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Stabilities of Isomeric Halonium Ions $C_2H_4X^+$ (X = Cl, Br) by Photoionization Mass Spectrometry and Ion Cyclotron Resonance Spectroscopy. General Considerations of the Relative Stabilities of Cyclic and Acyclic Isomeric Onium Ions

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Abstract: At least two noninterconverting structural isomers of the halonium ions $C_2H_4X^+$ (X = Cl, Br) are shown to exist in the gas phase. Threshold measurements of their formation through halide loss in the photoionization and fragmentation of corresponding dihaloethanes yield enthalpies of formation for these species. For X = Cl, the cyclic halonium ion is 5.6 kcal/mol less stable than the acyclic species CH_3CHCl^+. These stabilities are reversed for X = Br, with the cyclic isomer being more stable by 1.4 kcal/mol. In addition, relative stabilities of a larger class of onium ions are inferred from ion cyclotron resonance studies of exchange reactions between $C_2H_4X^+$ and HY to give $C_2H_4Y^+$ and HX (X, Y = Cl, Br, OH, SH, NH_2, PH_2). From the preferred direction of these processes, stability is inferred to increase in the order $X = OH < Cl < Br < SH, PH_2 < NH_2$ for the cyclic onium ions and $X = Cl < Br < SH, PH_2 < OH < NH_2$ for their acyclic isomers.

Introduction

The study of chemical reaction dynamics abounds with hypothetical intermediates which are convenient constructs based more on intuition than fact. With structures and properties inferred from related stable molecules and theoretical calculations, these species justify a myriad of observed kinetic phenomena. More recently, however, development of sophisticated instrumentation and novel experimental conditions have permitted many of these transients to be observed and characterized directly. For example, Roberts and Kimball[2] in 1937 proposed a cyclic bromonium ion intermediate to account for observed trans stereospecificity in addition of bromine to alkenes. Halonium ion intermediates have been suggested by other workers also.[3,4] In recent years these species have been investigated in both liquid and gas phase by a variety of techniques, including nuclear magnetic resonance,[5,6] ion cyclotron resonance (ICR),[7,8] and conventional mass spectrometry.[9-13] Theoretical studies have also been reported.[14,15] Among the more interesting questions addressed by these studies are considerations of the existence and relative stabilities of structural isomers of onium ions.

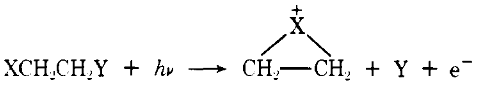
Several means exist to compare the stabilities of isomeric and congeneric onium ions. In the case of structural isomers, relative stabilities can be inferred directly from heats of formation. Halide and hydride affinities defined by

$$R^+ + X^- \rightarrow RX \qquad \Delta H^\circ = -A_{X^-} \tag{1}$$

(where X^- = halide ion or H^-) are also useful for comparing ion stabilities. Using eq 1 the stabilities of onium ions (as Lewis acids) can be compared with a common reference base. Relative stabilities can be inferred from studies of halide and hydride transfer reactions as generalized in the equation

$$R_1X + R_2^+ \rightleftharpoons R_2X + R_1^+ \tag{2}$$

In the present study we report detailed investigations of several small halonium ions $C_2H_4X^+$ (X = Cl, Br). Heats of formation are determined from photoionization mass spectrometric (PIMS) threshold measurements of reactions 3 and 4. Further, experiments are discussed that demonstrate the



$$XCH_2CH_2Y + h\nu \longrightarrow \overset{+}{X}(CH_2{-}CH_2) + Y + e^- \tag{3}$$

$$CH_3CHXY + h\nu \longrightarrow CH_3CHX^+ + Y + e^- \tag{4}$$

existence of two unique structural isomers, assumed to be the acyclic and cyclic species I and II, which yield different reaction products in mixtures containing NH_3. The isomers do not

