

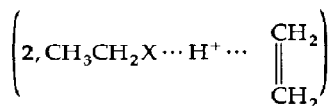
# A Tandem Mass Spectrometric Investigation of $(C_2H_5)_2X^+$ Ions ( $X = Cl, Br, I$ ): The Involvement of Classical and Nonclassical Ethyl Structures Therein

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The formation of diethyl halonium ions  $(C_2H_5)_2X^+$  ( $X = Cl, Br, I$ ) by a variety of ion-molecule reactions is described. The dissociation characteristics (metastable and collision-induced dissociation mass spectra) of these ions and their isomers were studied in detail. Some of the neutral fragmentation products were examined by their collision-induced dissociative ionization mass spectra.

The participation of classical (1,  $CH_3CH_2X^+CH_2CH_3$ ) and nonclassical



forms of the ions was considered. Dissociation reactions for which loss of positional identity of H-D atoms took place, for example,  $C_2H_4$  loss (a common fragmentation of metastable ions) and  $C_2H_5^+$  formation, were interpreted as involving nonclassical ions, **2**. It was concluded that the ion-molecule reactions produced both ion structures, but in different halogen-dependent proportions. For  $(C_2H_5)_2Cl^+$  ions, **2** is the major species, for  $(C_2H_5)_2Br^+$  both 1- and 2-type ions are generated, whereas for  $(C_2H_5)_2I^+$  the classical form **1** must be the predominant structure. (*J Am Soc Mass Spectrom* 1994, 5, 814-825)

**A** cyclic halonium ions  $RX^+R'$  ( $X = \text{halogen}$ ;  $R, R' = \text{alkyl}$ ) are well-known species in the condensed phase [1], where they are widely used as alkylating agents. Gas-phase alkyl halonium ions have been produced and studied by mass spectrometry [2]. Their ability to transfer an alkyl cation easily to a substrate has been used for the gas-phase alkylation of organic molecules [3] and for quantitative kinetic and thermochemical measurements [2d, 2e, 4-9]. For example, methyl cation affinities (MCA [3r, 5-7, 9] and ethyl cation affinities (ECA [3v]) of a variety of molecules have been determined.

The unimolecular decomposition of gas-phase halonium ions has not been studied widely. Bomse and Beauchamp [8] investigated the photoinduced dissociation of the  $(CH_3)_2Cl^+$  ion and its isomers by ion cyclotron resonance (ICR) spectroscopy [8]. Only  $(CD_3)_2Cl^+$  ions decomposed to  $CD_2Cl^+ + CD_4$ ,

whereas  $(CH_3)_2Cl^+$  and  $CD_3Cl^+CH_3$  were stable under the experimental conditions. Zappey et al. [10] studied the collision-induced dissociation of dimethyl halonium ions  $(CH_3)_2X^+$  ( $X = F, Cl, Br, I$ ) and their neutralization-reionization (NR) mass spectra. The major decomposition processes of these ions involved X-C bond cleavage, but some rearrangements also were proposed, for example, that formation of  $Br^+$  and  $I^+$  ions involved methyl radical coupling. C-H bond fission that leads to alkane ( $CH_4$ ) loss was not important [10], although it is a major product of ion-molecule reactions between  $CH_3^+$  and  $CH_3X$  [2g, 5].

Recovery signals were not found in the NR mass spectra of  $(CH_3)_2X^+$  ions [10]. Their neutralization with Xe was associated with cleavage of one of the carbon-halogen bonds in the generated (unstable) neutral species. In addition to  $CH_3X^+$  ions the NR mass spectra showed  $CH_2X^+$ ,  $CH_3^+$ ,  $X^+$ , and other ions whose relative abundances depend on the halogen atom [10].

Decomposition of the  $c\text{-}C_3H_5Br^+CH_3$  ions generated by reactions of  $(CH_3)_2X^+$  ( $X = F, Cl$ ) with cyclopropyl bromide was studied by Colosimo and Bucci [3d]. Rearrangements of these ions that lead to alkyl

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group coupling or result in Br<sup>·</sup> and HBr losses were explained by the formation of isomeric species with a methyl cation attached to carbon or halogen atoms [30].

The dissociation characteristics of protonated alkyl halides have been studied by several authors. Hollis et al. [2g] investigated the collision-induced fragmentation of protonated methyl halides  $CH_3X^+H$ . The common major decomposition was methyl cation formation. Hydrogen molecule loss also was observed for X = F, Cl, and Br, but not for protonated methyl iodide. An investigation of deuterated methyl chloride showed a low abundance of HCl and  $H_2$  in addition to DCl and HD loss, which indicates some H-D mixing prior to fragmentation. Heck et al. [11] studied in detail the collision-induced dissociation of labeled  $CH_3X^+H$  ions, and they showed that for nearly all fragmenting  $CH_3Cl^+D$  ions, deuterium was still bound to the halogen. Hydrogen exchange was detected within labeled  $CH_3Br^+H$ , and it was proposed that a stable halonium ion structure can interconvert with another structure in which the added proton is involved in a three-center, two-electron bond together with the carbon and methyl-group hydrogens. This type of structure was most favored by protonated iodomethane.

The collision-induced dissociations of protonated ethyl bromide and iodide were described by Wagner et al. [12]. Major reactions involved simple C—X and X—H bond cleavages that resulted in  $C_2H_5^+$ ,  $C_2H_3X^+$ , and  $XH^+$  ion formation.  $CH_2X^+$  ions also were observed, but their origin, as well as the possibility of hydrogen atom mixing prior to their formation, was not discussed.

No data on the decomposition of diethyl halonium ions have been reported.

The ethyl cation exhibits two structural forms [13]. The ground state, a symmetrical proton-bridged ethene, lies some 6–7 kcal mol<sup>-1</sup> below the classical form; the latter does not occupy a potential well and so at the corresponding energy, the hydrogen atoms can lose their positional identity [14]. However, the above two forms can be captured by a substrate molecule, for example, as in the  $C_2H_7O^+$  ions derived from protonated ethanol [15]. The two discrete  $C_2H_7O^+$  structures each occupy a potential well, and the classical (1; RX = H<sub>2</sub>O) configuration is about 12 kcal mol<sup>-1</sup> lower in energy than the symmetrical nonclassical form (2; RX = H<sub>2</sub>O) [16]. The lower energy (classical) form can be generated directly from a dissociative ionization, but the higher energy isomer so far has been produced only in admixture with the classical ion [15].



A similar situation may exist for diethyl halonium

ions with respect to isomeric ethyl cations and so the aim of this work is to investigate the decomposition of the symmetrical diethyl halonium ions  $(C_2H_5)_2X^+$  (X = Cl, Br, I) by tandem mass spectrometry and, with the aid of labeling studies, to attempt to assign structures to the ions.

## Experimental

Ethyl halides were purchased from Aldrich Chemical Co. (Milwaukee, WI). Deuterated ethyl bromides, ethyl iodides, and  $CH_3CD_2NO_2$  were purchased from Merck Sharp, and Dohme Isotopes (St. Louis, MO).  $CD_3CH_2NO_2$  and  $CHD_2CHDNO_2$  were synthesized by the standard procedure by using  $CD_3CH_2I$  or  $CHD_2CHDBr$  and  $AgNO_2$ .

Electron impact (ionizing electron energy 70 eV), metastable ion (MI), collision induced dissociation (CID), and collision-induced dissociative ionization (CIDI) mass spectra were recorded [17] via a modified VG Analytical Ltd. (Manchester, UK) ZAB-2F mass spectrometer with BEE geometry. Oxygen was used for the collisional activation of ions and the ionization of neutrals that originated from metastable and collisionally activated ions. In all cases the  $O_2$  pressure reduced the main beam by 15%. In the triple mass spectrometry ( $MS^3$ ) experiments, ions formed in the second field-free region (2-FFR) by the metastable or collision-induced dissociation of mass-selected precursor ions were transmitted into the third field-free region (3-FFR) and then collisionally activated. Recording the MI, CID, and CIDI mass spectra was carried out via the ZABCAT program [18]. Kinetic energy release (KER) measurements were performed on the same mass spectrometer at sufficient energy resolution to reduce the main ion beam width at half height to 3–5 V. The reproducibility of  $T_{0.5}$  values was better than 10%.

In the NR experiments, Xe and  $O_2$  were used for neutralization and reionization, respectively; their pressures were adjusted to give a main beam transmission of 85% for each stage. No survival signals were found in the NR mass spectra of  $(C_2H_5)_2X^+$ , which were dominated by the reionized alkyl halide ions and their dissociation products and thus did not provide any valuable information in addition to, for example, the CIDI mass spectra. For this reason NR mass spectra will not be discussed further in the present work.

