

The Ethyl Halides: Stable Neutral and Radical Cation Isomers [C₂, H₅, X] where X = F, Cl, Br, I

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The following isomers of the ethyl halide molecular ions have all been shown to be stable species in the gas phase: [CH₂CH₂FH]⁺⁺; [CH₃ClCH₂]⁺⁺ ($\Delta H_f^\circ = 1012 \text{ kJ mol}^{-1}$); [CH₃CHClH]⁺⁺ ($\Delta H_f^\circ = 971 \text{ kJ mol}^{-1}$); [CH₂CH₂ClH]⁺⁺; [CH₃BrCH₂]⁺⁺ ($\Delta H_f^\circ = 1058 \text{ kJ mol}^{-1}$); [CH₃CHBrH]⁺⁺ ($\Delta H_f^\circ = 995 \text{ kJ mol}^{-1}$) and [CH₂CH₂BrH]⁺⁺.

Neutralization-reionization mass spectrometry, employing Xe as the electron transfer target gas and O₂ as the target gas for reionization, indicated that the ylides CH₃ClCH₂ and CH₃BrCH₂ could not be generated by such means. However, the species CH₃CHClH, CH₂CH₂ClH and CH₂CH₂BrH (and possibly CH₃CHBrH) were unambiguously identified.

INTRODUCTION

In the past five years experimental and theoretical studies have firmly established the existence in the gas phase of simple organic ions having unusual structures and whose neutral counterparts are unknown or extremely reactive. An early example was the methyleneoxonium radical cation [CH₂OH₂]⁺⁺, an isomer of ionized methanol.^{1a,b} The isomeric pairs CH₃X⁺⁺ and CH₂XH⁺⁺ (for X = NH₂, SH, PH₂, F, Cl, Br, and I as well as OH) also have been well investigated via experiment¹⁻⁵ and by high-level *ab initio* molecular orbital theory calculations.⁶⁻¹⁰ Recently, a very thorough review by Hammerum about these species, both in the gas and condensed phase, has appeared.¹¹

The stable conventional and unconventional ionic species have some common features. Relatively high barriers to isomerization were calculated to separate the isomeric forms.¹⁰ The doubly charged [CH₂XH]²⁺ cation is significantly stable, while for the conventional ion, M²⁺ has only marginal stability.⁵ Following the pioneering experiments by Porter *et al.*,¹² the technique of neutralization-reionization mass spectrometry (NRMS) was used by Wesdemiotis *et al.*¹³ to investigate the stability of the neutral ylides CH₂FH, CH₂ClH, CH₂OH₂ and CH₂NH₃. In a NRMS experiment fast, gaseous neutral species are generated by the collision-induced charge exchange of their ionic counterparts in the first of two collision cells in the second field-free region (2nd FFR) of a reversed geometry, double focusing mass spectrometer. The stability and structure of the neutrals, isolated from the surviving ion flux by means of an ion beam deflector electrode, are then studied by their subsequent collision-induced dissociative reionization.¹⁴

Wesdemiotis *et al.*¹³ believed that they had identified all the above ylides but recent work from this laboratory¹⁵ was unable to confirm their conclusions. It should be noted that high-level calculations predict that these

ylides are unstable or situated in very shallow wells on their potential energy surfaces.^{7,8,10,16-18}

In the investigation of larger polyatomic systems, high level *ab initio* molecular orbital theory calculations are limited by cost, placing the emphasis for structure assignment upon experimental work. However, the unconventional isomers of ionized ethyl alcohol and dimethyl ether, namely the two ylidenes [CH₃CHOH₂]⁺⁺ and [CH₃OHCH₂]⁺⁺, and the distonic ion [CH₂CH₂OH₂]⁺⁺ have been characterized by both theory and experiment.^{19,20a,b,c}

The present work describes the neutral and radical-cation isomers of the ethyl halides, C₂H₅X, for X = F, Cl, Br and I. Some groundwork has already been laid in the investigation of the isomeric radical cations; in 1983 Schwarz *et al.*²¹ proposed that the electron impact induced loss of CO₂ from the esters XCH₂COOCH₃, generated [CH₃XCH₂]⁺⁺ for X = Cl, Br.



The collision-induced dissociation (CID) mass spectrum of the [C₂H₅X]⁺⁺ species contained the characteristic fragment [CH₃X]⁺⁺, whilst the ion [C₂H₂D₃X]⁺⁺, produced from XCH₂COOCD₃, specifically yielded [CD₃X]⁺⁺. The relative stabilities of [CH₃CH₂Cl]⁺⁺ and [CH₃ClCH₂]⁺⁺ were also investigated by *ab initio* molecular orbital theory calculations at the UMP2/6-31G*//STO-3G level which predicted ΔH_f° [CH₃ClCH₂]⁺⁺ to be some 27 kJ mol⁻¹ above that of ethyl chloride.

In contrast to the above, the [C₂H₅F]⁺⁺ ion from methylfluoroacetate, was concluded to be [CH₃CH₂F]⁺⁺, based on the almost identical CID mass spectra of the fragment ion and that of the ethylfluoride molecular ion.²² Also in 1983, Holmes *et al.*²³ reported generation of the ylidenes [CH₃CHXH]⁺⁺, X = Cl, Br, regarded as stable complexes between [CH₃CH]⁺⁺ and HX, via the loss of CO₂ from CH₃CHXCOOH.



The CID mass spectra were found to differ significantly from those of [CH₃CH₂X]⁺⁺ and [CH₃XCH₂]⁺⁺, and intense charge-stripping peaks were observed. Analysis

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of $[\text{CH}_3\text{CHClH}]^{+\bullet}$, $^{13}\text{CH}_3\text{CHClH}^{+\bullet}$ (generated from $^{13}\text{CH}_3\text{CHClCOOH}$), and $[\text{CD}_3\text{CHClH}]^{+\bullet}$ (generated from $\text{CD}_3\text{CHClCOOH}$), indicated that the methyl group in the precursor and product ion remained intact, in keeping with the proposed structure $[\text{CH}_3\text{CHClH}]^{+\bullet}$. The heat of formation, $\Delta H_f^\circ[\text{CH}_3\text{CHClH}]^{+\bullet} = 971 \text{ kJ mol}^{-1}$ was obtained from its measured appearance energy (*AE*) of 10.72 eV. The unimolecular fragmentation characteristics of $[\text{CH}_3\text{CH}_2\text{Cl}]^{+\bullet}$ and $[\text{CH}_3\text{CHClH}]^{+\bullet}$ and their deuterium labelled counterparts were also examined and $[\text{CH}_3\text{CHClH}]^{+\bullet}$ was proposed to isomerize to $[\text{CH}_3\text{CH}_2\text{Cl}]^{+\bullet}$ prior to metastable loss of HCl.

The purpose of this paper is two-fold: first, to extend the earlier work on the unconventional isomeric ions of the ethylhalides, to establish the existence of a third isomer, the distonic radical cation $\dot{\text{C}}\text{H}_2\text{CH}_2\text{XH}^+$, and second, via the recently introduced technique of neutralization-reionization mass spectrometry,^{24,25} to investigate the stabilities of the *neutral* counterparts of these stable, unconventional ions.