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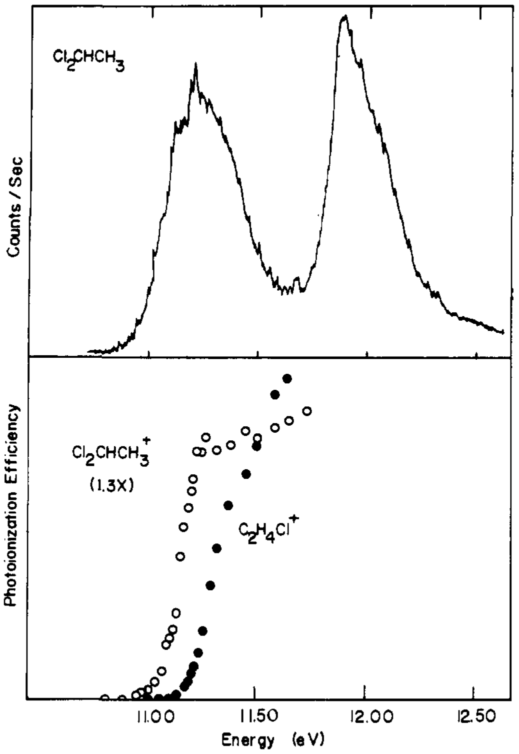
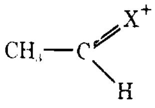


Figure 1. He I photoelectron spectrum of 1,1-dichloroethane between 10.5 and 12.5 eV and photoionization efficiency curves for $Cl_2CHCH_3^+$ and $C_2H_4Cl^+$ ions in Cl_2CHCH_3.



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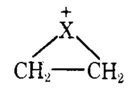
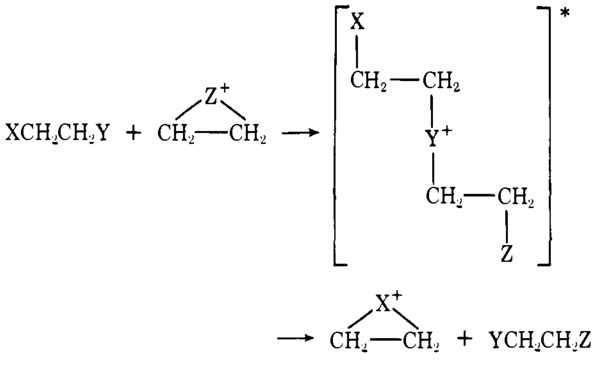


II

readily interconvert for X = Cl and Br once each is generated by electron impact and fragmentation of a specific dihaloethane neutral.

In addition, relative stabilities of a wider range of small onium ions I, II (S = Cl, Br, OH, SH, NH_2, and PH_2) are compared by examining the preferred direction of reactions 5, 6, 7, and 8 using ion cyclotron resonance spectroscopy.



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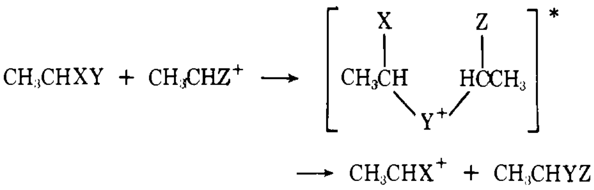
Experimental Section

The photoionization instrumentation used for these studies has been described in detail.[16,17] The hydrogen many-line spectrum was employed as the light source for this work. The monochromator was set for a resolution of 2 Å. Measurements were made solely at spectral maxima to minimize interference due to scattered light. Sample pressures were typically 2×10^{-4} Torr. To eliminate ion-molecule reactions at these pressures, the repeller voltage was maintained at 0.7 V positive with respect to the ionization chamber, yielding an ion residence time of 10 μs.



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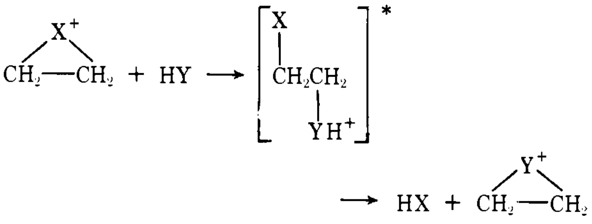

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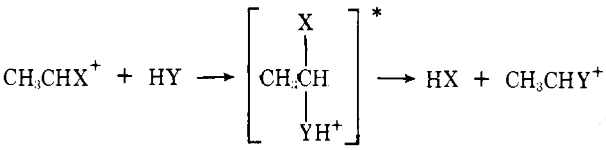

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ICR instrumentation and techniques used in these studies have been previously described in detail.[18-20] Most work was carried out at electron energies of 20 and 70 eV. Data reported for both ICR and PIMS experiments are corrected for ^{13}C isotope contributions. Concentrations of halogen-containing species are reported as the summation of all isotopic contributions.