To produce halonium ions, the ethyl halide or a mixture of ethyl halides was evaporated into a chemical ionization source so that the pressure measured above the ion source diffusion pump was in the range of  $3\text{--}9 \times 10^{-5}$  torr. Unsymmetrically labeled ethyl halonium ions were generated from mixtures of two halides by using similar partial pressures of each. In special cases (see Results and Discussion) these relative concentrations were varied widely. No ethyl group exchange was observed in ethyl chloride–ethyl bromide mixtures. When ethyl bromide with ethyl iodide

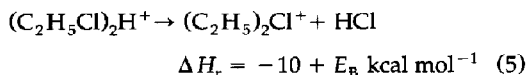
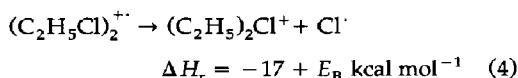
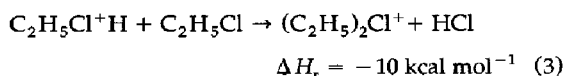
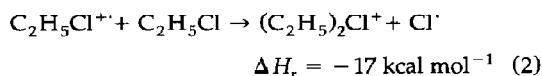
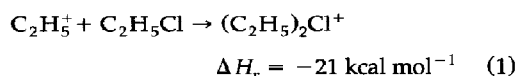
was evaporated via the same inlet system, some mixing was observed, but only after a delay of several minutes.

Modified neglect of differential overlap (MNDO) calculations of  $C_2H_4I^+$  ions were performed via the AMPAC program (Version 3) with full optimization of geometry.

## Results and Discussion

### $(C_2H_5)_2Cl^+$ Ions

It is first necessary to consider the origin of these ions.  $(C_2H_5)_2Cl^+$  ions were produced by ion-molecule reactions in the ionized vapors of ethyl chloride, and have been studied intensively by several authors [2b, 2f, 3-5]. Possible reactions that lead to diethyl chloronium ions are listed below together with their enthalpies ( $\Delta H_r$ ):

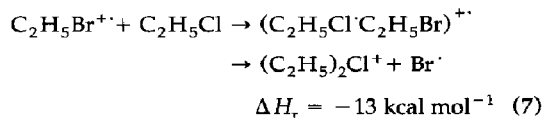
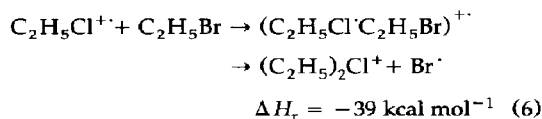


The reactant ions in eqs 1-5 are all observed in the high pressure mass spectrum of ethyl chloride. In general,  $C_2H_5Cl^{++}$  and  $C_2H_5Cl^+H$  are the most prominent species, and the reactants in eqs 4 and 5 are relatively much smaller (less than 0.1% of the most intense species, usually  $C_2H_5Cl^+$ ). Reaction 5 is accompanied by a metastable peak, whereas reaction 4 is not. In the calculation of  $\Delta H_r$  values,  $\Delta H_f[(C_2H_5)_2Cl^+] = 153 \text{ kcal mol}^{-1}$  was used (see Appendix); for these and all subsequent reactions, heats of formation were taken from ref 19 unless otherwise stated. Heats of formation of the ionized and proton-bound ethyl chloride dimers are unknown. The enthalpies for reactions 4 and 5 were calculated as for reactions 2 and 3, but the unknown binding energy was left as  $E_B$ . For reactions 4 and 5 to be endothermic (and therefore of relatively less importance) the binding energies would have to be greater than 17 and 10  $\text{kcal mol}^{-1}$ , respectively. For reaction 4 the reverse activation energy barrier was estimated to be approximately 7  $\text{kcal mol}^{-1}$  [2f], which indicates that  $(C_2H_5)_2Cl^+$  ions produced therefrom will contain some excess energy.

If the reaction of ionized ethyl chloride with an ethyl chloride molecule (reaction 2) leads to  $(C_2H_5)_2Cl^+$  formation, an intermediate ionized ethyl chloride dimer  $(C_2H_5Cl)_2^{++}$  might be observed. The latter was not found in ICR experiments [5], but its formation and decomposition by  $Cl^-$  loss were proposed by Weitzel et al. [2f]. Only weak signals at  $m/z$  128, 130, and 132, that correspond to the ionized dimer, were observed in our experiments, which indicates that routes in reactions 2 and 4 may be unlikely sources of the  $(C_2H_5)_2Cl^+$  ion. Moreover, the MI and CID mass spectra of the dimer ions did not show a signal due to chlorine atom loss. Instead  $C_2H_5Cl^{++}$  and  $C_4H_9Cl^+$  ions were observed in both spectra ( $C_2H_5Cl$  and  $HCl$  losses, respectively).

Formation of the diethyl chloronium ion by reaction 3 was established by ICR spectroscopy [5] and high pressure mass spectrometry [3]. The proton-bound alkyl chloride dimers were considered as an intermediate [2b, 5], and  $(C_2H_5Cl)_2H^+$  ions were observed in the present work. Their metastable and collision-induced dissociations both involve  $HCl$  loss to produce  $(C_2H_5)_2Cl^+$ .

To produce diethyl chloronium ions that contain one labeled ethyl group, mixtures of  $C_2H_5Cl$  with the appropriate deuterium-labeled ethyl bromides were used. Theard and Hamill [2a] observed no ion-molecule reaction products in  $C_2H_5Cl$ - $C_2H_5Br$  mixtures, but we found significant yields of  $C_2H_5Cl^+Et^*$  ( $Et^*$  denotes a labeled ethyl group) and  $(C_2H_5Cl^+Et^*Br)^+$  ions in the mass spectra of  $C_2H_5Cl$ - $Et^*Br$  mixtures. The mixed dimers may originate from a molecular ion addition to the neutral molecules (reactions 6 and 7):

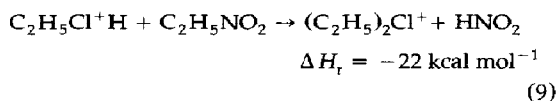
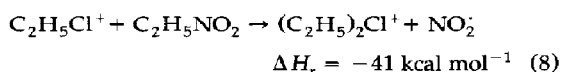


The MI mass spectra of the mixed ionized dimers  $(C_2H_5Cl^+Et^*Br)^+$  contained a peak due to  $Br^-$  loss, which indicates that these reactions produce at least part of the diethyl chloronium ions in the above mixtures. Note that the CID mass spectra (measured in the 3-FFR) of the labeled diethyl chloronium ions that originate from the *metastable* ionized dimers are the same as the spectra of ion-source-generated species and therefore we conclude that the same species are produced irrespective of their origin.

Note that the metastable ionized dimer only loses  $C_2H_5Cl$  by forming an  $Et^*Br^{++}$  ion. Moreover, the  $Et^*Br^{++}$  ions so produced showed no evidence for the loss of position of a deuterium label, for example, the CID mass spectrum of metastably generated

CD<sub>3</sub>CH<sub>2</sub>Br<sup>+</sup> ions displayed only CH<sub>2</sub>Br<sup>+</sup> fragments (no CHDBr<sup>+</sup> or CD<sub>2</sub>Br<sup>+</sup>). Thus there is no ethyl-group exchange between the halogen atoms in the mixed dimer ions, nor is there any H-D mixing within the ethyl group(s).

Nitroethane (and isotopomers) was also used in experiments with ethyl chloride because it is an excellent source of C<sub>2</sub>H<sub>5</sub><sup>+</sup> ions (base peak in the normal electron impact mass spectrum) and it has no molecular ion. It was therefore surprising to observe CH<sub>3</sub>CD<sub>2</sub>Cl<sup>+</sup>+C<sub>2</sub>H<sub>5</sub> ions from a mixture of CH<sub>3</sub>CD<sub>2</sub>NO<sub>2</sub> with C<sub>2</sub>H<sub>5</sub>Cl. The dimer (CH<sub>3</sub>CD<sub>2</sub>NO<sub>2</sub>+C<sub>2</sub>H<sub>5</sub>Cl)<sup>+</sup> and its proton-bound analog were *not* observed; these comprise reasonable intermediates for reactions 8 and 9, but the origin of the CH<sub>3</sub>CD<sub>2</sub>Cl<sup>+</sup>+C<sub>2</sub>H<sub>5</sub> ions remains uncertain:



Direct addition of CH<sub>3</sub>CD<sub>2</sub><sup>+</sup> to C<sub>2</sub>H<sub>5</sub>Cl cannot be ruled out.