EXPERIMENTAL

Metastable ion (MI) and collision-induced dissociation (CID) mass spectra were recorded as described previously using a Vacuum Generators ZAB-2F double focusing mass spectrometer.²⁶ A 100 μA electron beam of ionizing energy 70 eV was used. The ion source temperature was 200 °C and the accelerating voltage 8 kV. Oxygen was used as the collision gas at a pressure corresponding to 90% main beam transmission.²⁷

Neutralization-reionization mass spectra were recorded using a modified ZAB-2F mass spectrometer as described in Reference 28. The 2nd FFR of the spectrometer contains two electrically isolated collision cells with a beam deflector electrode between them. In NR experiments the mass selected ions undergo charge-transfer neutralization with xenon in the first cell. The xenon pressure is set to give 90% main beam transmission. All remaining ions in the beam are deflected away, and the neutrals are reionized by collision with oxygen (pressure adjusted to give 90% transmission) in the second cell. In all cases contributions from natural isotopic abundances from adjacent ions of lower mass were considered, and corrected for where applicable.

In all the above collision experiments beam-defining slits were fully open to obtain maximum signal strength and to minimize energy-resolving effects. Metastable peak shapes were, however, recorded under conditions of good energy resolution, with main beam widths of 2 V or less; kinetic energy releases were evaluated using established methods.²⁹

To distinguish ions generated metastably from those produced by collision in CID experiments, the second collision cell was floated at an appropriate voltage (usually at -500 V or +500 V). Similarly, NR mass spectra were corrected for neutral species arising from metastable ion fragmentations by applying a voltage to the *first* cell.

All ionization and appearance energies, unless otherwise referenced, were recorded in this laboratory using

energy-selected electrons.³⁰ The appearance energy of the metastable fragment ion, $[\text{C}_2\text{H}_5\text{F}]^{+\bullet}$, from methyl fluoroacetate was measured on a Kratos-AEI MS 902S mass spectrometer using a comparative method.³¹ The metastable characteristics of the $[\text{C}_2\text{H}_5\text{Br}]^{+\bullet}$ fragment ion from methyl bromoacetate were also examined in the 1st FFR of this instrument.

The majority of the samples obtained commercially were of research grade, and were used without further purification. $\text{FCH}_2\text{CH}_2\text{CH}_2\text{OH}$ was prepared from 3-chloro-1-propanol, anhydrous KF and ethylene glycol,³² and purified by gas chromatography (GC). $\text{ClCH}_2\text{COOCD}_3$ was prepared by esterification of ClCH_2COOH by CD_3OD . $\text{CH}_3\text{CHClCOOD}$ was obtained within the ion source via deuterium exchange using D_2O . Signal averaging³³ was required only for the charge stripping (CS) and NR mass spectra of the $[\text{C}_2\text{H}_5\text{X}]^{+\bullet}$ from $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OH}$ and $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}$.

RESULTS AND DISCUSSION

Thermochemistry

The heats of formation of the conventional and ylid isomers of the $[\text{C}_2\text{H}_5\text{X}]^{+\bullet}$ ions have been calculated from their respective ionization (*IE*) and appearance (*AE*) energies, measured using energy-selected electrons.³⁰ Previously published work is included for completeness, see Table 1.

The $\text{C}_2\text{H}_5\text{F}$ isomers

The $[\text{C}_2\text{H}_5\text{F}]^{+\bullet}$ radical cations obtained from ethylfluoride and methyl fluoroacetate generated closely similar MI and CID mass spectra, in general agreement with earlier results.²²

The measured appearance energies for $[\text{C}_2\text{H}_5\text{F}]^{+\bullet}$ (see Table 1) resulted in a heat of formation of the $[\text{C}_2\text{H}_5\text{F}]^{+\bullet}$ fragment ion from methyl fluoroacetate which was equal, within experimental error, to that of ionized ethylfluoride. Note that without the *adiabatic IE* for ethyl fluoride it could have been concluded that the ion derived from the ester was a new, thermodynamically more stable species than $[\text{CH}_3\text{CH}_2\text{F}]^{+\bullet}$. The unusually large difference of 0.65 eV between the vertical and adiabatic *IE* indicates a considerable geometry change between the neutral and ionized species, and that ionization via electron impact, a mainly vertical process, will produce highly excited ions. With the dissociation energy for the process;



at 912 kJ mol^{-1} (*AE* of $m/z = 47$ is 12.14 eV) vertical ionization must account for the rather low intensity of the molecular ion (~12%) relative to hydrogen loss (base peak) in the electron impact (EI) mass spectrum of ethylfluoride.

Thus, although $[\text{CH}_2\text{XH}]^{+\bullet}$ and $[\text{CH}_3\text{XCH}_2]^{+\bullet}$ are stable for $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and $\text{X} = \text{Cl}, \text{Br}$ respectively, the ylidion $[\text{CH}_3\text{FCH}_2]^{+\bullet}$ has not been obtained via the

Table 1. Experimental heats of formation of the C_2H_5X isomers (ΔH_f° values in kJ mol^{-1})

Precursor	ΔH_f°	Neutral fragment	IE or AE (eV \pm .05)	Ion	ΔH_f°
CH_3CH_2F	-263 ³⁴	-	12.43 (v) ³⁵	$[CH_3CH_2F]^{++}$	936
			11.78 (ad)	$[CH_3CH_2F]^{++}$	873
FCH_2COOCH_3	-570 ^a	CO_2^b	10.90	$[CH_3CH_2F]^{++}$	875
			11.1 ± 0.2^c	$[C_2H_5F]^{++*}$	894
CH_3CH_2Cl	-112 ³⁷	-	11.01 ³⁸	$[CH_3CH_2Cl]^{++}$	950
$ClCH_2COOCH_3$	-414 ^a	CO_2	10.7 ± 0.2	$[CH_3ClCH_2]^{++}$	1012
$CH_3CHClCOOH$	-456 ^a	CO_2	10.72 ²³	$[CH_3CHClH]^{++}$	971
CH_3CH_2Br	-62 ³⁷	-	10.28 ³⁸	$[CH_3CH_2Br]^{++}$	930
$BrCH_2COOCH_3$	-377 ^a	CO_2	10.8 ± 0.2	$[CH_3BrCH_2]^{++}$	1058
$CH_3CHBrCOOH$	-431 ^a	CO_2	10.70	$[CH_3CHBrH]^{++}$	995
CH_3CH_2I	-7.5 ³⁷	-	9.34 ³⁹	$[CH_3CH_2I]^{++}$	894

^a by additivity,³⁶ with a correction of $+15 \text{ kJ mol}^{-1}$ for F adjacent to carbonyl.

^b $\Delta H_f^\circ[CO_2] = -393 \text{ kJ mol}^{-1}$.³⁷

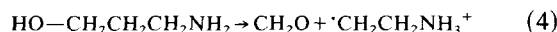
^c as in Ref. 31.

appropriate analogous experiment. In FCH_2COOCH_3 , $IE = 10.56 \text{ eV}$ (this work), the charge site is at the carbonyl function; in the chloro and bromo esters a lone pair electron is removed from the halo-atom and methyl migration to Cl and Br may then be facilitated.

Neutralization-reionization mass spectrometry has allowed the generation of the neutral counterparts of fast, stable ions. The NR and CID mass spectra of ethylfluoride, see Fig. 1, are nearly superimposable within experimental error, but $[^{13}CCH_4F]^+$ ions account for all of the m/z 48 peak in the NR mass spectrum. The close similarity of the spectra (Fig. 1) indicate that neutral CH_3CH_2F is produced. Note that CH_3CH_2F requires $\sim 250 \text{ kJ mol}^{-1}$ internal energy in order to dissociate by loss of HF,⁴⁰ its decomposition of lowest

energy requirement. We propose that the collision-induced ionization, a wholly vertical process, cannot regenerate stable $[C_2H_5F]^{++}$ ions.