Photoelectron spectra were obtained using a photoelectron spectrometer (PES) built at Caltech employing a He(I) resonance lamp and a cylindrical 127 °C electrostatic analyzer. A complete description of this instrument and its operation can be found elsewhere.[21] Resolution was maintained at 28 meV for these studies.

All experiments were performed at ambient temperature (20-25 °C). Chemicals used in this work were obtained from commercial sources and used without further purification except for several freeze-pump-thaw cycles at liquid N_2 temperature to remove noncondensable gases.

Results

Halonium Ion Formation by Photoionization and Fragmentation of the Dihaloethanes. PIMS studies of dihaloethanes furnish heats of formation for the several halonium ions investigated. These results are shown in Figures 1-4. In each, photoionization efficiency curves are presented for parent ion formation and halonium ion production through halide loss, reactions 3 and 4, along with other prevalent low-energy fragmentation processes where they occur.

For 1,1-dichloroethane (Figure 1) and 1,2-dichloroethane (Figure 2) the first band of the PES spectrum is included for comparison. Within experimental error, the PES and PIMS data yield identical parent ion thresholds in all cases. PIMS onset energies for all fragment ions reported lie within the first complex band of each respective PES spectrum. The lowest ionization processes observed in the PES spectra of dihaloethanes have been assigned[22-24] to halogen lone pair orbitals with multiplet character due to interhalogen interactions and spin-orbit splitting, accompanied by broadening from vibrational and conformational contributions. This results in a broad region over which the internal energy of the molecular ion may be continuously varied as the photon energy is increased. Onsets recorded in this range are reasonably well defined and should represent true thresholds provided that there are no significant kinetic shifts and the effects of thermal energy are accounted for. These complications have been discussed elsewhere.[25-27] Briefly, the thermal energy content of the parent neutral contributes to the total internal energy of the molecular ion, decreasing the additional energy required for dissociation. This shifts the observed threshold to lower energy. The kinetic shift gives rise to contrasting behavior, shifting the onset to

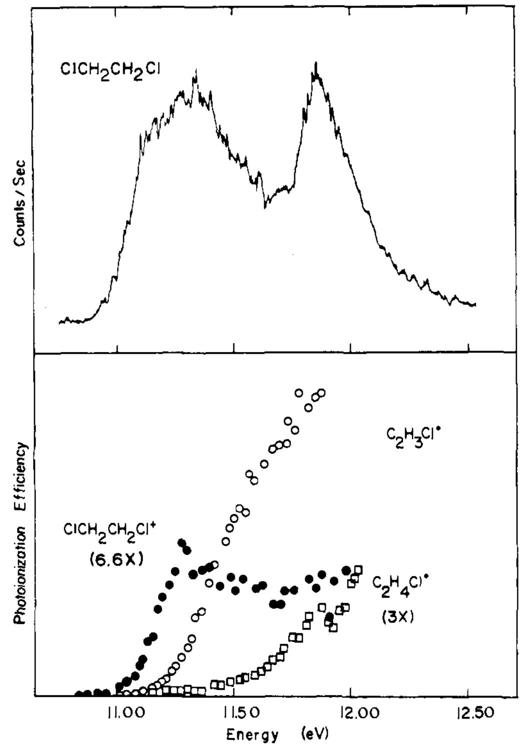


Figure 2. He I photoelectron spectrum of 1,2-dichloroethane between 10.5 and 12.5 eV and photoionization efficiency curves for $ClCH_2CH_2Cl^+$, $C_2H_3Cl^+$, and $C_2H_4Cl^+$ ions in $ClCH_2CH_2Cl$.