Dissociation products of the metastable and collisionally activated diethyl chloronium ions together with their enthalpies and corresponding kinetic energy releases are listed in Table 1. The major metastable reaction is C<sub>2</sub>H<sub>6</sub> loss. It may produce ClCH<sub>2</sub>CH<sub>2</sub><sup>+</sup> and CH<sub>3</sub>CH<sup>+</sup>+Cl ions, whose heats of formation are close (200 and 198 kcal mol<sup>-1</sup>, respectively [20]). To characterize the structure of the C<sub>2</sub>H<sub>4</sub>Cl<sup>+</sup> ions formed by this reaction, the CID mass spectrum of these ions, generated from metastable (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl<sup>+</sup> in the 2-FFR, was measured in the 3-FFR. The resulting CID mass spectrum was very similar to that of the C<sub>2</sub>H<sub>4</sub>Cl<sup>+</sup> ion that originated from CH<sub>3</sub>CHClX [X = CH<sub>3</sub>, COOC<sub>2</sub>H<sub>5</sub> [21] and Br (Yan An and J. L. Holmes, in preparation)]; it had peaks corresponding to CCl<sup>+</sup>, CHCl<sup>+</sup> and, unlike the C<sub>2</sub>H<sub>4</sub>Cl<sup>+</sup> ion from ClCH<sub>2</sub>CH<sub>2</sub>X [X = OC<sub>6</sub>H<sub>5</sub>, COOC<sub>2</sub>H<sub>5</sub>, OH [21] and Br (Yan An and J. L. Holmes, in preparation)], only a weak signal at *m/z* 49, CH<sub>2</sub>Cl<sup>+</sup>. We therefore propose that this C<sub>2</sub>H<sub>6</sub> loss produces only CH<sub>3</sub>CH<sup>+</sup>+Cl ions following the transfer of an α-H atom from one ethyl group to the other.

**Table 1.** Decomposition of metastable (MI) and collisionally activated (CID) (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl<sup>+</sup> ions

Decomposition	ΔH <sub>f</sub> (kcal/mol)	Int. (%)		KER (meV)	
		MI	CID	MI	CID
C <sub>2</sub> H <sub>5</sub> ClH <sup>+</sup> +C <sub>2</sub> H <sub>4</sub>	30	0.7	59.4	5	25
C <sub>2</sub> H <sub>4</sub> Cl <sup>+</sup> +C <sub>2</sub> H <sub>6</sub>	25	74.0	9.1	13	20
C <sub>4</sub> H <sub>9</sub> <sup>+</sup> +HCl	28	0.8	1.5	36	a
C <sub>2</sub> H <sub>6</sub> <sup>+</sup> +C <sub>2</sub> H <sub>5</sub> Cl	36	24.5	30.0	8	16

<sup>a</sup> Not measured

Deuterium-labeled ions showed loss of positional identity of H-D atoms within the labeled ethyl group(s). The MI mass spectrum of C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>+CH<sub>2</sub>CD<sub>3</sub> displayed C<sub>2</sub>H<sub>3</sub>D<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>D, and C<sub>2</sub>H<sub>6</sub> loss (Table 2) forming C<sub>2</sub>H<sub>4</sub>Cl<sup>+</sup>, C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>Cl<sup>+</sup>, and C<sub>2</sub>HD<sub>3</sub>Cl<sup>+</sup> ions, respectively. The CID mass spectra of the latter two product ions (3-FFR experiments) showed both CHCl<sup>+</sup> and CCl<sup>+</sup> ions. Similar results were found for C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>+CD<sub>2</sub>CH<sub>3</sub> ions decomposing by C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>5</sub>D loss. These results together with the very close similarity between the MI mass spectra of C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>+CH<sub>2</sub>CD<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>+CHDCHD<sub>2</sub> ions unequivocally confirm that H-D mixing within each ethyl group (but not between the groups) precedes ethane loss. The C<sub>2</sub>H<sub>6</sub>-C<sub>2</sub>H<sub>5</sub>D loss ratios from C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>+C<sub>2</sub>H<sub>2</sub>D<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>+C<sub>2</sub>H<sub>3</sub>D<sub>2</sub> (47:53 and 65:35, respectively) are not far from the statistical values (40:60 and 60:40, respectively) which shows however, a small hydrogen isotope effect *k*<sub>H-D</sub> ≈ 1.3 (i.e., observed ratio:statistical ratio).

Ethyl cation formation is the second most abundant reaction of metastable (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl<sup>+</sup> ions. It is characterized by a small KER, appropriate for a simple bond cleavage that has little or no reverse activation energy barrier. Note that this simple bond cleavage is not the metastable ion fragmentation of lowest energy requirement (Table 1). It follows that the C<sub>2</sub>H<sub>6</sub> elimination must have an appreciable reverse energy barrier of up to approximately 10 kcal mol<sup>-1</sup>. It is also worth noting that the C<sub>2</sub>H<sub>6</sub> loss, unlike C<sub>2</sub>H<sub>5</sub>Cl loss, is *insensitive* to collision gas, which indicates that an intermediate structure, accessed via a barrier close to the dissociation limit, is involved in this reaction.

The MI mass spectra of the labeled species C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>+Et<sup>+</sup> show peaks due to both the labeled and unlabeled ethyl cations. In all cases the latter are more

**Table 2.** Neutral lost from metastable (MI) and collisionally activated (CID) labeled diethyl chloronium ions, C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>R (sum of intensities = 100)

R		C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>3</sub> D	C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	C <sub>2</sub> HD <sub>3</sub>	RH	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> D	HCl	DCI	C <sub>2</sub> H <sub>5</sub> Cl	RCI
CD <sub>2</sub> CH <sub>3</sub>	MI	1.8	—	< 1.8	—	29.0	< 20.8	11.1	0.9	a	14.1	21.1
	CID	28.6	8.2	< 16.1	—	1.1	< 1.1	1.1	2.2	0.2	21.4	18.6
CH <sub>2</sub> CD <sub>3</sub>	MI	3.4	—	< 1.7	< 1.7	22.6	< 15.8	< 18.1	0.6	a	13.3	26.3
	CID	30.4	—	< 11.4	< 9.8	1.0	< 1.0	< 1.0	2.0	0.3	23.6	20.9
CHDCHD <sub>2</sub>	MI	3.4	—	< 1.7	< 1.7	26.1	< 16.2	< 17.5	0.7	0.1	12.5	31.3
	CID	15.1	—	< 6.8	< 7.0	2.0	< 1.0	< 1.0	1.3	0.3	23.5	36.0

<sup>a</sup> Trace.

abundant. The neutral labeled ethyl chloride products were analyzed by CIDI mass spectrometry to investigate hydrogen atom mixing therein. The CIDI mass spectra of  $C_2H_5Cl^+CD_2CH_3$  and  $C_2H_5Cl^+CH_2CD_3$  show molecular ions of both unlabeled and labeled ethyl chlorides and their decomposition products; the simple C—C bond cleavage yielded peaks that correspond to  $CH_2Cl^+$ ,  $CHDCl^+$ , and  $CD_2Cl^+$  ions, again clearly indicating that a loss of a positional identity of H-D atoms has taken place before the metastable decomposition of the diethyl chloronium ions. Note that (for example) the molecular ion of  $CD_3CH_2Cl^{++}$  yields a CID mass spectrum that contains  $CCl^+$ ,  $CHCl^+$ ; and  $CH_2Cl^+$  only, which shows no mixing within ionized ethyl chloride that has insufficient energy to fragment.

Ethene loss from the metastable  $(C_2H_5)_2Cl^+$  ions is only a very minor reaction (Table 1), although its enthalpy is only 5 kcal mol<sup>-1</sup> higher than that for formation of  $CH_3CHCl^+ + C_2H_6$  and even lower than that for  $C_2H_5^+ + C_2H_5Cl$ . It follows that this reaction has a substantial energy barrier that is well above that for the simple bond cleavage. However, this ethene loss is the most collision-sensitive reaction (Table 1) and therefore, for the highest energy ions accessed by collision, the reaction may well be a simple bond cleavage in an ion of non-classical form, for example, 2. Such species would account also for the collision-induced formation of a nonclassical  $C_2H_5^+$  ion. The relative abundances of the CID fragment ions  $C_2H_5^+$  and  $C_2H_5Cl^+H$  (Table 1) are also in keeping with the relative proton affinities (PA) of the components of this hydrogen-bridged ion:  $PA(C_2H_4) = 162.6$  kcal mol<sup>-1</sup> [22] and  $PA(C_2H_5Cl) = 167$  kcal mol<sup>-1</sup> [5].

The kinetic energy releases that accompany the collision-induced  $C_2H_4$  and  $C_2H_5Cl$  losses are unremarkable and in spite of a significant reverse energy barrier, the KER for ethene loss is only 25 meV.

It is likely that the weak signal for loss of  $C_2H_4$  and HCl in the MI mass spectrum arises from residual collision-induced processes. For the minor loss of hydrogen chloride, both HCl and DCl eliminations were observed from the labelled species. As can be seen in Table 2, the level of H-D mixing in the collision-induced ethene loss is similar to that for metastable ethane loss, and therefore a similar isotope effect may be proposed.