A weak peak at m/z 48, $[C_2H_5F]^{++}$, was observed in the EI mass spectrum of the molecular ion of 3-fluoropropanol, corresponding to loss of CH_2O . Similar CH_2O losses from ionized 3-aminopropanol and 1,3-dihydroxypropane have been studied.¹¹ Both yield distonic ions, for example,



The CID mass spectrum of the $[C_2H_5F]^{++}$ fragment ion, presented in Fig. 2, is proposed to result from the distonic structure $[CH_2CH_2FH]^{++}$. The lack of intensity of CH_3^+ and FCH_2^+ , the intense $C_2H_4^{++}$ and HF^{++} ions are good supporting evidence for this proposal.

The MI characteristics of $[CH_2CH_2FH]^{++}$ and $[CH_3CH_2F]^{++}$ are similar, both showing H and H_2 losses, but the former has an intense, broad peak at m/z 28, $T_{0.5} \sim 600 \text{ meV}$. Note that a weak, broad peak at m/z 28 does appear in the MI mass spectrum of $[CH_3CH_2F]^{++}$ but this arises entirely from $[^{13}CCH_4F]^+$ losing HF. The heat of formation of the new ion could not successfully be measured from an AE and the low intensity of the peak precluded a NRMS experiment.

Recent theoretical calculations at the MP2/6-31G*//6-31G*⁴¹ and MP2/6-31G*//3-21G*⁴² levels have predicted the heats of formation of the distonic ions $[CH_2CH_2XH]^{++}$ for $X = F, Cl$. In the former case, comparison was also made with their bridged counterparts. The energies of the fluoro species, 1 and 2, relative to

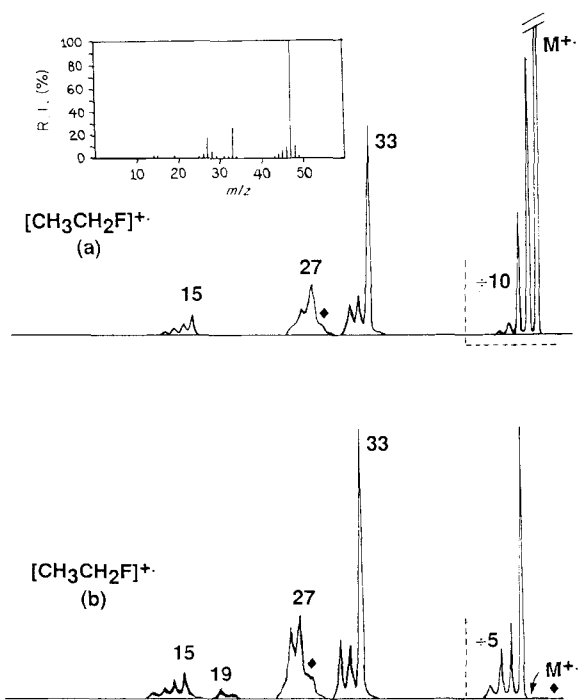


Figure 1. For ethylfluoride, (a) the CID and (b) NR mass spectra; \blacklozenge indicates peaks which have been corrected for ^{13}C contributions from $[C_2H_4F]^+$. Insert: the EI mass spectrum of ethylfluoride.

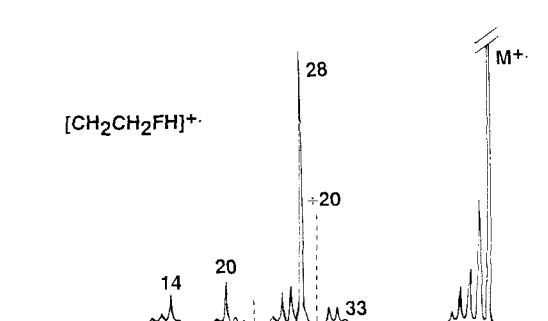


Figure 2. The CID mass spectrum of $[CH_2CH_2FH]^{++}$.

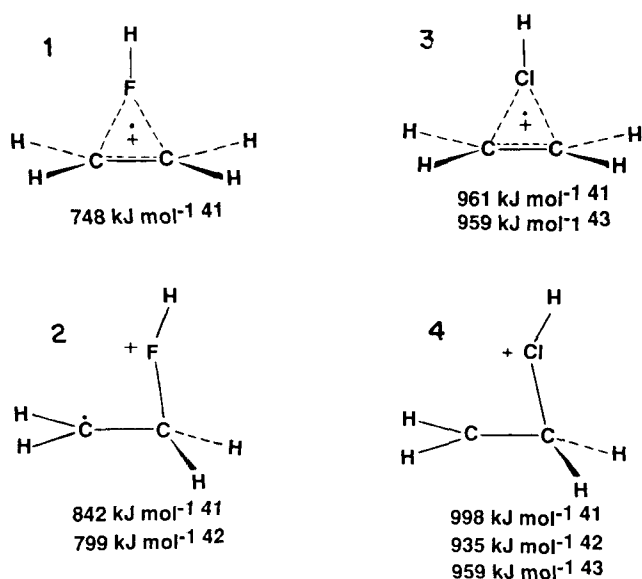


Figure 3. The distonic isomers, **2** and **4**, of ethylfluoride and chloride, and their bridged counterparts, **1** and **3**. The predicted heats of formation of these ions are included, see text.

$[\text{CH}_3\text{CH}_2\text{F}]^{+\cdot}$, were calculated to be -125 kJ mol^{-1} ⁴¹ for the symmetrically bridged, and -31 kJ mol^{-1} ⁴¹ and -74 kJ mol^{-1} ⁴² for the distonic, indicating that the unconventional $[\text{C}_2\text{H}_5\text{F}]^{+\cdot}$ ion structure may be considerably more thermodynamically stable than $[\text{CH}_3\text{CH}_2\text{F}]^{+\cdot}$. Either the distonic or bridged structure is compatible with the observed dissociation characteristics.

The $\text{C}_2\text{H}_5\text{Cl}$ isomers

Both $[\text{CH}_3\text{ClCH}_2]^{+\cdot}$ (*a*) and $[\text{CH}_3\text{CHClH}]^{+\cdot}$ (*b*) are produced via Eqns (1) and (2) respectively, and their measured appearance energies and corresponding heats of formation are presented in Table 1. Their MI and CID characteristics have been reported^{21,23} and are in full agreement with the present work, except that *a* is not observed to be generated *metastably* from $\text{XCH}_2\text{COOCH}_3$, the peaks²¹ ($T_{0.5} \sim 29$ and 40 meV, for $\text{X} = \text{Cl}$ and Br respectively) were found to arise from

collision-induced fragmentations; CH_3^{\cdot} loss from *a* is also not a metastable process. The CID mass spectra of *a* and *b* are given in Figs. 5 and 6 respectively.

Both of these ylids generate a composite and a Gaussian metastable peak corresponding to the losses of HCl and Cl^{\cdot} , respectively; in contrast, the MI mass spectrum of ethylchloride contains only the intense Gaussian peak for the loss of HCl . Experiments were performed using deuterium labelled precursors and the appropriate kinetic energy release data, metastable peak shapes and relative abundances, are given in Table 2.