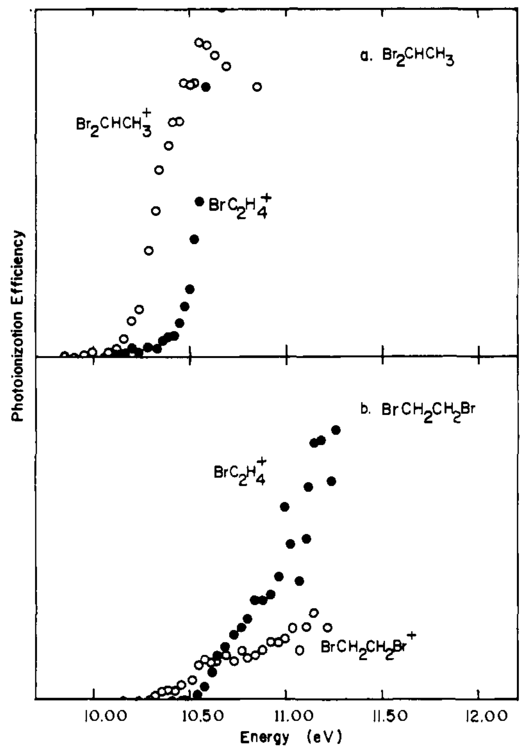


Figure 3. (a) Photoionization efficiency curves for $Br_2CHCH_3^+$ and $BrC_2H_4^+$ ions in Br_2CHCH_3. (b) Photoionization efficiency curves for $BrCH_2CH_2Br^+$ and $BrC_2H_4^+$ ions in $BrCH_2CH_2Br$.

higher energy. This is due to the requirement that the dissociation rate, which increases with increasing energy above threshold, be sufficient for the fragment ions to be formed and detected within the time scale of the experiment. If the species of interest is the major fragment near threshold, i.e., the lowest energy fragmentation process observed, the above effects are often comparable in magnitude and thus tend to cancel each other. However, if fragmentation must compete with other low-energy processes which are kinetically favorable, the kinetic shift can be substantial owing to the reduction in time scale for reaction determined by the frequency factor of the competing process. Except as noted below, halonium ion production is the lowest energy process observed. Onsets were chosen by matching slopes with the parent ion curve as discussed previously.[27]

The PIMS results for $ClCH_2CH_2Cl$, Figure 2, indicate formation of $C_2H_3Cl^+$ through loss of HCl to be the lowest energy process. Hence, exemplifying the above discussion, $C_2H_4Cl^+$ exhibits a gently increasing cross section in the threshold region, making determination of the onset difficult. All thresholds for the ions observed are presented in Table I in addition to heats of formation derived from this data. Lack of thermochemical data for $BrCH_2CH_2Cl$ and $BrClCHCH_3$ parent neutrals presents a problem in calculating halonium ion heats of formation when produced from these species. However, $\Delta H°_f$ (II, X = Br) = 206.5 kcal/mol produced from $BrCH_2CH_2Br$ implies $\Delta H°_f$ ($BrCH_2CH_2Cl$) = −15.7 kcal/mol. Using this value, $\Delta H°_f$ (II, X = Cl) becomes 204.8 kcal/mol when produced from $ClCH_2CH_2Br$ in good agreement with $\Delta H°_f$ (II, X = Cl) = 204.4 kcal/mol derived from $ClCH_2CH_2Cl$. Similarly $\Delta H°_f$ ($BrClCHCH_3$) = −17.1 kcal/mol based on $\Delta H°_f$ (I, X = Cl) = 198.8 kcal/mol produced from Cl_2CHCH_3. In this system, unfortunately, the presence of a relatively large concentration of I (X = Cl) masks the true onset for I (X = Br) by contributing bromonium ion intensity below threshold through the ion-molecule reaction.

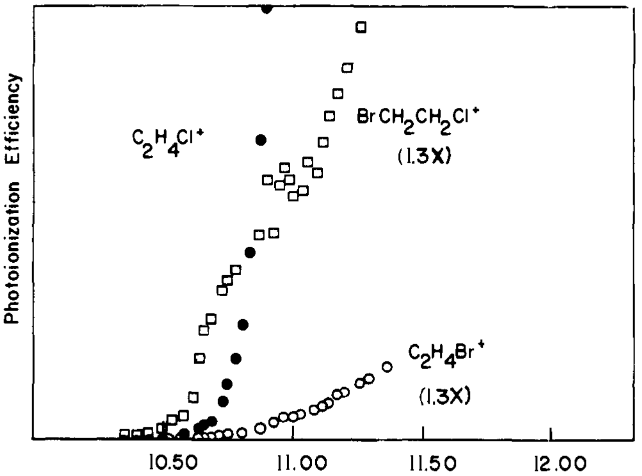


Figure 4. Photoionization efficiency curves for $BrCH_2CH_2Cl^+$, $BrC_2H_4^+$, and $ClC_2H_4^+$ ions in $BrCH_2CH_2Cl$.

$$CH_3CHCl^+ + ClBrCHCH_3 \rightarrow CH_3CHBr^+ + Cl_2CHCH_3 \quad (9)$$

Based on the above results, recommended heats of formation for the isomeric onium ions $C_2H_4X^+$ (X = Cl, Br) are summarized in Table II.