### $(C_2H_5)_2Cl^+$ Ion, Structures

By analogy with the  $C_2H_5O^+H_2$  ion [15, 16], two ground-state forms for the diethyl chloronium ion must be considered: a classical and nonclassical species (1 and 2; RX =  $CH_3CH_2Cl$ ). The relative stabilities of the above ions are not known, but the following simplest explanations of the present results do not need that information. Our proposals are illustrated schematically in Figure 1. In this Figure the ground state for 2 is shown to be above that for 1, but only by analogy with

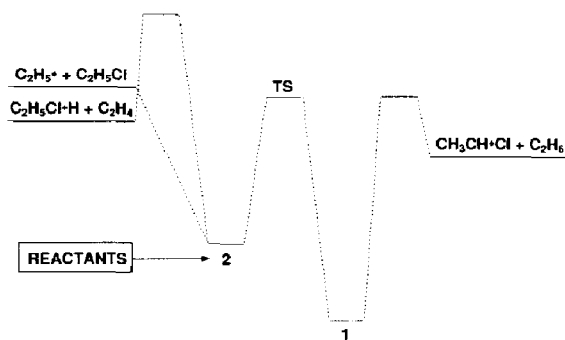
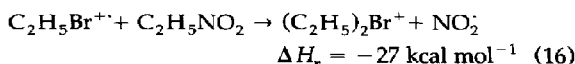
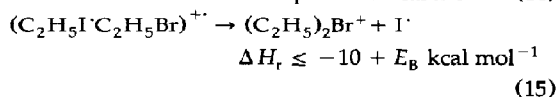
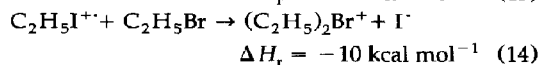
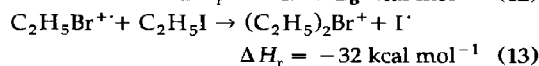
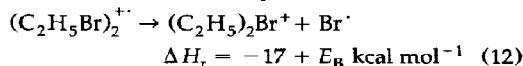
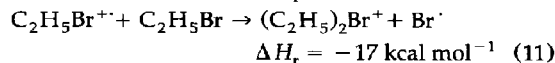
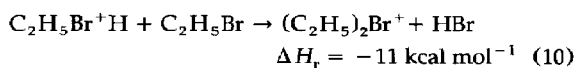


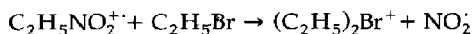
Figure 1. The energy diagram for  $(C_2H_5)_2Cl^+$  ion decomposition. (The relative ground-state energies of 2 and 1 are not known.)

the ethyl oxonium ion [16]. We propose that (1) the ion-molecule process that generates the diethyl chloronium ions produces a nonclassical (2) structure and (2) there is a high barrier separating 2 from 1. This barrier lies close to the dissociation limit for the (collision-insensitive) production of the  $CH_3CH^+Cl$  ion by a simple H transfer in the isomeric 1-type ion. The production of 2-type ions can account for the (complete) H-D mixing in each ethyl group, assuming a facile classical-nonclassical isomerization of each ethyl moiety within an ion of structure 2. This mixing must either be very fast for ions above the transition state or the nonclassical ions can mix H-D atoms in each ethyl group via another (unknown) intermediate that lies in a low potential well. Dissociations to  $C_2H_5^+$  and  $C_2H_5Cl^+H$  from 2 were discussed above.

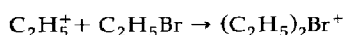
### $(C_2H_5)_2Br^+$ Ions

Diethyl bromonium ions were produced by ion-molecule reactions in the ionized vapors of ethyl bromide and its isotopomers or their mixtures with labeled and unlabeled ethyl iodide and nitroethane:





$$\Delta H_r = -40 \text{ kcal mol}^{-1} \quad (17)$$



$$\Delta H_r = -38 \text{ kcal mol}^{-1} \quad (18)$$

Some of these reactions, namely, reactions 10 and 11, have already been reported as the precursors for Et<sup>\*</sup>Br<sup>+</sup> [2a, 5]. However, we consider that reaction 10 is an unlikely source for (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Br<sup>+</sup> ions in our experimental conditions because of the low concentration of protonated ethyl bromide. An investigation of these reactions by ICR spectroscopy showed that bromine atoms from both reactants were present equally in the products [5], and therefore it can be proposed that reaction 11 involves formation of a symmetrical intermediate—the ionized ethyl bromide dimer. Formation of stable (C<sub>2</sub>H<sub>5</sub>Br)<sub>2</sub><sup>+</sup> in the gas phase has been observed by several authors [2a, 23]. In the present work the metastable and collisionally induced decomposition of (C<sub>2</sub>H<sub>5</sub>Br)<sub>2</sub><sup>+</sup> resulted in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Br<sup>+</sup> formation (reaction 12).

C<sub>2</sub>H<sub>5</sub>Br<sup>+</sup>Et<sup>\*</sup> ions also were observed in Et<sup>\*</sup>Br–C<sub>2</sub>H<sub>5</sub>X and C<sub>2</sub>H<sub>5</sub>Br–Et<sup>\*</sup>X (X = I, NO<sub>2</sub>) mixtures, where they originated from reactions 13–16. In the case of the ethyl bromide–ethyl iodide mixtures, formation of the mixed ionized dimers was observed. These dimers decomposed metastably and under collisional activation to yield C<sub>2</sub>H<sub>5</sub>Br<sup>+</sup>Et<sup>\*</sup>, reactions 13 and 14. Simple deuterium labeling experiments showed that there is no ethyl-group exchange between halogen atoms in the ionized dimers. MS<sup>3</sup> and CIDI experiments also clearly showed no H–D mixing within the ethyl groups, for example, collisionally activated CD<sub>3</sub>CH<sub>2</sub>I<sup>+</sup> ions and collisionally ionized CD<sub>3</sub>CH<sub>2</sub>Br, produced from metastable (CD<sub>3</sub>CH<sub>2</sub>I)<sup>+</sup>(C<sub>2</sub>H<sub>5</sub>Br)<sup>+</sup> and (C<sub>2</sub>H<sub>5</sub>I)(CD<sub>3</sub>CH<sub>2</sub>Br)<sup>+</sup>, respectively, did not yield any CHDX<sup>+</sup> or CD<sub>2</sub>X<sup>+</sup> ions.

Reaction 17 cannot be a source for diethyl bromonium ions in ethyl bromide–nitroethane mixtures, again because nitroethane has no stable molecular ion. Peaks that correspond to mixed ionized dimers (Et<sup>\*</sup>Br)<sup>+</sup>(Et<sup>\*</sup>NO<sub>2</sub>)<sup>+</sup> were present, but they did not decompose to form Et<sup>\*</sup>Br<sup>+</sup>. These observations lead us to propose that although direct ethyl cation addition to ethyl bromide (reaction 18) may occur, its efficiency is low compared with substitution reactions 11, 13, and 14.

The heat of formation of (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Br<sup>+</sup> is unknown, but it can be estimated from available proton, methyl, and ethyl cation affinities (see Appendix) as 163 kcal mol<sup>-1</sup>. Thus all the above reactions are exothermic and will lead to products that have excess internal energy. The enthalpies of reactions 12 and 15 could not be calculated because of the unknown binding energies

E<sub>B</sub> in the dimers, but it seems unlikely that they will be of sufficient magnitude to make the reaction endothermic.

The MI mass spectrum of (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Br<sup>+</sup> displays ions that correspond to C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> loss and C<sub>2</sub>H<sub>5</sub><sup>+</sup> ion formation (Table 3). The latter is a minor reaction, but it is characterized by the lowest KER.

That the ethane loss leads to CH<sub>3</sub>CHBr<sup>+</sup> and not CH<sub>2</sub>CH<sub>2</sub>Br<sup>+</sup> was shown from a comparison of the CID mass spectrum of the above ion, which originated from metastable (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Br<sup>+</sup>, with the CID mass spectra of CH<sub>3</sub>CH<sup>+</sup>Br [produced from CH<sub>3</sub>CHBr<sub>2</sub> (Yan An and J. L. Holmes, in preparation)] and C<sub>2</sub>H<sub>4</sub>Br<sup>+</sup> [produced from BrCH<sub>2</sub>CH<sub>2</sub>Br (Yan An and J. L. Holmes, in preparation)]. For the first two species only a trace signal due to CH<sub>2</sub>Br<sup>+</sup> ion was found, which indicates that they have the CH<sub>3</sub>CHBr<sup>+</sup> structure. Thus C<sub>2</sub>H<sub>6</sub> loss may result from a simple methylene hydrogen transfer from one ethyl group to the other in an ion of classical configuration.