The first unexpected result was that the uniquely 1,2-hydrogen chloride elimination from $[\text{CH}_3\text{CH}_2\text{Cl}]^{+\cdot}$ ions produced a composite metastable peak for DCI loss from $[\text{CD}_3\text{CH}_2\text{Cl}]^{+\cdot}$. This reaction takes place at the thermochemical threshold (983 kJ mol^{-1} ³⁹); this energy lies only $\sim 30 \text{ kJ mol}^{-1}$ above the ground state of $[\text{CH}_3\text{CH}_2\text{Cl}]^{+\cdot}$ (950 kJ mol^{-1} ³⁹) and so might well be expected *not* to be metastable, the low critical energy giving rise to too low a density of states for the fragmentation to linger on into the μs time frame. It is however possible that the metastable peak arises from the participation of a thermodynamically more stable $[\text{C}_2\text{H}_5\text{Cl}]^{+\cdot}$ isomer, perhaps the distonic ion $[\text{CH}_2\text{CH}_2\text{ClH}]^{+\cdot}$, and that the composite metastable peak reflects the involvement of two reacting configurations in the metastable time frame, for example, $[\text{CD}_2\text{CH}_2\cdots\text{ClD}]^{+\cdot}$ and a four-centered elimination from $[\text{CD}_3\text{CH}_2\text{Cl}]^{+\cdot}$ ions.

Ab initio molecular orbital theory calculations by Clark and Symons⁴¹ and by Yates, Bouma and Radom⁴² have been used to investigate the stability of such distonic type ions. The former authors found no stable species with a ΔH_f° below that of ionized ethyl chloride but Yates *et al.* established that a stable, non-linear distonic ion lay 15 kJ mol^{-1} below $[\text{CH}_3\text{CH}_2\text{Cl}]^{+\cdot}$. A more recent calculation by Hoz *et al.*,⁴³ at a lower level of theory found the distonic ion to be stable but to lie 9 kJ mol^{-1} above $[\text{CH}_3\text{CH}_2\text{Cl}]^{+\cdot}$.

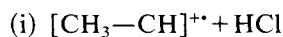
We propose that the composite nature of the HCl loss peaks for the ylids (*a* and *b*) results from the generation of two daughter ions at $m/z = 28$, $[\text{CH}_2=\text{CH}_2]^{+\cdot}$ and $[\text{CH}_3-\text{CH}]^{+\cdot}$. The heat of formation of the ethylene radical cation is 1075 kJ mol^{-1} ,³⁹ while $\Delta H_f^\circ[\text{CH}_3-\text{CH}]^{+\cdot}$ is estimated to be 1155 kJ mol^{-1} , from

Table 2. Kinetic energy releases ($T_{0.5}$)^a for the fragmentation $\text{C}_2\text{H}_5\text{Cl}^{+\cdot} \rightarrow \text{C}_2\text{H}_4^{+\cdot} + \text{HCl}$

Ion	Loss	Peak shape	$T_{0.5}$ (meV)	Rel. ab.
$[\text{CH}_3\text{CH}_2\text{Cl}]^{+\cdot}$	HCl	Gaussian type	24	
$[\text{CH}_3\text{CH}_2\text{Cl}]^{+\cdot}$	DCI	Composite	69	
$[\text{CH}_3\text{ClCH}_2]^{+\cdot}$	HCl	-no-signal-		
$[\text{CH}_3\text{ClCH}_2]^{+\cdot}$	HCl	Composite (Gaussian type)	~ 30	20
$[\text{CH}_3\text{ClCH}_2]^{+\cdot}$	HCl	(dished)	~ 450	100
$[\text{CD}_3\text{ClCH}_2]^{+\cdot}$	DCI	Composite (Gaussian type)	~ 28	10
$[\text{CD}_3\text{ClCH}_2]^{+\cdot}$	DCI	(dished)	~ 460	100
$[\text{CH}_3\text{CHClH}]^{+\cdot}$	HCl	Gaussian type	30	34
$[\text{CH}_3\text{CHClH}]^{+\cdot}$	HCl	Composite (Gaussian type)	~ 11	5
$[\text{CH}_3\text{CHClH}]^{+\cdot}$	HCl	(dished)	~ 300	100
$[\text{CH}_3\text{CHClD}]^{+\cdot}$	DCI	Composite	-	v. weak
$[\text{CH}_3\text{CHClD}]^{+\cdot}$	HCl	Composite (Gaussian type)	~ 30	9
$[\text{CH}_3\text{CHClD}]^{+\cdot}$	HCl	(dished)	~ 340	100

^a Kinetic energy releases calculated from the peak width at half height.²⁹ Those for the composite peaks are estimated from deconvolution.

$\Delta H_f^\circ[\text{CH}_2]^{++} = 1398 \text{ kJ mol}^{-1}$ ³⁹ and the (extrapolated) stabilization effect of CH_3 substitution on a charge-bearing site.⁴⁴



$$\Delta H_f^\circ(\text{prod}) = 1155 - 92$$
³⁷ = 1063 kJ mol⁻¹



$$\Delta H_f^\circ(\text{prod}) = 1075 - 92$$
³⁷ = 983 kJ mol⁻¹

Although the existence of the $[\text{CH}_3\text{CH}]^{++}$ ion in the gas phase remains undemonstrated, its production is proposed to give rise here to the narrow component in the composite metastable peak, the fragments having been generated near threshold. The *AE* for $m/z = 28$ from $[\text{CH}_3\text{CHClH}]^{++}$ was measured to be $\leq 11.5 \text{ eV}$,²³ 1109 kJ mol⁻¹, consistent with the threshold calculated from the estimated value for $\Delta H_f^\circ[\text{CH}_3\text{—CH}]^{++}$. The generation of an ethylene radical cation via a barrier of similar height is then proposed to be the origin of the very broad component of the composite $[\text{C}_2\text{H}_4]^{++}$ peak.

The results of the labelling experiments are less easy to interpret. For $[\text{CD}_3\text{ClCH}_2]^{++}$ ions, only loss of DCl is associated with the large kinetic energy release process, compatible with rearrangement to 'hot' $[\text{CD}_3\text{CH}_2\text{Cl}]^{++}$ ions. The small kinetic energy release involves both HCl and DCl with the former predominant. The major composite peak for the loss of HCl from $[\text{CH}_3\text{CHClD}]^{++}$ cannot readily be explained. Clearly, a solution to the above mechanistic problems must await a more detailed understanding of the $[\text{C}_2\text{H}_5\text{Cl}]^{++}$ potential energy surface.

By analogy with the fluoro analogue it was expected that the $[\text{C}_2\text{H}_5\text{Cl}]^{++}$ fragment ion in the EI mass spectrum of 3-chloropropanol has the distonic structure, $[\text{CH}_2\text{CH}_2\text{ClH}]^{++}$. The CID mass spectrum (Fig. 7) of the $m/z = 64$ ion contains major peaks corresponding to CH_2^+ , HCl^{++} and $[\text{C}_2\text{H}_4]^{++}$; these, and the lack of $[\text{C}_2\text{H}_5]^{++}$ are consistent with the distonic form. Unlike the $[\text{C}_2\text{H}_5\text{Cl}]^{++}$ isomers, $[\text{CH}_3\text{CH}_2\text{Cl}]^{++}$, $[\text{CH}_3\text{ClCH}_2]^{++}$ and $[\text{CH}_3\text{CHClH}]^{++}$, there is no loss of Cl^\bullet and only a possible minor HCl loss observed for this ion in the metastable time frame. Although unobtainable by experiment, the heats of formation of the distonic ion and its bridged counterpart, (shown in Fig. 3), have been calculated by *ab initio* molecular orbital theory. The energies of the chloro species **3** and **4**, relative to $[\text{CH}_3\text{CH}_2\text{Cl}]^{++}$, were calculated to be +11 kJ mol⁻¹⁴¹ and +9 kJ mol⁻¹⁴³ for the symmetrically bridged, and +48 kJ mol⁻¹,⁴¹ -15 kJ mol⁻¹⁴² and +9 kJ mol⁻¹⁴³ for the distonic ion respectively.

