Stable $C_2H_5X^{+\cdot}$ (X=Cl, Br) Radical Cations of Structure $[CH_3CHXH^{+\cdot}]$: Their Energetics and Dissociation Characteristics†

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A new radical cation having the methyl carbene type structure $[CH_3CHClH]^{+\cdot}$ has been characterized in the gas phase. It is readily generated by the dissociative ionization $[CH_3CHClCO_2H]^{+\cdot} \rightarrow CO_2 + [CH_3CHClH]^{+\cdot}$. Its enthalpy of formation has been estimated to be 951 kJ mol^{-1}, close to that of $[CH_3CH_2Cl]^{+\cdot}$. The principal fragmentation characteristics (loss of HCl and Cl$^{\cdot}$) of the ion are discussed. A brief description of the bromo analogue $[CH_3CHBrH]^{+\cdot}$ is also given.

INTRODUCTION

Unusual molecules, which because of intermolecular interactions are inaccessible in condensed phases, can be generated and examined in the gas phase.[1,2] This applies particularly to ions whose inherent properties can only be determined experimentally in the gas phase. Recently, small cation radicals having uncommon structural properties have been both observed in the gas phase[3-6] and predicted theoretically to exist on the basis of extended *ab initio* calculations.[7,8] A number of these ions can be represented as $[CH_2]^{+\cdot}XH$ (X = OH, SH, NH$_2$, halogen) and such relatively small ions may play a role in interstellar chemistry. It is noteworthy that their neutral carbene counterpart (and related species) bonded to metal atoms are of central importance in organometallic chemistry.[9] Such species have been considered as radical ion/dipole complexes by virtue of their dissociation characteristics[6] although the calculated charge distribution in the ground state of these ions may not be in keeping with the above name.[5,7] This problem has also recently been attacked by some of us.[10] The notion that interactions in transition states for gas-phase ion rearrangements and fragmentations can be rationalized in terms of even-electron ion/dipole combinations, was proposed some years ago[11] but firm evidence for this type of complex has yet to be provided.[12,13]

The novel radical cations of unconventional structure referenced above were chiefly characterized by their collisionally activated fragmentations (CAD) which, in general, were markedly different from those of their ionic counterparts of conventional structure.

Another important difference was found in the charge stripping (CS), the former yielding intense doubly charged ions, often absent in the spectra of the latter. Differences in metastable ion characteristics were sometimes significant and in a number of cases the heat of formation (ΔH_f^0) of the complex ion was shown to be less than those of any isomeric ion of conventional structure.

In this paper we report the existence of similar stable complexes between ionized methyl carbene, $[CH_3CH]^{+\cdot}$, and HCl, namely $[CH_3CHClH]^{+\cdot}$. Brief mention is also made of the bromo analogue, i.e. $[CH_3CHBrH]^{+\cdot}$. These experiments constitute an extension of earlier work on halogenated complexes.[4,6,10]
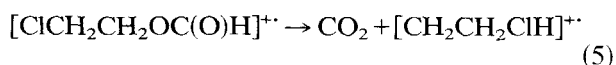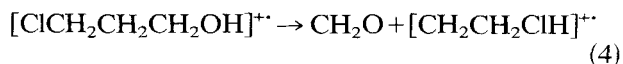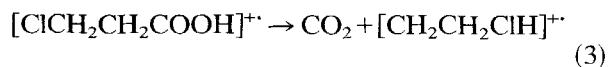
RESULTS AND DISCUSSION

The dissociative ionizations (1) and (2) (X = Cl, Br) were used in this study

$$[XCH_2COOCH_3]^{+\cdot} \rightarrow CO_2 + [CH_2XCH_3]^{+\cdot} \quad (1)$$

$$[CH_3CHXCOOH]^{+\cdot} \rightarrow CO_2 + [CH_3CHXH]^{+\cdot} \quad (2)$$

to generate the radical ions. Although of potential interest, iodine-containing analogues could not be studied, as CO_2 loss does not take place for X = I, their fragmentations being dominated by loss of I$^{\cdot}$. Studies on fluoro-containing compounds are in progress.