The results will be discussed below with the aid of the energy diagram (Figure 2). This is similar to Figure 1, but the energy barriers have different relative magnitudes. Results of deuterium labeling experiments are given in Table 4. This table shows that the relative ion abundances do not depend on the origin of the ion. For example, the relative abundance of ions in the MI and CID mass spectra of C<sub>2</sub>H<sub>5</sub>Br<sup>+</sup>CD<sub>2</sub>CH<sub>3</sub> ions that originate from the C<sub>2</sub>H<sub>5</sub>Br–CH<sub>3</sub>CD<sub>2</sub>Br, C<sub>2</sub>H<sub>5</sub>I–CH<sub>3</sub>CD<sub>2</sub>Br, C<sub>2</sub>H<sub>5</sub>Br–CH<sub>3</sub>CD<sub>2</sub>I, C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>–CH<sub>3</sub>CD<sub>2</sub>Br, and C<sub>2</sub>H<sub>5</sub>Br–CH<sub>3</sub>CD<sub>2</sub>NO<sub>2</sub> mixtures are quantitatively similar. There is no hydrogen mixing between the two ethyl groups, as indicated, for example, by the MI mass spectrum of C<sub>2</sub>H<sub>5</sub>Br<sup>+</sup>C<sub>2</sub>D<sub>5</sub>, which shows C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub> and no C<sub>2</sub>H<sub>4–n</sub>D<sub>n</sub> (n = 1–3) loss, and C<sub>2</sub>H<sub>5</sub>D and C<sub>2</sub>D<sub>5</sub>H with no loss of C<sub>2</sub>H<sub>6–n</sub>D<sub>n</sub> (n = 2–4).

First, to extend discussion of the C<sub>2</sub>H<sub>6</sub> loss process, the labeling experiments show that H–D mixing precedes the fragmentation, but with an H–D isotope effect of approximately 1.5. MS<sup>3</sup> experiments on the labeled fragment CH<sub>3</sub>CH<sup>+</sup>Br ions generated from (CD<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>Br<sup>+</sup> and (CH<sub>3</sub>CD<sub>2</sub>)<sub>2</sub>Br<sup>+</sup> both show peaks that correspond to CHBr<sup>+</sup> and CDBr<sup>+</sup> in their CID mass spectra. Note that unlike this reaction for (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl<sup>+</sup> ions, the collision-induced ethane loss involved appreciably less H–D mixing, for example, C<sub>2</sub>H<sub>3</sub>D<sub>3</sub> loss is favored from both (CH<sub>3</sub>CD<sub>2</sub>)<sub>2</sub>Br<sup>+</sup> and

**Table 3.** Decomposition of metastable (MI) and collisionally activated (CID) (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Br<sup>+</sup> ions

Decomposition	ΔH <sub>r</sub> (kcal/mol)	Int. (%)		KER (meV)	
		MI	CID	MI	CID
C <sub>2</sub> H <sub>5</sub> Br <sup>+</sup> H + C <sub>2</sub> H <sub>4</sub>	36	57.9	56.7	16	17
CH <sub>3</sub> CHBr <sup>+</sup> + C <sub>2</sub> H <sub>6</sub>	31	39.3	4.9	17	18
C <sub>2</sub> H <sub>5</sub> Br <sup>+</sup> + C <sub>2</sub> H <sub>5</sub>	97	—	4.9	—	a
C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + C <sub>2</sub> H <sub>5</sub> Br	44	2.8	33.5	14	24

<sup>a</sup> Not measured.

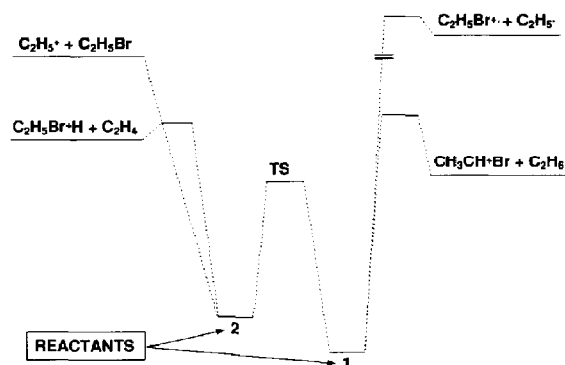


Figure 2. The energy diagram for  $(C_2H_5)_2Br^+$  ion decomposition. (The relative ground-state energies of 2 and 1 are not known.)

$(CD_3CH_2)_2Br^+$  relative to metastable ions. We propose, therefore, that at least some  $(C_2H_5)_2Br^+$  ions are produced that have classical ethyl group structures with unmixed H atoms.

A minor, but significant, collision-induced process generated  $C_2H_5Br^+$  ions (Table 3). These ions were transmitted from the 2-FFR to the 3-FFR and their CID mass spectrum was examined. For ethyl bromide ions that originate from collisionally excited  $(CD_3CH_2)_2Br^+$ , only  $CH_2Br^+$  fragment ions were observed (no  $CHDBr^+$  or  $CD_2Br^+$ ) and therefore for these ions no H-D mixing preceded their generation. This result emphasizes the presence of  $(C_2H_5)_2Br^+$  ions of classical structure. It remains to be decided whether there is evidence to show that a nonclassical ion is cogenerated. Note that the simplest explanation for H-D mixing involves equilibration between classical and nonclassical isomers.

The data for the ethene loss clearly show that hydrogen mixing occurs within each ethyl group. This is indicated by  $C_2HD_3$  loss from a  $CD_3CH_2$  group and  $C_2H_3D$  loss from a  $CH_3CD_2$  group (Table 4). That such mixing is complete can be concluded from the

similarity of the  $C_2H_2D_2-C_2HD_3$  loss ratios from metastable ions that contain  $CD_3CH_2$  and  $CHD_2CHD$  groups. For all partially deuterated ethyl radicals, the preferred loss of a more heavily deuterated ethene was observed, irrespective of the initial position of deuterium atom(s) and their number in the ethyl group. Thus the  $C_2H_3D-C_2H_4$  loss ratio from metastable  $CH_2DCH_2Br^+Et^+$  ions, the  $C_2H_2D_2-C_2H_3D$  loss ratio from  $CH_3CD_2Br^+Et^+$  ions, and the  $C_2HD_3-C_2H_2D_2$  loss ratios from  $CD_3CH_2Br^+Et^+$  and  $CHD_2CHDBr^+Et^+$  ions all exceeded the statistical values (80:20, 60:40 and 40:60, respectively). This can be explained by a hydrogen isotope effect, the magnitude of which is almost independent of the initial position of H and D atoms in the ethyl group(s) and varies from about 3 to 3.8. This isotope effect is substantially higher than the analogous value observed for diethyl chloronium ions (approximately 1.3), in keeping with the lower barrier for  $C_2H_4$  loss for the  $(C_2H_5)_2Br^+$  ions (cf. Figures 1 and 2).

For collisionally excited ions, the loss of more heavily deuterated ethenes is relatively smaller. Moreover the increase in the  $C_2H_3D-C_2H_2D_2$  loss ratio from  $(CH_3CD_2)_2Br^+$  ions indicates *no* increase in any simple  $\beta$ -hydrogen shift in ions of classical structure—if it takes place at all. Note too that for the collisionally excited processes the isotope effect is diminished ( $k_{H-D} = 1.3-2.0$ ).

The reaction that generates  $C_2H_5^+$  ions also can be used to probe H-D mixing in the  $(C_2H_5)_2Br^+$  precursor by means of the CIDI mass spectrum of the neutral (labeled)  $C_2H_5Br$ . For example,  $(CD_3CH_2)_2Br^+$  ions gave a CIDI mass spectrum that contained  $CH_2Br^+$ ,  $CHDBr^+$ , and  $CD_2Br^+$  ions, which clearly indicates that H-D mixing had taken place.

We propose that in this system, both the classical and nonclassical  $(C_2H_5)_2Br^+$  ions are generated, although there is no conclusive evidence for the latter species. However, if it is *not* generated, special kinetic arguments concerning H-D mixing in excited ions of classical structure have to be imposed, that is, all

Table 4. Neutral loss from metastable (MI) and collisionally activated (CID) labeled diethyl bromonium ions,  $RBr^+R'$  (sum of intensities = 100)

R	R'		$C_2H_4$	$C_2H_3D$	$C_2H_2D_2$	$C_2HD_3$	$C_2D_4$	RH	RD	R'H	R'D	RBr	R'Br
$C_2H_5$	$CH_2CH_2D$	MI	42	30	—	—	—	12	< 1	16	—	a	a
$C_2H_5$	$C_2D_5$	MI	81	—	—	—	6	—	< 1	9	—	1	3
$CH_2CH_2D$	$CH_2CH_2D$	MI	5	71	—	—	—	20	4	b	b	a	a
$CD_2CH_3$	$CD_2CH_3$	MI	—	13	67	—	—	12	6	b	b	2	b
		CID	—	13	37	—	—	3	2	b	b	41	b
$CH_2CD_3$	$CH_2CD_3$	MI	—	—	28	56	—	5	5	b	b	6	b
		CID	—	—	22	11	—	5	1	b	b	53	b
$CHDCHD_2$	$CHDCHD_2$	MI	—	—	24	53	—	8	3	b	b	7	b
		CID	—	—	18	19	—	3	2	b	b	54	b
$CD_2CH_3$	$C_2D_5$	MI	—	16	53	—	21	—	5	3	2	a	a
$CHDCHD_2$	$C_2D_5$	MI	—	—	24	41	28	—	3	2	2	a	a
$CH_2CD_3$	$C_2D_5$	MI	—	—	15	29	36	—	5	2	4	4	5
$C_2D_5$	$C_2D_5$	MI	—	—	—	—	94	—	6	—	b	a	a

<sup>a</sup> Not measured.