The CS mass spectra of the four chloro-isomers are given in Table 3. The CS mass spectra are clearly structure characteristic, with (doubly charged) $m/z = 32$ ions dominating the spectra for $[\text{CH}_3\text{CHClH}]^{++}$ and $[\text{CH}_2\text{CH}_2\text{ClH}]^{++}$, behaviour analogous to the lower homologues $[\text{CH}_3\text{Cl}]^{++}$ and $[\text{CH}_2\text{ClH}]^{++}$.⁵

The $[\text{C}_2\text{H}_5\text{Br}]^{++}$ isomers

Heats of formation for the ions $[\text{CH}_3\text{CH}_2\text{Br}]^{++}$, $[\text{CH}_3\text{BrCH}_2]^{++}$ and $[\text{CH}_3\text{CHBrH}]^{++}$ are given in Table 1. The ΔH_f° for $[\text{CH}_2\text{CH}_2\text{BrH}]^{++}$ could not be measured,

Table 3. Charge stripping mass spectra of $[\text{C}_2\text{H}_5\text{Cl}]^{++}$ ions

Ion structure	M^{2+}	$[M-1]^{2+}$	$[M-2]^{2+}$	$[M-3]^{2+}$	Relative cross-section ^a
$[\text{CH}_3\text{CH}_2\text{Cl}]^{++}$	—	4	100	36	1/300
$[\text{CH}_3\text{ClCH}_2]^{++}$	100	very weak			1/1000
$[\text{CH}_3\text{CHClH}]^{++}$	100	14	1	3	1/50
$[\text{CH}_2\text{CH}_2\text{ClH}]^{++}$	100	36	44	2	1/150

^a Ratio of the sum of the CS peaks to that of the singly charged CID fragment ions.

and no theoretical calculations have been made for the bromo-ions. Note that the two ylidsions have ΔH_f° values above that for $[\text{CH}_3\text{CH}_2\text{Br}]^{++}$. The CID mass spectra of these isomeric ions are structure-characteristic and are presented later (see discussion of neutral analogues). The EI mass spectrum of 3-bromopropanol contains a small peak ($\sim 1\%$ of the base peak, $m/z = 31$) at $m/z = 108$, corresponding to the possible generation of the distonic ions $[\text{CH}_2\text{CH}_2\text{BrH}]^{++}$. The metastable ion mass spectra for the bromo-ions are given in Table 4. All peaks are of Gaussian type and, in contrast with the chloro-analogues, hydrogen bromide loss is only a minor process.

Note that unlike the $[\text{C}_2\text{H}_5\text{Cl}]^{++}$ system (where HCl loss is favoured over Cl^\bullet loss, i.e. $\Delta H_f^\circ[\text{C}_2\text{H}_4]^{++} + \Delta H_f^\circ[\text{HCl}] = 983 \text{ kJ mol}^{-1}$,³⁹ $\Delta H_f^\circ[\text{C}_2\text{H}_5]^{++} + \Delta H_f^\circ[\text{Cl}^\bullet] = 1039 \text{ kJ mol}^{-1}$ ³⁹) loss of Br^\bullet is the less energy demanding fragmentation and so is the expectedly predominant metastable process; $\Delta H_f^\circ[\text{C}_2\text{H}_5]^{++} + \Delta H_f^\circ[\text{Br}^\bullet] = 1029 \text{ kJ mol}^{-1}$ ³⁹ $\Delta H_f^\circ[\text{C}_2\text{H}_4]^{++} + \Delta H_f^\circ[\text{HBr}] = 1039 \text{ kJ mol}^{-1}$.³⁹ It is proposed that Br^\bullet loss proceeds via $[\text{CH}_3\text{CH}_2\text{Br}]^{++}$ ions. The kinetic energy releases for Br^\bullet loss from $[\text{CH}_3\text{BrCH}_2]^{++}$ and $[\text{CH}_3\text{CHBrH}]^{++}$ are compatible with the relative energies of these ions and $[\text{CH}_3\text{CH}_2\text{Br}]^{++}$.

The $[\text{C}_2\text{H}_5\text{I}]^{++}$ isomers

The iodo analogues of the precursor molecules which successfully led to $[\text{C}_2\text{H}_5\text{Cl}]^{++}$ and $[\text{C}_2\text{H}_5\text{Br}]^{++}$ isomeric ions do not produce any $[\text{C}_2\text{H}_5\text{I}]^{++}$ daughter ions and so no isomers of ethyl iodide have so far been observed.

Neutral isomers of $[\text{C}_2\text{H}_5\text{Cl}]^{++}$ and $[\text{C}_2\text{H}_5\text{Br}]^{++}$

Neutralization-reionization mass spectra were recorded as described in the experimental section. Theoretical calculations have indicated that the ylides derived from

Table 4. Metastable peak characteristics of $[\text{C}_2\text{H}_5\text{Br}]^{++}$ ions

Ion	Loss	$T_{0.5}$ (meV)	Rel. Ab.
$[\text{CH}_3\text{CH}_2\text{Br}]^{++}$	Br^\bullet	—	v. weak peak
$[\text{CH}_3\text{BrCH}_2]^{++}$	HBr	40	1
	Br^\bullet	43	40
$[\text{CH}_3\text{CHBrH}]^{++}$	HBr	12	1
	Br^\bullet	24	40
$[\text{CH}_2\text{CH}_2\text{BrH}]^{++}$	Br^\bullet	7	—

the lower homologues, CH_2ClH , are unstable or, at best, lie in a very shallow potential well.^{8a,10} Although the interpretation of experiments by Wesdemiotis *et al.*¹³ and by ourselves¹⁵ are at odds over the stability of the above species, it is nevertheless possible that the ylide CH_2ClH survives for sufficient time (μs) to be weakly observable. It was therefore of considerable interest to examine the present isomeric $[\text{C}_2\text{H}_5\text{Cl}]^{+\bullet}$ and $[\text{C}_2\text{H}_5\text{Br}]^{+\bullet}$ ions by the NR technique.

Figure 4 shows the NR mass spectra for $[\text{CH}_3\text{CH}_2\text{Cl}]^{+\bullet}$ and $[\text{CH}_3\text{CH}_2\text{Br}]^{+\bullet}$ with the CID mass spectra for comparison. Stable, neutral $\text{CH}_3\text{CH}_2\text{X}$ species are clearly generated, and (unlike $\text{CH}_3\text{CH}_2\text{F}$) ^{13}C correction to the recovered $[\text{CH}_3\text{CH}_2\text{X}]^{+\bullet}$ peaks was insignificant. The major collision-generated neutrals (Cl^\bullet and Br^\bullet) comprise the only significant differences in the spectra.