The molecular ion of ethyl chloride (*a*) is a stable gas-phase ion and its collisional activation (CA) characteristics have previously been reported and used to distinguish it from the product ion of reaction (1), $[CH_3ClCH_2]^{+\cdot}$ (*b*).[10] The relative stabilities of these two ions, *a* and *b*, have been investigated computationally; *b* was predicted to have ΔH_f^0 ca. 46 kJ mol^{-1}

higher than a, but their ready interconversion is precluded by a high energy barrier. Ion b can be regarded as a homologue of $[CH_2ClH]^{+\cdot}$; however, the possible existence of the isomeric forms of b, $[CH_3CHClH]^{+\cdot}$ (c) and $[CH_2CH_2ClH]^{+\cdot}$ (d), should also be explored. For example c could be produced by reaction (2) above, and d by the process (3) or, by analogy with the formation of the stable radical ion/dipole complex $[CH_2CH_2OH_2]^{+\cdot}$, by either reaction (4) or (5).

$$[ClCH_2CH_2COOH]^{+\cdot} \rightarrow CO_2 + [CH_2CH_2ClH]^{+\cdot} \tag{3}$$

$$[ClCH_2CH_2CH_2OH]^{+\cdot} \rightarrow CH_2O + [CH_2CH_2ClH]^{+\cdot} \tag{4}$$

$$[ClCH_2CH_2OC(O)H]^{+\cdot} \rightarrow CO_2 + [CH_2CH_2ClH]^{+\cdot} \tag{5}$$

Reaction (2) (X = Cl) indeed produced intense signals at m/z 64 and 66, $[M - CO_2]^{+\cdot}$; however, neither CO_2 loss according to processes (3) and (5) nor CH_2O elimination via (4) were observed to take place.
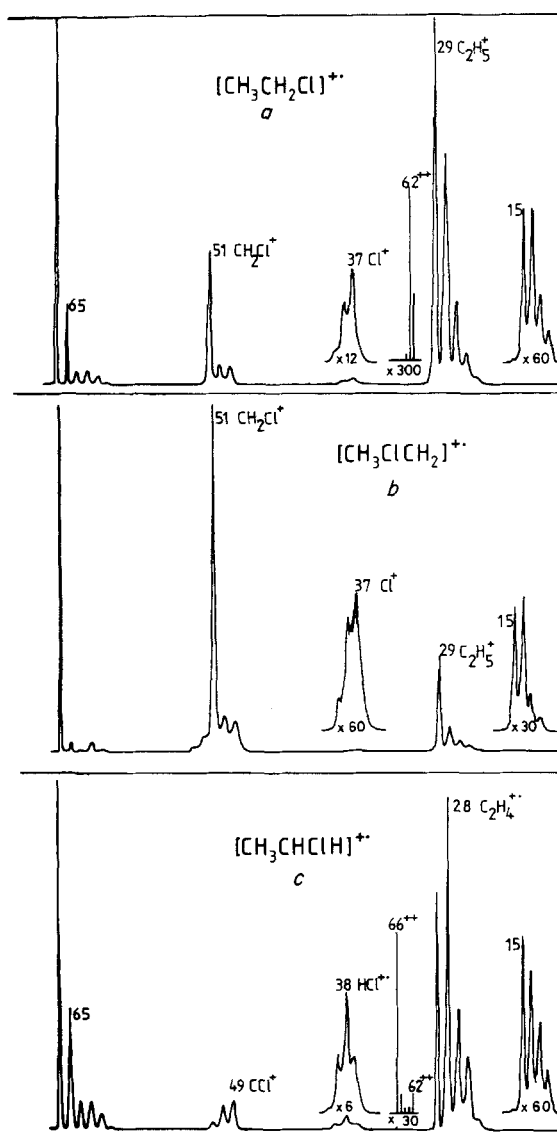

Figure 1. CA mass spectra of ions m/z 66: $[CH_3CH_2{}^{37}Cl]^{+\cdot}$ (a), $[CH_3{}^{37}ClCH_2]^{+\cdot}$ (b) and $[CH_3CH^{37}ClH]^{+\cdot}$ (c).