Gas Phase Ion Chemistry of Dihaloethanes. The gas phase ion chemistry of each dihaloethane species alone was characterized using ion cyclotron resonance spectroscopy. Studies of 1,2- and 1,1-chlorobromoethane serve as examples of the observed processes. All reactions are confirmed by double resonance.

Electron impact ionization of 1,2-chlorobromoethane at 20 eV leads to formation of the molecular ion $BrCH_2CH_2Cl^+$ (16%), the halonium ions $C_2H_4Cl^+$ (58%) and $C_2H_4Br^+$ (4%), and the fragment $C_2H_3^+$ (19%) as abundant species. The

Table I. PIMS Thresholds Measured for Dihaloethane Fragment Ions and Derived Heats of Formation

parent	$\Delta H^\circ{}_f$[a]	ion	IP, eV (PES)[b]	IP, eV (PIMS)	AP, eV (PIMS)	$\Delta H^\circ{}_f$, kcal/mol
$ClCH_2CH_2Cl$	−31.23	$ClCH_2CH_2Cl^+$	11.04	11.05		
		II (X = Cl)			11.47[c]	204.4
		$C_2H_3Cl^+$			11.1[d]	
Cl_2CHCH_3	−30.6	$Cl_2CHCH_3{}^+$	11.02	11.06		
		I (X = Cl)			11.20	198.8
$BrCH_2CH_2Br$	−9.6	$BrCH_2CH_2Br^+$	10.42	10.37[e]		
		II (X = Br)			10.53[e]	206.5
Br_2CHCH_3	−7	$Br_2CHCH_3{}^+$	10.17	10.17		
		I (X = Br)			10.48	207.9
$BrCH_2CH_2Cl$	(−15.7)[g]	$BrCH_2CH_2Cl^+$	10.52	10.55		
		II (X = Cl)			10.72	204.8
		II (X = Br)			10.89	(206.5)[f]
$BrClCHCH_3$	(−17.1)[g]	$BrClCHCH_3{}^+$	10.37	10.42		
		I (X =Cl)			10.52	(198.8)[h]
		I (X = Br)			(10.57)[i]	

[a] Except as noted, data is from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970; the heat of formation of Br_2CHCH_3 has not been experimentally determined and is estimated from group equivalents. [b] Adiabatic first ionization potentials. [c] A somewhat higher threshold of 11.60 eV has been reported for the identical process in a photoion-photoelectron coincidence experiment.[9] [d] This is considerably above the thermodynamic threshold of 10.73 eV for this process. [e] R. R. Corderman and J. L. Beauchamp, unpublished results. [f] Assumes $\Delta H^\circ{}_f$ II (X = Br) is correct as derived from $BrCH_2CH_2Br$; $\Delta H^\circ{}_f$ ($ClCH_2CH_2Br$) = −15.7 calculated from this (see text). [g] See discussion in text. [h] Assumes $\Delta H^\circ{}_f$ I (X = Cl) is correct as derived from Cl_2CHCH_3; $\Delta H^\circ{}_f$ ($ClBrCHCH_3$) = −17.1 calculated from this (see text). [i] This is well below the thermodynamic threshold at 11.01 eV due to ion intensity contribution from an ion-molecule reaction (see text).

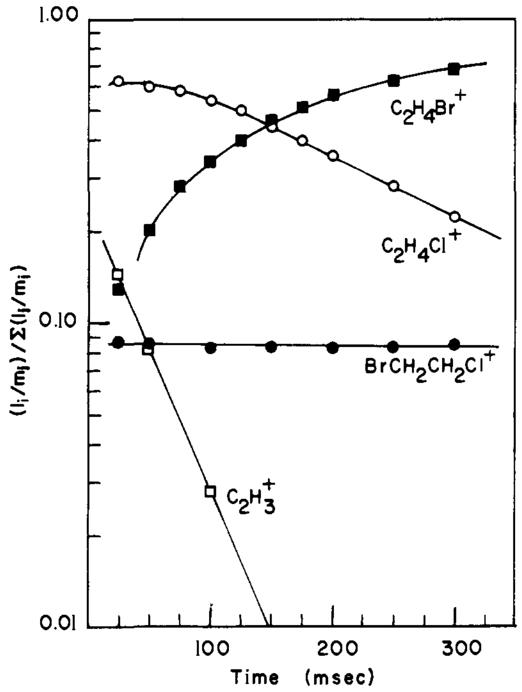
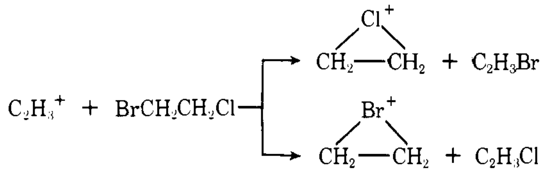