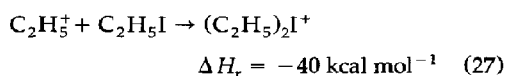
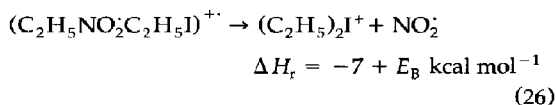
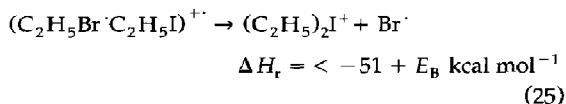
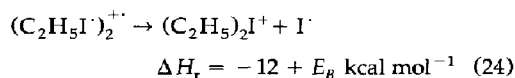
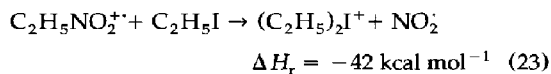
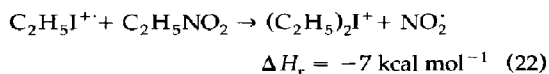
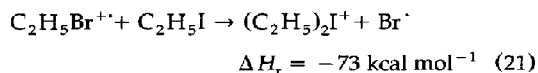
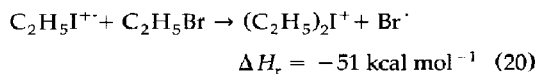
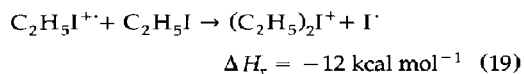
<sup>b</sup> R' = R.

classical ions with sufficient energy to decompose by C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>5</sub>Br losses must undergo very fast reversible isomerization with the nonclassical ion. It is the latter species that most probably yields the C<sub>2</sub>H<sub>5</sub>Br<sup>+</sup>H and (nonclassical) C<sub>2</sub>H<sub>5</sub><sup>+</sup> ions.

### CH<sub>3</sub>CH<sub>2</sub>I<sup>+</sup> + CH<sub>2</sub>CH<sub>3</sub> Ions

Diethyl iodonium ions (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> are always present in the chemical ionization mass spectrum of ethyl iodide. To produce symmetrically labeled species Et<sub>2</sub><sup>+</sup>I<sup>+</sup>, the appropriately deuterated ethyl iodides were used. Unsymmetrical ions C<sub>2</sub>H<sub>5</sub>I<sup>+</sup>Et\* were generated from mixtures of ethyl iodides or ethyl iodide with ethyl bromide, nitroethane, diethyl carbonate, and 3-pentanone; one of the components was labeled.

Possible reactions that leads to diethyl iodonium ion formation, together with their enthalpies are.



In these calculations  $\Delta H_r^\circ[(\text{C}_2\text{H}_5)_2\text{I}^+] = 174 \text{ kcal mol}^{-1}$  was used (see Appendix). The enthalpies of reactions 24-26 could not be calculated, again because of unknown binding energies  $E_B$  in the ionized dimers. All other reactions (reactions 19-23) are exothermic relative to the ground state of the (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> ion.

Reactions 19-23 are molecular ion-molecule reactions with elimination of an atom or a radical. Reaction 23, which involves ionized nitroethane, can be ruled

out (see above). Reactions 19-22 may involve formation of an intermediate adduct ion. As has been reported elsewhere [23] the ionized ethyl iodide dimer also was observed in the mass spectrum of C<sub>2</sub>H<sub>5</sub>I. Metastable ion and collision-induced dissociations of these dimers involve I atom loss that results in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup>. Note that the dissociation characteristics of the latter ions (and their labeled analogs) were independent of their origin, for example, for (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> from the ion source, or produced from metastable dimer ions. Thus (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> is a common intermediate for the formation of (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> ions in the chemical ionization mass spectra of ethyl iodide, its labeled analogs, and their mixtures. It should be noted that no hydrogen atom exchange was observed in the ionized ethyl iodide dimers, indicated by the CID mass spectra of labeled ethyl iodide molecular ions that metastably originate from (Et\*<sub>2</sub>I)<sup>++</sup>. For example, collisional activation of CD<sub>3</sub>CH<sub>2</sub>I<sup>++</sup> generated from (CD<sub>3</sub>CH<sub>2</sub>)<sub>2</sub><sup>+</sup> showed CH<sub>2</sub>I<sup>+</sup> and no CHDI<sup>+</sup> or CD<sub>2</sub>I<sup>+</sup> ions.

(C<sub>2</sub>H<sub>5</sub>Br<sup>+</sup>C<sub>2</sub>H<sub>5</sub>I)<sup>++</sup> gave rise to only a very weak (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> ion under collisional activation, making reaction 25 an unlikely source for diethyl iodonium ions. Adduct ions (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub><sup>+</sup>C<sub>2</sub>H<sub>5</sub>I)<sup>++</sup> were found in the mass spectra of ethyl iodide-nitroethane mixtures, but they did not decompose to (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> in either their MI or CID mass spectra, which rules out reaction 26.

A study of reaction 27 as a potential source for (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> was of special interest because stable adduct formation between the ethyl cation and ethyl iodide has not been reported before and by analogy with the C<sub>2</sub>H<sub>5</sub><sup>+</sup> ion reactivity toward other ethyl halides (see above), hydrogen transfer that results in protonated ethyl iodide would be expected. C<sub>2</sub>H<sub>5</sub>I<sup>+</sup>Et\* ions appeared in the mass spectra of ethyl iodide mixtures with Et\*NO<sub>2</sub> and Et\*<sub>2</sub>CO, and for Et\*I mixed with C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CO, and (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>CO, the nitro, keto, and carbonate derivatives are good sources for the C<sub>2</sub>H<sub>5</sub><sup>+</sup> (or Et\*<sup>+</sup>) cations. The yields of C<sub>2</sub>H<sub>5</sub>I<sup>+</sup>Et\* ions were low, but, as will be shown, the dissociation characteristics of these ions that originates from the C<sub>2</sub>H<sub>5</sub>I-Et\*NO<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>I-Et\*<sub>2</sub>CO mixtures were quantitatively different from the same ions formed in the mass spectra of mixed ethyl halides and from C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>-Et\*I mixtures. These results allow us to consider reaction 27 as a possible source for diethyl iodonium ions. Its efficiency, however, is much lower than, for example, that of reaction 19.

In summary, diethyl iodonium ions were produced from a variety of molecular ion-molecule reactions, some of which involved formation of intermediate dimer ions. Direct addition of the ethyl cation to ethyl iodide can also occur. Note that effective stabilization *must* precede the transmission of (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> ions generated by reactions 20, 21, and 27 to the 2-FFR; otherwise their MI mass spectra would show C<sub>2</sub>H<sub>4</sub>I<sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> ions in addition to C<sub>2</sub>H<sub>6</sub>I<sup>+</sup> (for the energy requirements, see Table 5 and the discussion below).



**Table 5.** Decomposition of metastable (MI) and collisionally activated (CID)  $(C_2H_5)_2I^+$  ions

Decomposition	$\Delta H_f$ (kcal/mol <sup>-1</sup> )	Int. (%)		KER (meV)	
		MI	CID	MI	CID
$C_2H_5I^+ + H + C_2H_4$	40	100	88.1	14	19
$CH_3CHI^+ + C_2H_6$	33	—	2.7	—	87
$C_2H_5I^+ + C_2H_5$	70	—	6.4	—	68
$CH_2I^+ + (C_3H_8)^a$	59	—	0.6	—	b
$I^+ + (C_4H_{10})^c$	75	—	1.1	—	b
$C_2H_5^+ + C_2H_5I$	53	—	0.7	—	42
$C_2H_3^+ + C_2H_5I + H_2$	103	—	0.1	—	b

<sup>a</sup> For  $C_3H_8$  = propane.<sup>b</sup> Not measured.<sup>c</sup> For  $C_4H_{10}$  = butane.

This stabilization may involve removal of the excess internal energy via the halogen atom lost in reactions 20 and 21 or by collisions with neutral molecules in the ion source.

The MI and CID mass spectra of the  $(C_2H_5)_2I^+$  ion together with reaction enthalpies and corresponding kinetic energy releases are shown in Table 5. Ethene loss is the only fragmentation of metastable ions. The accompanying kinetic energy release is small. This reaction is also the major collision-induced dissociation.