The CA mass spectra of ionized $C_2H_5{}^{37}Cl$ and the isobaric species generated by reactions (1) and (2) are shown in Fig. 1; the CA mass spectra for a, b and deuterium-labelled a and b have been discussed in detail and presented in tabular form elsewhere.[10] It is clear from the CA mass spectrum derived from $[CH_3CHClCO_2H]^{+\cdot}$ that a third $[C_2H_5Cl]^{+\cdot}$ ion structure is produced. Note for example the very significant presence of the doubly charged ion $[C_2H_5Cl]^{++}$, absent in the CA spectra of a and b. Also noteworthy for the new ion is the greater abundance of m/z 38 $[H^{37}Cl]^{+\cdot}$, the quite weak signal of m/z 51, $[CH_2{}^{37}Cl]^{+\cdot}$, and the different abundances of ions m/z 29 and 28. These results alone do not readily permit any distinction to be made between the possible structures c and d, and so the following isotopic labelling experiments were performed. The CA mass spectra of the $[M - CO_2]^{+\cdot}$ ions derived from $^{13}CH_3CHClCOOH$ and $CD_3CHClCOOH$ both showed ions in the group m/z 49–51 ($[C^{37}Cl]^+$, $[CH^{37}Cl]^{+\cdot}$, $[CH_2{}^{37}Cl]^+$) having the same abundance ratios as those of the unlabelled compound. Thus, the methyl group in the precursor and product ion must remain intact; this result strongly indicates that the unsymmetrical ion c is produced rather than d.

The appearance energy (AE) of m/z 64 from $CH_3CHClCO_2H$ was measured using energy-selected electrons;[14] this, 10.72 eV, together with

$$\Delta H_f^0[CH_3CHClCO_2H] = -477 \text{ kJ mol}^{-1} \text{ } ^{15}$$

and

$$\Delta H_f^0[CO_2] = -393.5 \text{ kJ mol}^{-1} \text{ } ^{16}$$

leads to ΔH_f^0 $[CH_3CHClH]^{+\cdot} = 951 \pm 4$ kJ mol^{-1}. This is within experimental error identical with $\Delta H_f^0[CH_3CH_2Cl]^{+\cdot} = 950$ kJ mol^{-1}.[16] These results are in good agreement with *ab initio* calculations performed at the 6-31G/4-31G level which gave a difference of $\simeq 13$ kJ mol^{-1} in favour of the conventional ion structure a.

The unimolecular fragmentation characteristics of $[CH_3CH_2Cl]^{+\cdot}$ and $[CH_3CHClH]^{+\cdot}$ were examined. The former has been shown to dissociate to yield $[C_2H_4]^{+\cdot} + HCl$ and $[C_2H_5]^+ + Cl^\cdot$ at the thermochemical threshold for these reactions.[16] The metastable peaks for these decompositions are both of Gaussian type ($T_{0.5} = 18$ meV) but as expected from its lower threshold (see Fig. 2) the unimolecular loss of HCl prevails by a factor of c. 50.

The cation c also shows the unimolecular losses of $Cl^\cdot$ and HCl but it differs in two aspects from $[CH_3CH_2Cl]^{+\cdot}$ ions: (i) the loss of $Cl^\cdot$ relative to that of HCl is greatly enhanced (3 : 1 by height) and (ii) the metastable peak for the loss of HCl (see Fig. 3(a)) is a broad composite with a half-height energy release of 300 meV for the broad component.

The AE of both metastable transitions was measured and found to be the same within experimental error (11.4 eV for loss of $Cl^\cdot$ and ≤ 11.5 eV for loss of HCl). The common threshold energy for these two reactions (of which the HCl loss proceeds above the thermochemical threshold) leads us to propose that ion c rearranges to energy-rich $[CH_3CH_2Cl]^{+\cdot}$ before dissociation, in keeping with the larger kinetic energy
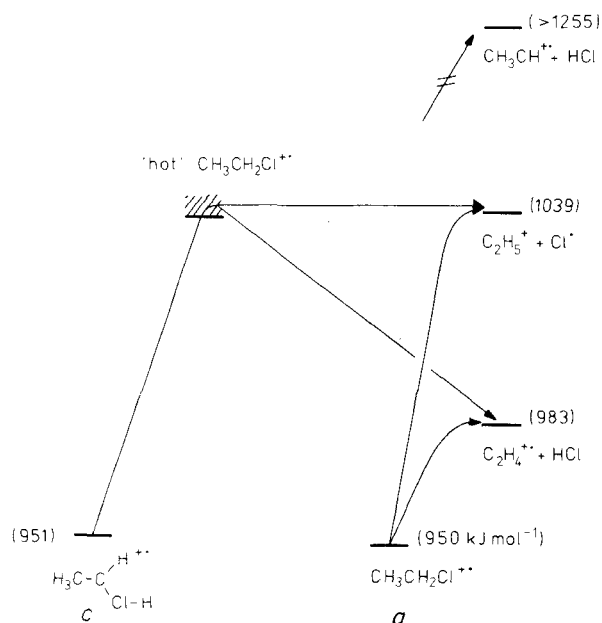
Figure 2. Energy diagram showing the unimolecular losses of HCl and Cl˙ from [CH₃CH₂Cl]⁺˙ (*a*) and [CH₃CHClH]⁺˙ (*c*). Numbers in parentheses refer to ΔH_f^0 values, given in kJ mol⁻¹.

