems untenable, except possibly as a transition state for the methane loss—a reaction in which H-atom positional exchange is unobservable, but in which the presence of D in the methane product retards the metastable reaction, relative to the propane loss and to the main ion beam intensity, (see Table 1).

In marked contrast, the propane-loss reaction is enhanced by the participation of D (see Table 1). This is particularly so when two D transfers have to be made from the 1-CD_3 group to generate the $CH_3CD_2CH_3$ neutral product. At shorter times (first field-free region metastable peaks; see Table 1), there is a reduction in this specificity of D placement in the neutral product. In terms of the ion II, it may be that for metastable ions the H^+-bridged species is more important than the D^+-bridged analogue, an effect which may partially account for the observations. Such a preference has recently been described in the collision-induced decomposition of H^+- and D^+-bound water molecule clusters.[9] In that work it was also concluded that deuterium is preferentially located in the neutral water molecules in the solvent shell surrounding the core species. It must be stated, however, that the magnitudes of the isotopic preferences referred to above would alone be insufficient to account for the extraordinarily large effect found in this study.

In an attempt to identify the possible presence of ions of structure II, the Xe/O_2 neutralization–reionization (NR) mass spectrum was recorded and compared with that obtained using He in place of Xe. The purpose of the second experiment was to discover the reionization mass spectrum of the neutral species generated by collision-induced dissociation, He being (relative to Xe) a very poor target gas for electron transfer because of its high *IE* of 24.6 eV.[6] The two spectra were qualitatively very similar, except that only in the Xe/O_2 NR mass spectrum were *m/z* 45, 55 and 73 observed, having relative abundances similar to those in the normal electron-impact mass spectrum. We conclude that at least some molecular ions retain their structure (note that a recovered molecular ion, *m/z* 88, would probably be too weak for observation). The presence of many ions of structure II would have been expected to produce a mixture of $[CH_2CHOH]$ and $[CH_3\dot{C}HCH_3]$; the latter would have dominated the NR mass spectrum, having a much lower *IE* than vinyl alcohol. Although the ions of *m/z* 38–43 were the most intense group of peaks in the NR mass spectrum, peaks of similar intensity were also present in the He/O_2 mass spectrum, making the NR mass spectrum inconclusive with regard to the presence of proton bridged ions.

The CA mass spectrum of the $[CD_3CH(OH)CH(CH_3)_2]^{+\cdot}$ ions provides evidence in support of the proposed proton bridged species II. After correction for MI processes (see Experimental), peaks remain at *m/z* 45, 46, 47 and 48 (relative intensities 6:11:6:9), to which can be assigned the structures $[CDHCHOH]^{+\cdot}$, $[CD_2CHOH]^{+\cdot}$, $[CD_2HCHOH]^+$ and $[CD_3CHOH]^+$, respectively (correspondig to neutral products $C_3H_6D_2$, C_3H_7D, $C_3H_6D^\cdot$ and $C_3H_7^\cdot$). Thus H/D exchange between C(1) and C(3) has already taken place among these non-fragmenting ions; note that in the ion source, *m/z* 45, $[CH_3\overset{+}{C}HOH]$, is wholly displaced to *m/z* 48, showing that H/D mixing does not take place among ions thus generated. These results will indeed reflect the isotope distribution among non-fragmenting ions, provided that collisional excitation is followed by very rapid decomposition, i.e. before any further H/D exchange is possible. To accommodate the behaviour of the lower energy metastable ions (those fragmenting in the second field-free region), a large isotope effect is still required to explain the very high yields of propane-d_2. Collision-induced methyl loss is a very weak process, but only $CD_2H^\cdot$ and $CD_3^\cdot$ losses are observed in the CA mass spectrum (approximately equal abundances), again reconcilable with specific H/D mixing in the long-lived (non-fragmenting) precursor molecular ion.

Similar results were observed for the ions $[CH_2DCH(OH)CH(CH_3)_2]^{+\cdot}$ and $[CH_3CH(OH)CD(CH_3)_2]^{+\cdot}$, both showing collision-induced dissociations leading to $[C_2H_4O]^{+\cdot}$, $[C_2H_3DO]^{+\cdot}$, $[C_2H_5O]^+$ and $[C_2H_4DO]^{+\cdot}$. Positional mixing among these ions was not complete, with *m/z* 46 being greater than *m/z* 44 (ratio 41:24) for $[CH_2DCH(OH)CH(CH_3)_2]^{+\cdot}$ and vice versa for $[CH_3CH(OH)CD(CH_3)_2]^{+\cdot}$ (ratio 21:35). These observations are in keeping with an ion of structure II being the predominant low-energy form of the molecular ion. Moreover, with ion II as the predominant species, the lower energy route to *m/z* 73 (loss of $CH_3^\cdot$) can indeed effectively be reduced in importance.

The results of this study are far from conclusive. The lack of a definitive solution shows the limitations of currently available experimental methods for the study of the intermediates which must govern the behaviour of many ion fragmentations. At worst, however, studies of this kind can reduce the choice of fragmentation mechanisms to a small enough number to be examined by advanced *ab initio* theoretical calculations.

EXPERIMENTAL

Electron-impact, metastable-ion (MI) and collisional-activation (CA) mass spectra were recorded using a VG Analytical ZAB-2F mass spectrometer. CA mass spectra were measured using He as collision gas under essentially single collision conditions[10] (~10% beam reduction). MI and CA contributions to CA mass spectra were separated by raising the collision cell from ground potential to +1000 V. Neutralization (Xe, 90% transmission)–reionization (O_2, 90% transmission) (NR) mass spectra were recorded using the same mass spectrometer, modified as described elsewhere.[11] Except when kinetic energy releases were being determined, all energy-resolving slits were wide open to avoid instrument discrimination effects.

Metastable peak appearance energies were measured by a comparitive method using a Kratos MS902S mass spectrometer.[5] For appearance energies measured with energy-selected electrons an apparatus consisting of an electrostatic electron monochromator and mini-computer data system was used.[12]

3-Methylbutan-2-ol was obtained from Wiley Organics. The compounds labelled at C(1) were all prepared by a Grignard reaction using appropriately labelled methylmagnesium iodide and isobutyraldehyde. The OD-labelled alcohol was prepared by exchange with D_2O; the 3-deuteriated derivative was prepared by reacting methylmagnesium iodide with isobutyraldehyde-2-d_1. The reaction of $(CD_3)_2CHMgBr$ with acetaldehyde furnished the hexadeuterio alcohol. All labelled compounds were obtained from Merck, Sharp and Dohme.

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