For a particular neutral structure to be 'detectable' by NRMS, the energy of the vertically neutralized species should be lower than that of transition states for subsequent rearrangement or fragmentation.^{8a} This is true of ethylchloride and ethylbromide. The similar CID and NR mass spectra clearly point to a similar geometry for ion and neutral, while the intensity of the regenerated molecular radical cations, the survivors, indicates stability of the neutral following collision-induced vertical neutralization of the ion.

The NR mass spectrum of $[\text{CH}_3\text{ClCH}_2]^{+\bullet}$ (shown together with its CID mass spectrum in Fig. 5), was composed entirely of fragment ions, neither $[\text{C}_2\text{H}_5\text{Cl}]^{+\bullet}$ survivors nor even their hydrogen loss species were observed. Unlike ethylfluoride, this absence results from the instability of the neutral, not the regenerated radical cation. The fragments are characteristic of the ylid structure, indicating that isomerization cannot precede

decomposition. Note the absence of any C_2 fragments (indicating no $\text{C}-\text{C}$ bond), and the very similar intensity of the $[\text{CH}_2\text{Cl}]^+$ and $[\text{CH}_3\text{Cl}]^{+\bullet}$ fragments. Decomposition of the ylide to $\text{CH}_3^\bullet + \text{CH}_2\text{Cl}^\bullet$ is favoured over dissociation to $\text{CH}_3\text{Cl} + \text{CH}_2$ by 54 kJ mol^{-1} ($\Delta H_f^\circ[\text{CH}_3^\bullet]$, 142 kJ mol^{-1} ³⁹ + $\Delta H_f^\circ[\text{CH}_2\text{Cl}^\bullet]$, 115 kJ mol^{-1} ⁴⁵ = 257 kJ mol^{-1} ; $\Delta H_f^\circ[\text{CH}_3\text{Cl}]$, -82 kJ mol^{-1} ³⁷ + $\Delta H_f^\circ[\text{CH}_2]$, 392 kJ mol^{-1} ³⁹ = 310 kJ mol^{-1}) but the signals of similar abundance in the NRMS must result from widely different reionization cross-sections, favouring CH_3Cl .

Figure 5 also shows the results for $[\text{CH}_3\text{BrCH}_2]^{+\bullet}$ ions, whose behaviour was very similar. Thus neutralization-reionization can sometimes provide a good alternative means of structure assignment, as strikingly illustrated for these ylids. The NRMS are much more characteristic of the $[\text{CH}_3\text{XCH}_2]^{+\bullet}$ structure than the CID mass spectra. Indeed, the earlier identification of the ions required deuterium labelling to differentiate their CID mass spectra from those of the conventional isomer.²¹

The NR mass spectra of the other ylids $[\text{CH}_3\text{CHClH}]^{+\bullet}$ and $[\text{CH}_3\text{CHBrH}]^{+\bullet}$, shown in Fig. 6 with the corresponding CID mass spectra, contain signals corresponding to surviving neutral counterparts. This was unexpected; corrections for ^{13}C (i.e. $^{13}\text{CCH}_4\text{X}^+$ species) did not significantly reduce the peaks. The $[\text{CH}_3\text{CHBrH}]^{+\bullet}$ signal is indeed small and so it is not impossible that it arises from the presence of some $[\text{CH}_3\text{CH}_2\text{Br}]^{+\bullet}$ ions in the initial ion flux. However, for the chloro-analogue such an explanation is not possible, there being insufficient m/z 29 and m/z 49 in the NR mass spectrum (compare Figs 4 and 6); moreover the CID and NRMS of these ylids are remarkably similar.

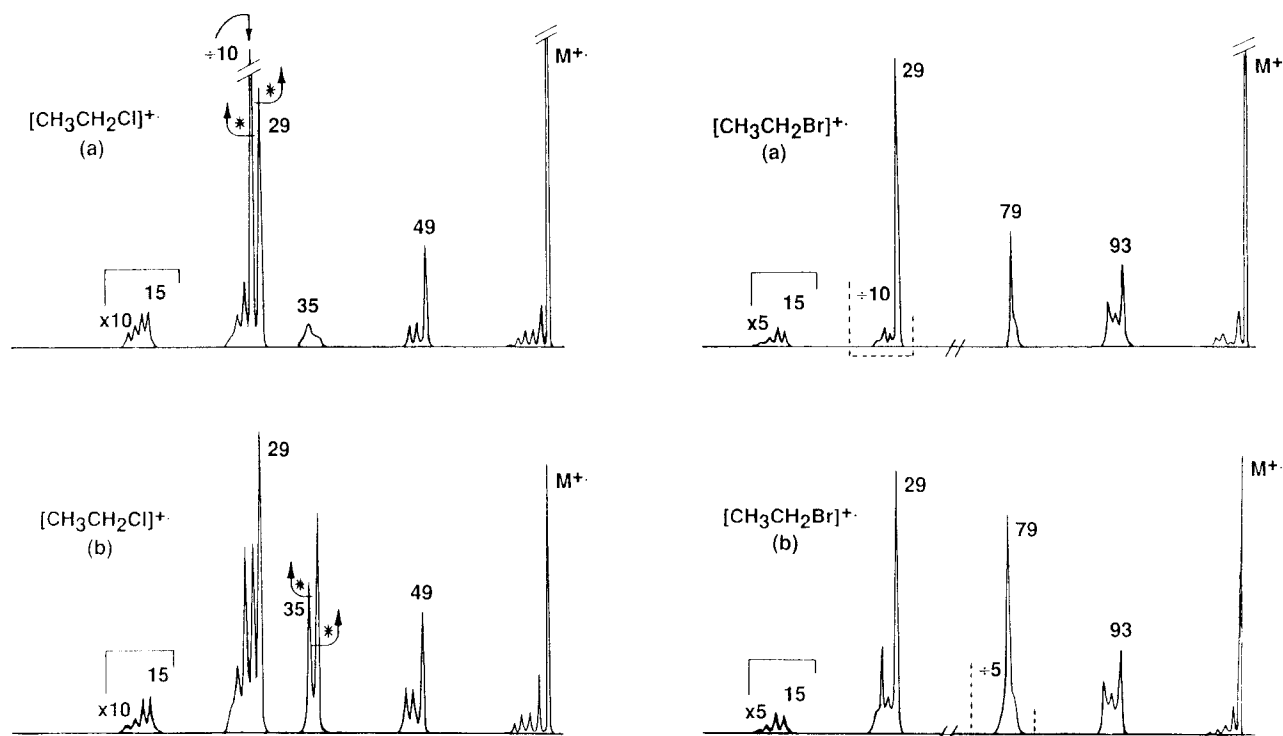


Figure 4. For ethylchloride and ethylbromide, (a) the CID and (b) NR mass spectra; where indicated, *, peak heights have been corrected for metastable processes occurring prior to the collision cell.