release component in the metastable peak ($T_{0.5}$ = 300 meV). These results are shown in Fig. 2.

Note that direct loss of Cl˙ from ion *c* is not possible for low-energy ions and, similarly, that direct loss of HCl without rearrangement leads to the high-energy [CH₃CH]⁺˙ ion (see Fig. 2). However, the latter reaction dominates the CA mass spectrum (see Fig. 3(b)); for example, the ions [CH₃CHClD]⁺˙ and [CH₃CDClH]⁺˙ derived from CH₃CHClCOOD and CH₃CDClCOOH showed an almost exclusive loss of DCl and HCl, respectively.

For the *unimolecular* HCl loss from [CH₃CHClH]⁺˙ and its labelled isotopomers the following results were obtained: (i) the relative intensities of the two components of the composite metastable peak remain practically the same for all isotopomers studied; (ii)
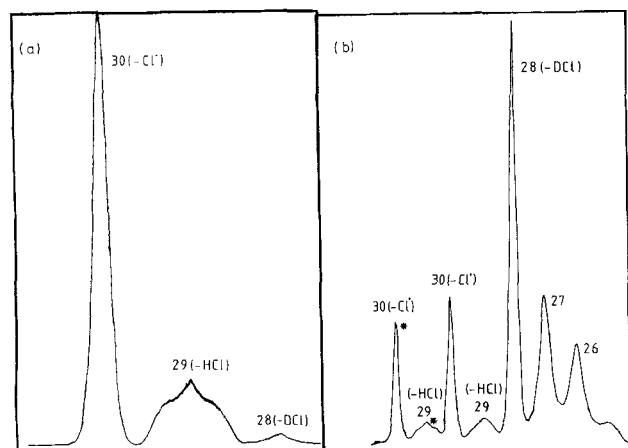

Figure 3. Partial MI (a) and CA (b) spectra of the *m/z* 67 ion [CH₃CH³⁷ClD]⁺˙ derived from CH₃CHClCO₂D showing the preferred losses of H³⁷Cl and D³⁷Cl in unimolecular and collisionally activated dissociations, respectively. The CA spectrum was recorded at a collision gas cell potential of -400 V and the peaks denoted with an asterisk (largely) result from unimolecular dissociations outside the cell.
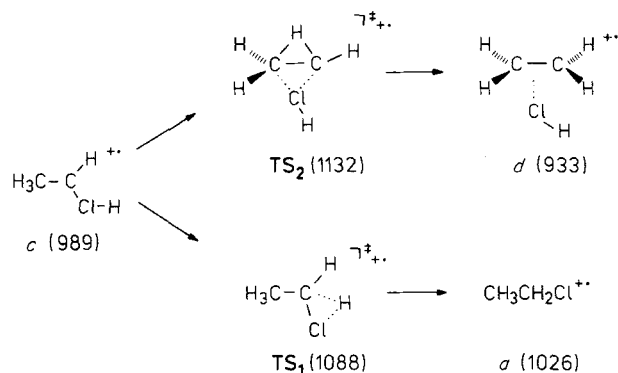

Figure 4. MNDO isomerization paths for [CH₃CHClH]⁺˙. (Note: complete geometry data and charge distributions can be obtained on request from the authors.)

[CH₃CHClD]⁺˙ and [CH₃CDClH]⁺˙ lose HCl almost exclusively whereas both HCl and DCl are eliminated from [CD₃CHClH]⁺˙ (ratio 1:2.1). From the results of either [CH₃CHClD]⁺˙ or [CH₃CDClH]⁺˙ one may conclude that these ions undergo isomerization to an energy rich [CH₃CHDCl]⁺˙ ion which, via a formal [1.2]-elimination involving the hydrogen atoms of the intact methyl group, decomposes to HCl and [CH₂CHD]⁺˙ (*m/z* 29).