Loss of alkane (ethane) is the reaction of lowest energy requirement, but it is not a metastable ion fragmentation and is only a weak peak in the CID mass spectrum (Table 5). This process must, therefore, have a high energy barrier, which is supported by the high  $T_{0.5}$  value. Ethane loss may result in formation of  $CH_2CH_2I^+$  or the  $CH_3CHI^+$  ion; the latter is a reaction of higher exothermicity. (The heat of formation of  $ICH_2CH_2^+$  ion has been determined experimentally as 212 kcal mol<sup>-1</sup> [20]. Our calculations by the MNDO method predict that the stability of  $CH_3CH^+I$  must be approximately 1.5 kcal mol<sup>-1</sup> lower than that of  $CH_2CH_2I^+$ , whose ground state is a cyclic iodonium ion.) The low abundance of the fragment ion did not, however, allow the characterization of the  $C_2H_4I^+$  ions that originate from  $(C_2H_5)_2I^+$  by their CID mass spectrum. Collisional activation of  $(CD_3CH_2)_2I^+$ , however, results in  $C_2H_3D_3$  loss, and a peak that corresponds to  $C_2H_2D_4$  loss was not found. This result indicates that no significant H-D mixing precedes ethane loss and has been taken (as discussed above) as evidence for the classical structure.

The other collision-induced dissociations of  $(C_2H_5)_2I^+$ , their energies, and kinetic energy releases are listed in Table 5. Simple I— $C_2H_5$  bond cleavage leads to  $C_2H_5^+ + C_2H_5I$ , and  $C_2H_5I^+ + C_2H_5$ . Even though the latter reaction is less endothermic, the  $C_2H_5I^+$  ion is more abundant than  $C_2H_5^+$  in the CID mass spectrum. If the reactions involved similar transition states it would be expected that the process of lower energy would be accompanied by a higher KER. Table 5 shows, however, the opposite result; the reaction of lower endothermicity shows the lower  $T_{0.5}$

value. We propose that formation of  $C_2H_5^+$  and  $C_2H_5I^+$  involves different transition states, possibly related to isomeric classical and non-classical structures of diethyl iodonium ions (1 and 2;  $RX = C_2H_5I$ ). MS<sup>3</sup> experiments with labeled ethyl iodides that originate from collisionally activated  $Et_2^+I^+$  ions showed no H-D mixing, again in keeping with a classical type ion. Note also that the CID mass spectra of the neutral labeled  $C_2H_5I$  from collisionally activated, labeled  $(C_2H_5)_2I^+$  did not show any significant H-D mixing therein. The latter result may indicate that the nonclassical form of the  $(C_2H_5)_2I^+$  ions formed by collisional excitation of its classical isomer is not stable and dissociates rather than undergoing reverse isomerization.

Tables 6-8 show the results of labeling experiments for the loss of ethene from metastable and collisionally activated  $(C_2H_5)_2I^+$  ions. The following conclusions can be drawn for metastable ions.

1. There is no H-D mixing between the ethyl groups. For example, the MI mass spectrum of  $C_2H_5I^+C_2D_5$  shows only loss of  $C_2H_4$  and  $C_2D_4$  (no  $C_2H_3D$ ,  $C_2H_2D_2$  or  $C_2HD_3$ ).
2. Loss of ethene is favored from the less deuterated ethyl group, which indicates a secondary isotope effect. This preference rises from 1.3 (for  $CH_3CD_2I^+C_2H_5$ ) to 3.1 (for  $CD_3CH_2I^+C_2H_5$ ) to 4.5 (for  $C_2D_5I^+C_2H_5$ ), and falls again for  $CH_3CD_2I^+C_2D_5$  (2.8) and  $CD_3CH_2I^+C_2D_5$  (1.5).
3. H-D positional interchange takes place within each ethyl group and apparently reaches random statistical values at long times (Table 8) for an ethyl group that contains  $CD_3CH_2$  but not for a  $CH_3CD_2$  group.
4. Ions that originate from mixtures of labeled  $C_2H_5NO_2$  or  $(C_2H_5)_2CO$  with unlabeled  $C_2H_5I$  show reduced  $C_2H_2D_2$  loss abundances compared with ions produced from the other mixtures, including that of  $C_2H_5NO_2$  with  $Et^+I$ .

Decomposition of metastable  $CH_3CD_2I^+Et^+$  ions may be reconciled with complete H-D mixing in the ethyl group before ethene loss with an isotope effect ( $k_{H-D} > 4$ ) in favor of hydrogen over deuterium migration to the iodine atom, which results in more deuterated ethene loss. The  $C_2H_3D-C_2H_2D_2$  ratio from  $CH_3CD_2I^+Et^+$  does not show any significant dependence on ion lifetime (Table 8), which indicates that H-D mixing is complete in less than 15  $\mu s$  (see Table 8).

The data for the  $CD_3CH_2I^+Et^+$  ion again show that hydrogen mixing takes place, as indicated by  $C_2HD_3$  loss. The  $C_2H_2D_2-C_2HD_3$  loss ratio exceeds the statistical value (60:40) for most of the ions listed in Table 7. The degree of deuterium atom migration decreases as the ion lifetime increases (Table 8) and reaches the statistical value for ions with lifetimes approximately 30  $\mu s$ . For short-lived metastable or collisionally activated ions, a direct one-step ethene loss via a  $\beta$ -deuterium shift competes with H-D mixing.

**Table 6.** The deuterium content in the ethene lost from metastable (MI) and collisionally activated (CID)  $CH_3CD_2IEt^+$  and  $(CH_3CD_2)_2I^+$  ions<sup>a</sup>

Ion		$-C_2H_4$	$-C_2H_3D$	$-C_2H_2D_2$
$(CH_3CD_2)_2I^+$ from	MI	—	13	87
$CH_3CD_2I$	CID	—	13	87
$CH_3CD_2I^+Et$ from	MI	58	6 (14)	36 (86)
$CH_3CD_2I + C_2H_5I$	CID	53	6 (13)	41 (87)
$CH_3CD_2I^+Et$ from	MI	56	6 (12)	38 (88)
$CH_3CD_2I + C_2H_5Br$	CID	51	5 (10)	44 (90)
$CH_3CD_2I^+Et$ from	MI	60	6 (14)	34 (86)
$CH_3CD_2Br + C_2H_5I$	CID	52	5 (10)	43 (90)
$CH_3CD_2I^+Et$ from	MI	61	5 (12)	34 (88)
$CH_3CD_2I + C_2H_5NO_2$	CID	51	4 (8)	47 (92)
$CH_3CD_2I^+Et$ from	MI	62	5 (14)	33 (86)
$CH_3CD_2I + (C_2H_5O)_2CO$	CID	52	6 (10)	42 (90)
$CH_3CD_2I^+Et$ from	MI	58	9 (19)	33 (81)
$CH_3CD_2NO_2 + C_2H_5I$	CID	52	7 (14)	41 (86)
$CH_3CD_2I^+Et$ from	MI	61	8 (21)	31 (79)
$(CH_3CD_2)CO + C_2H_5I$	CID	51	11 (21)	38 (79)

<sup>a</sup>  $C_2H_3D/C_2H_2D_2$  loss ratios are given in parentheses.**Table 7.** The deuterium content in the ethene lost from metastable (MI) and collisionally activated (CID)  $C_2H_2D_3I^+C_2H_5$  and  $(C_2H_2D_3)_2I^+$  ions<sup>a</sup>

Ion		$-C_2H_4$	$-C_2H_2D_2$	$-C_2HD_3$
$(CD_3CH_2)_2I^+$ from	MI	—	67	33
$CD_3CH_2I$	CID	—	72	28
$CD_3CH_2I^+Et$ from	MI	74	17 (67)	9 (33)
$CD_3CH_2I + C_2H_5I$	CID <sup>b</sup>	—	(76)	(24)
$CD_3CH_2I^+Et$ from	MI	75	16 (65)	9 (35)
$CD_3CH_2Br + C_2H_5I$	CID	62	26 (69)	12 (31)
$CD_3CH_2I^+Et$ from	MI	73	18 (67)	9 (33)
$CD_3CH_2I + C_2H_5Br$	CID	56	33 (76)	11 (24)
$CD_3CH_2I^+Et$ from	MI	76	17 (67)	7 (33)
$CD_3CH_2I + C_2H_5NO_2$	CID	55	32 (70)	13 (30)
$CD_3CH_2I^+Et$ from	MI	75	16 (65)	9 (35)
$CD_3CH_2I + (C_2H_5O)_2CO$	CID	56	31 (71)	13 (29)
$CD_3CH_2I^+Et$ from	MI	72	15 (54)	13 (46)
$CD_3CH_2NO_2 + C_2H_5I$	CID	55	31 (67)	15 (33)
$(CHD_2CHD)_2I^+$ from	MI	—	40	60
$CHD_2CHDBr + C_2H_5I$	CID	—	49	51
$CHD_2CHDI^+Et$ from	MI	58	15 (38)	27 (62)
$CHD_2CHDBr + C_2H_5I$	CID	53	24 (51)	23 (49)
$CHD_2CHDI^+Et$ from	MI	69	11 (34)	20 (66)
$CHD_2CHDNO_2 + C_2H_5I$	CID	54	23 (51)	23 (49)

<sup>a</sup>  $C_2H_2D_2/C_2HD_3$  ratios are given in parentheses.<sup>b</sup> Only  $C_2H_2D_2/C_2HD_3$  ratio has been measured.