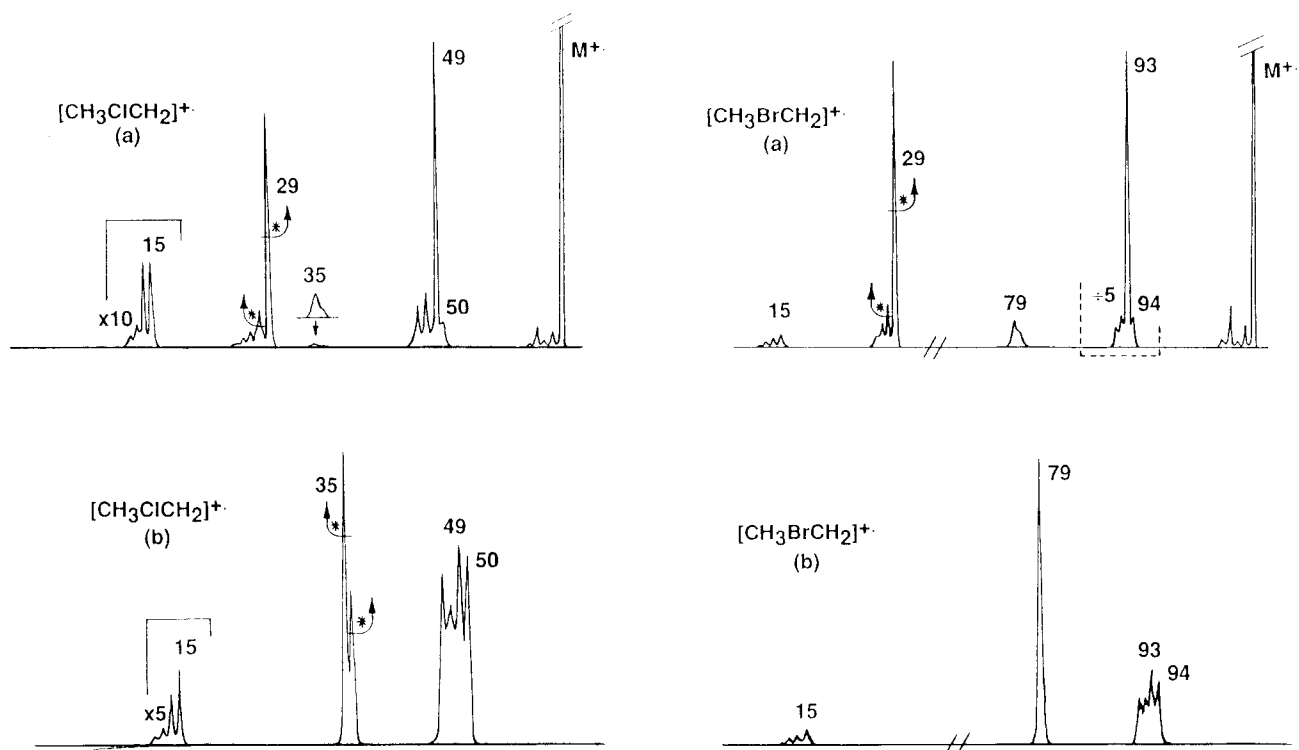


Figure 5. For the ylidyons $[\text{CH}_3\text{CICH}_2]^+$ and $[\text{CH}_3\text{BrCH}_2]^+$, (a) the CID and (b) NR mass spectra; where indicated, *, peak heights have been corrected for metastable processes occurring prior to the collision cell.

The NR mass spectra of the distonic ions $[\text{CH}_2\text{CH}_2\text{CIH}]^+$ and $[\text{CH}_2\text{CH}_2\text{BrH}]^+$ were also examined. Again, relatively large yields of surviving $[\text{C}_2\text{H}_5\text{X}]^+$ ions were observed (Fig. 7) and moreover,

the spectra were not compatible with the involvement of the conventional ethyl halide ions.

For completeness of data, the CID and NR mass spectra of $[\text{CH}_3\text{CH}_2\text{I}]^+$ are presented in Fig. 8.

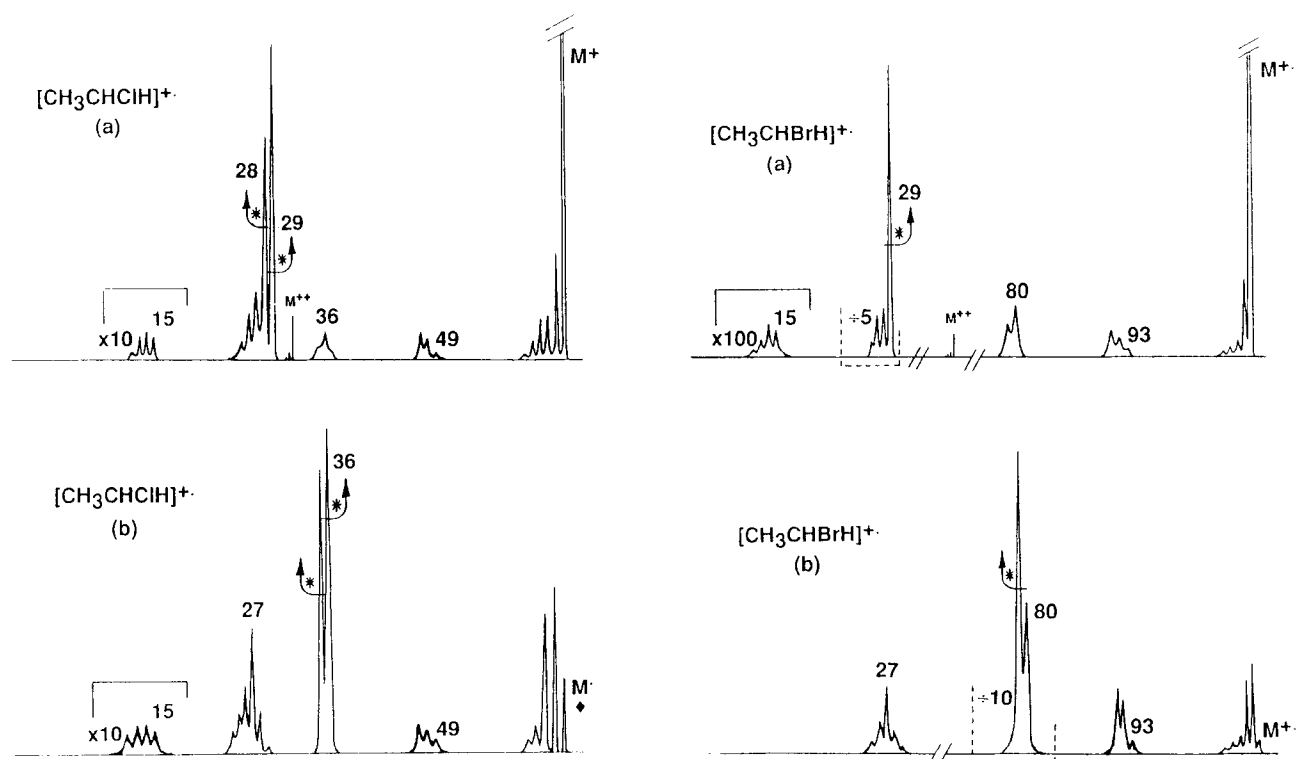


Figure 6. For the ylidyons $[\text{CH}_3\text{CHCIH}]^+$ and $[\text{CH}_3\text{CHBrH}]^+$, (a) the CID and (b) NR mass spectra; ● indicates correction made for ^{13}C contribution from $[\text{C}_2\text{H}_4\text{Cl}]^+$, * indicates corrections made for the metastable processes occurring prior to the collision cell.