This interpretation is aided by semi-empirical molecular orbital calculations of the energetics for some rearrangement pathways of ion *c* using Dewar's MNDO procedure.[17] The results are summarized in Fig. 4, which shows two reasonable pathways. The energetically favoured route proceeds from *c* to *a* via transition state TS₁, and it may well be that this path mainly accounts for the unimolecular HCl loss from *c*.
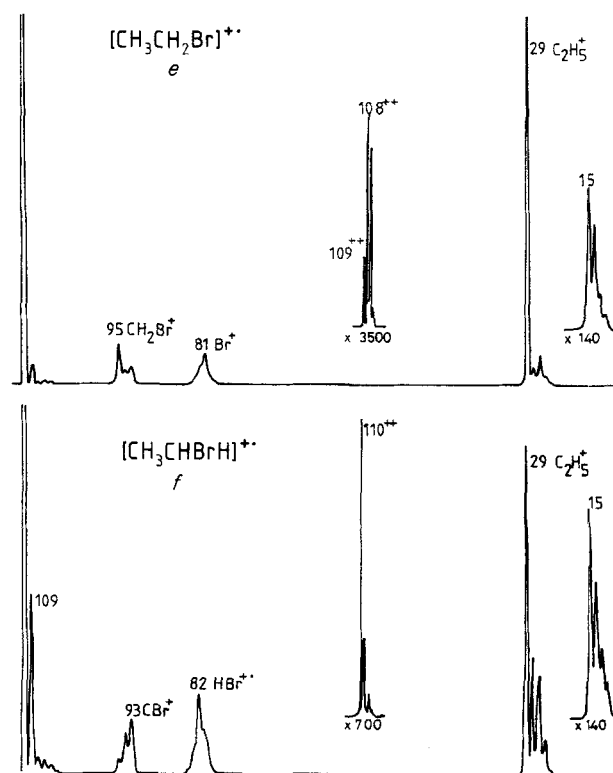

Figure 5. CA mass spectra of ions *m/z* 110: [CH₃CH₂⁸¹Br]⁺˙ (*e*) and [CH₃CH⁸¹BrH]⁺˙ (*f*).

As shown in Fig. 4 there exists another, energetically less favoured, route via TS_2 to yield the as yet unobserved ion d. It cannot be decided, however, whether it is due to this pathway or an additional, yet unexplored, mechanism that partial hydrogen exchange between the methyl group and the Cl—H unit of c takes place prior to dissociation. Other explanations for the observed losses of both HCl and DCl from $[CD_3CHClH]^{+\cdot}$ and the clean reactions of $[CH_3CDClH]^{+\cdot}$ and $[CH_3CHClD]^{+\cdot}$ can be envisaged by invoking kinetic isotope effects. That at least two different mechanisms operate in the HCl elimination from $[CH_3CHClH]^{+\cdot}$ is indicated by the composite shape of the metastable peak.

The CA mass spectra of the $[CH_3CH_2{}^{81}Br]^{+\cdot}$ ion (e), generated via direct electron impact ionization of CH_3CH_2Br, and $[CH_3CH^{81}BrH]^{+\cdot}$ (f), derived via reaction (2) (X = Br), were also studied. Although less striking than for the chloro analogues (see Fig. 5), it was clear that a new ion structure was generated different from that of the ion generated via reaction (1).[10] Note the abundant signal for the doubly charged $[C_2H_5Br]^{++}$ ion in the CA mass spectrum of f, absent in e. The much greater abundance of m/z 82 $[H^{81}Br]^{+\cdot}$ in f, and the lower relative abundance of m/z 95

$[CH_2{}^{81}Br]^+$ in f are both in keeping with the structure $[CH_3CHBrH]^{+\cdot}$. These observations are directly analogous with those for the chloro compounds.

EXPERIMENTAL

CA and MI mass spectra were measured as described elsewhere[18] using the VG ZAB-2f mass spectrometer in Utrecht. Metastable peak appearance energies were obtained, as previously described,[19] on a KRATOS AEI MS 902 instrument. Compounds were prepared by conventional methods, purified by GC and characterized by NMR.

Acknowledgements

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