Diethyl iodonium ions that contain  $CHDCHD_2$  group(s) do not display the same behavior as isotopomeric  $CD_3CH_2$  containing ions, the former show a lower  $C_2H_2D_2-C_2HD_3$  loss ratio (Table 7). This behavior is significantly different from the chloro and bromo analogs (see above). The decomposition of labeled  $(C_2H_5)_2I^+$  can be described as the combination of an initial H or D transfer from the  $\beta$ -position of the ethyl group. Hydrogen atom transfer, by analogy with  $CH_3CD_2I^+Et^*$  ions, leads to a  $C_2H_2D_2/C_2HD_3$  loss ratio of approximately 13:87, whereas D migration is expected to lead to 67% of  $C_2H_2D_2$  and 33% of  $C_2HD_3$  loss. Combination of these two values in a 1:1

ratio gives the observed  $C_2H_2D_2-C_2HD_3$  loss ratio (40:60) from  $(CHD_2CHD)_2I^+$ . Taking into account that one hydrogen and two deuterium atoms are able to migrate from the  $CHD_2$  group, the hydrogen isotope effect ( $\beta$ -H versus  $\beta$ -D migration) will be approximately 2, which is comparable with the secondary isotope effect discussed above.

The MI mass spectra of  $C_2H_5I^+Et^*$  ions that originate from the  $C_2H_5I-Et^*NO_2$  and  $C_2H_5I-Et^*_2CO$  mixtures show reduced  $C_2H_2D_2$  abundances compared with other ions, including those that originate from mixtures of the labeled ethyl iodide with unlabeled nitroethane (Tables 6 and 7). This can be explained by

**Table 8.** The deuterium content in the ethene lost from metastable  $(CD_3CH_2)_2I^+$  and  $CD_3CH_2I^+Et$  and  $(CH_3CD_2)_2I^+$  ions vs. ion life times ( $\tau$ ,  $\mu s$ )

ion	$\tau$	$-C_2H_4$	$-C_2H_3D$	$-C_2H_2D_2$	$-C_2HD_3$
$(CD_3CH_2)_2I^+$	2 <sup>b</sup>	—	—	75	25
	15 <sup>c</sup>	—	—	67	33
	30 <sup>d</sup>	—	—	59	41
$CD_3CH_2I^+Et$	15 <sup>c</sup>	74	—	17 (67)	8 (33)
	30 <sup>d</sup>	77	—	14 (61)	9 (39)
$(CH_3CD_2)_2I^+$	15 <sup>c</sup>	—	15	85	—
	30 <sup>d</sup>	—	11	89	—

<sup>a</sup> For ions produced by ion molecule reactions in  $CD_3CH_2I$ ,  $CH_3CD_2I$  or  $CD_3CH_2I-C_2H_5I$  mixture.

<sup>b</sup> First field free region of MS902 mass spectrometer.

<sup>c</sup> Second field free region of ZAB-2F mass spectrometer.

<sup>d</sup> Third field free region of ZAB-2F mass spectrometer.

the two origins for  $(C_2H_5)_2I^+$  ions: the molecular ion-molecule reactions produce them via an intermediate adduct in which no H-D mixing takes place. However,  $C_2H_5^+$  undergoes facile H-D mixing at a low internal energy [14] and therefore adduct ions from labeled  $C_2H_5^+$  and unlabeled  $C_2H_5I$  will contain an ethyl group with fully (or partially) mixed H-D atoms.

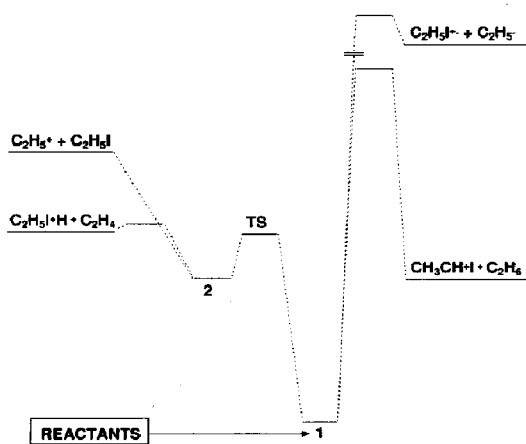
The effect of collisional activation on the decomposition of  $CH_3CD_2I^+Et^*$  and  $C_2H_2D_3I^+Et^*$  ions, unlike their bromonium analog, is the same (Tables 6 and 7), and results in increased  $C_2H_2D_2$  loss relative to  $C_2H_3D$  and  $C_2HD_3$ , respectively, which is associated with ethene loss via a simple  $\beta$ -H or  $\beta$ -D migration.

The  $(C_2H_5)_2I^+$  results can be summarized in conjunction with the energy diagram (Figure 3) and explained by invoking the formation of a classical  $(C_2H_5)_2I^+$  ion from the dimer association reaction. We suggest that the stability of this 1-type ion is greater for iodine than for the other halides, relative to the nonclassical ion 2. The latter may well be formed in the addition of an ethyl cation to ethyl iodide, although we cannot rule out that the reaction cogenerates 1-type ions. The collision-induced dissociation experiments

not only identify 1-type ions, but also show that H-D mixing via 2 is less facile than for the other diethyl halonium analogs. For this reason a shallower well is also shown for ion 2 in Figure 3.

## Appendix

A number of methyl and ethyl cation affinities (MCA and ECA) are known, although only a few have been directly measured [5-7, 19]. From the proton affinity (PA) values for the methyl and ethyl halides [5], the MCA and ECA for the hydrogen halides can be calculated and these are shown in Table 9. Direct experimental values for the MCA of HCl and HBr have been reported (55.1 and 61.2 kcal mol<sup>-1</sup> [7] and 51.7 and 55.4 [6], respectively). We have not included the direct MCA values in Table 9 because the analogous ECA values have not been determined. From the data in Table 9 the mean value for MCA(HX)-ECA(HX) is  $32 \pm 2$  kcal mol<sup>-1</sup>. The MCA of  $CH_3Cl$  and  $CH_3Br$  have been determined experimentally as 62 and 63.3 kcal mol<sup>-1</sup> [6] and the MCA of  $CH_3I$  was estimated from a plot of PA values for  $CH_3X$  ( $X = F, Cl, Br$ ) against their MCA values. The good straight line that resulted gave an interpolated value of 65.2 kcal mol<sup>-1</sup> for the MCA of methyl iodide. By using the above difference between MCA and ECA for the halogen acids, ECA values for  $CH_3Cl$ ,  $CH_3Br$ , and  $CH_3I$  can be estimated (Table 10). This permits the estimation of heats of formation of  $C_2H_5X^+CH_3$ , and hence MCA values for ethyl halides (Table 10). We propose that the difference between the MCA values for the methyl and ethyl halides will be reproduced in the ECA values for



**Figure 3.** The energy diagram for  $(C_2H_5)_2I^+$  ion decomposition.

**Table 9<sup>a</sup>**

RX	PA <sup>b</sup>	MCA(HX)	ECA(HX)	MCA(HX)-ECA(HX)
$CH_3Cl$	160	53		31
$C_2H_5Cl$	167		22	
$CH_3Br$	163	58		32
$C_2H_5Br$	170		26	
$CH_3I$	170	67		34
$C_2H_5I$	175		33	

<sup>a</sup> All values in kilocalories per mole.

<sup>b</sup> From ref. 5.

Table 10<sup>a</sup>

RX	MCA	ECA	$\Delta_f H_f^\circ(\text{RX}^+ \text{C}_2\text{H}_5)$
CH <sub>3</sub> Cl	62 <sup>b</sup>	30 ± 2	166
CH <sub>3</sub> Br	63 <sup>b</sup>	31 ± 2	176
CH <sub>3</sub> I	65	33 ± 2	187
C <sub>2</sub> H <sub>5</sub> Cl	68 ± 2	36 ± 2	153
C <sub>2</sub> H <sub>5</sub> Br	70 ± 2	38 ± 2	163
C <sub>2</sub> H <sub>5</sub> I	72 ± 2	40 ± 2	174

<sup>a</sup>All values in kilocalories per mole.<sup>b</sup>From ref. 6.

the same molecules, that is, giving the values shown in Table 10. From these results and assumptions, the  $\Delta H_f^\circ$  values for the diethyl halonium ions were derived. Note that our estimated heats of formation of C<sub>2</sub>H<sub>5</sub>Cl<sup>+</sup>CH<sub>3</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl<sup>+</sup> are in very satisfactory agreement with those chosen by Mathews and Stone [3w] (164 and 155 kcal mol<sup>-1</sup>, respectively).

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