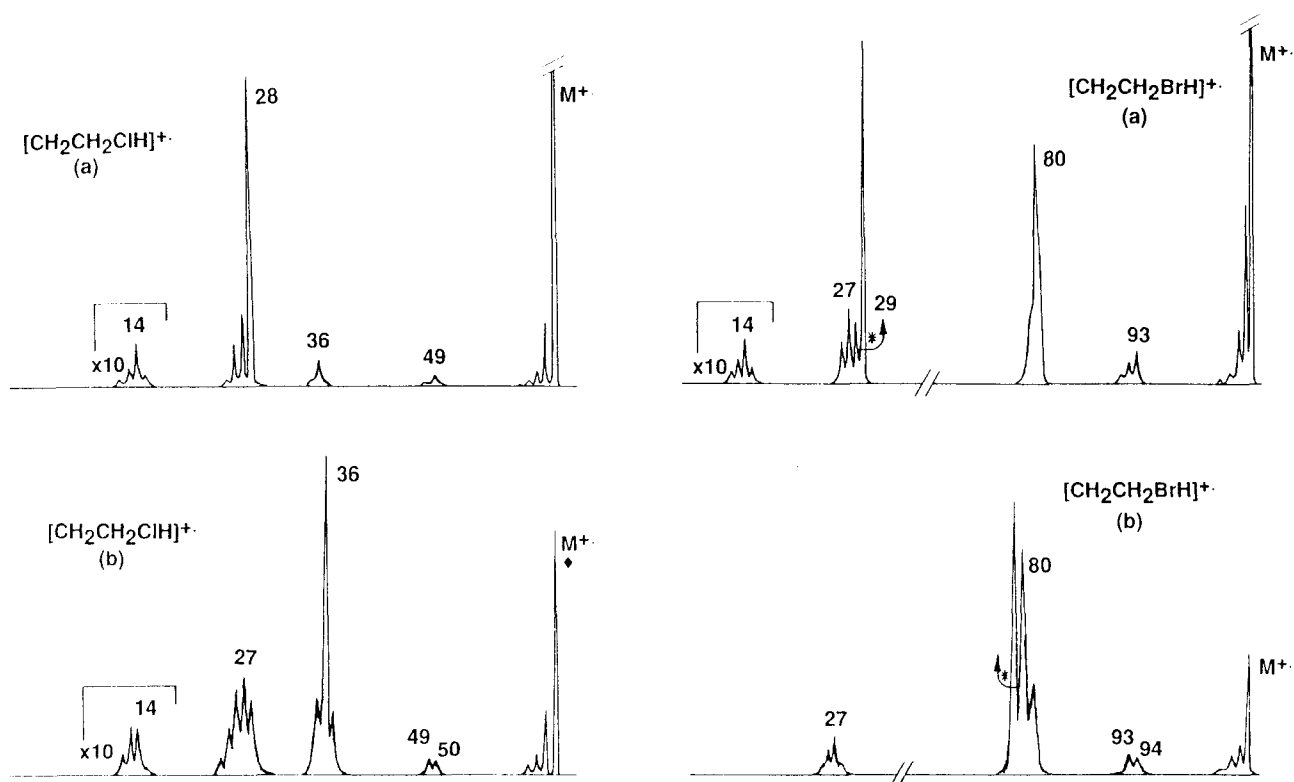


Figure 7. For the distonic ions $[\text{CH}_2\text{CH}_2\text{ClH}]^{+\bullet}$ and $[\text{CH}_2\text{CH}_2\text{BrH}]^{+\bullet}$, (a) the CID and (b) the signal-averaged NR mass spectra; ♦ indicates correction made for ^{13}C contribution from $[\text{C}_2\text{H}_4\text{Cl}]^{+\bullet}$, * indicates corrections made for the metastable process occurring prior to the collision cell.

CONCLUSIONS

The adiabatic IE of ethylfluoride and the AE of $[\text{C}_2\text{H}_5\text{F}]^{+\bullet}$ from $\text{FCH}_2\text{COOCH}_3$ have been obtained and gave heats of formation equivalent within experimental error, supporting the conclusion²² that the $[\text{CH}_3\text{CH}_2\text{F}]^{+\bullet}$ ion is produced.

The heats of formation of $[\text{CH}_3\text{ClCCH}_2]^{+\bullet}$, $[\text{CH}_3\text{BrCH}_2]^{+\bullet}$ and $[\text{CH}_3\text{CHBrH}]^{+\bullet}$, 1012, 1058, and 995 kJ mol^{-1} respectively, have been obtained from the measured AE 's from their respective precursors, (Eqns 1 and 2).

The $T_{0.5}$ values of the metastable processes of these unconventional ions have also been recorded, and we have proposed the formation of both $[\text{CH}_2=\text{CH}_2]^{+\bullet}$ and $[\text{CH}_3-\text{CH}]^{+\bullet}$ to explain the composite nature of the metastable peak at m/z 28 from the $[\text{C}_2\text{H}_5\text{Cl}]^{+\bullet}$ ylidions.

The neutral counterparts of the stable radical cations discussed above, have been investigated by the most recently introduced technique, neutralization-reionization mass spectrometry. For the ethylhalides, where $X = \text{Cl}, \text{Br}, \text{I}$, vertical neutralization yields stable neutral counterparts. For $X = \text{F}$, a stable neutral is proposed; the lack of survivors results from the instability of the ion generated by the vertical process of collision-induced reionization. Consistent with the trend observed in the hydrogen analogues, the neutral counterparts of the ylidions $[\text{CH}_3\text{ClCH}_2]^{+\bullet}$ and $[\text{CH}_3\text{BrCH}_2]^{+\bullet}$ are unstable, and dissociate directly upon formation. The unconventional ions, $[\text{CH}_3\text{CHXH}]^{+\bullet}$ and $[\text{CH}_2\text{CH}_2\text{XH}]^{+\bullet}$ (for

$X = \text{Cl}, \text{Br}$), contrary to expectations, generated NR mass spectra which are not composed entirely of fragment ions, and which are similar to their CID mass spectra. The 'survivors' observed are accounted for by

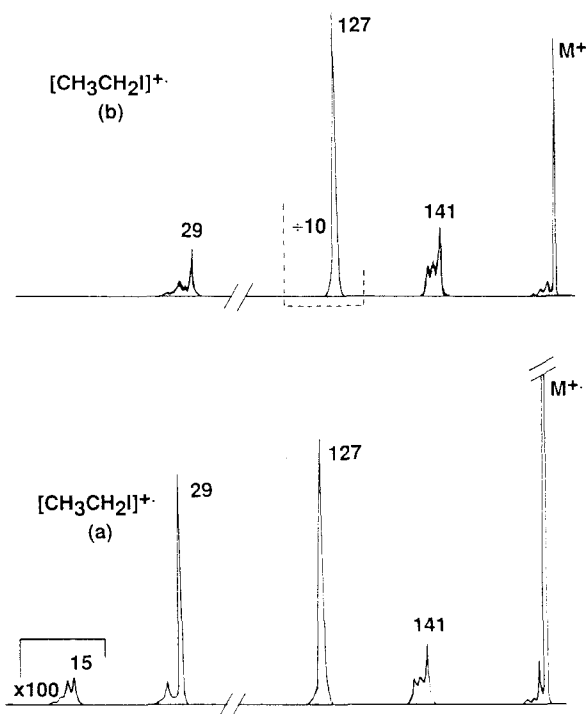


Figure 8. For ethyl iodide, (a) the CID and (b) NR mass spectra.

neither ^{13}C contributions nor an interfering flux of the conventional isomer. And thus without evidence to the contrary, the neutral ylides, CH_3CHXH and $\text{CH}_2\text{CH}_2\text{XH}$, are proposed to be stable.

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