Figure 5. Variation of ion abundance with time following a 10-ms, 20-eV electron beam pulse in $ClCH_2CH_2Br$ at 6.4×10^{-7} Torr.

trapped ion data shown in Figure 5 indicate that the molecular ion is unreactive. $C_2H_3{}^+$ reacts to generate both halonium ions (reactions 10 and 11). The chloronium ion reacts more slowly at long times to generate the bromonium ion (reaction 12).



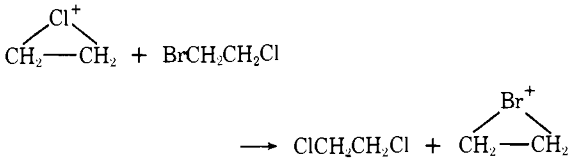
(10)

(11)

Table II. Thermodynamics of Onium Ions and HX Neutrals

ion	$\Delta H^\circ{}_f$, kcal/mol	HX	$\Delta H^\circ{}_f$, kcal/mol	PA(HX)[g]
I (X = F)	165.9[a]	HF	−65.14[g]	112.7
II (X = F)	201[b]			
I (X = Cl)	198.8	HCl	−22.06[g]	136.0
II (X = Cl)	204.4			
I (X = Br)	207.9	HBr	−8.71[g]	140.0
II (X = Br)	206.5			
I (X = OH)	143[c]	HOH	−57.80[g]	170.3
II (X = OH)	169[c]			
I (X = SH)	197[d]	HSH	−4.88[g]	173.9
II (X = SH)	194[e]			
I (X = NH_2)	154[f]	HNH_2	−10.97[g]	202.3
II (X = NH_2)	173[e]			
I (X = PH_2)	214 ± 8[i]	HPH_2	+5.5[g]	187.4
II (X = PH_2)	205 ± 16[i]			

[a] Reference 27. [b] Reference 39. [c] Reference 30. [d] B. G. Keyes and A. G. Harrison, *J. Am. Chem. Soc.*, **90**, 5671 (1968). [e] D. H. Aue, private communication. [f] Reference 37. [g] "JANAF Thermochemical Tables", 2nd ed., NSRDS-NBS 37 (1971). [h] Reference 43. [i] Estimates based on observed exchange reactions in the ICR.



(12)

The electron impact fragmentation and subsequent reactions observed in the case of 1,1-bromochloroethane are analogous to 1,2-bromochloroethane, except that the molecular ion reacts rapidly to yield $C_2H_4Cl^+$ and $C_2H_4Br^+$, presumably in collision-induced decompositions. The halide transfer (process 9) is again observed to be slow. The trapped ion data in Figure 6 show that $C_2H_4Br^+$ is the only remaining ion at long times. Using the data in Table II, the halide transfer reactions 12 and 9 are calculated to be exothermic by 13.4 and 4.4 kcal/mol, respectively. Rates for these processes are summarized in Table III.

Table III. Approximate Halonium Ion Reaction Rates and Exothermicities

	reaction no.	rate[a]	$\Delta H^{\circ\, b}$
A. Halide Transfer Reactions			
I (X = Cl) + $ClBrCHCH_3 \rightarrow$ I (X = Br) + Cl_2CHCH_3	(9)	4.0	−4.4
II (X = Cl) + $ClCH_2CH_2Br \rightarrow$ II (X = Br) + $ClCH_2CH_2Cl$	(12)	2.0	−13.4
B. HX Exchange Reactions			
II (X = Br) + $NH_3 \rightarrow$ II (X = NH_2) + HBr	(13)	0.09	−31.2
II (X = Cl) + $NH_3 \rightarrow$ II (X = NH_2) + HCl	(17)	5.0	−42.5
C. Proton Transfer			
I (X = Br) + $NH_3 \rightarrow NH_4^+ + C_2H_3Br$	(14)	30.0	−24.3
I (X = Cl) + $NH_3 \rightarrow NH_4^+ + C_2H_3Cl$	(18)	10.0	−25.3

[a] 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] kcal/mol, based on thermochemical data in Table VII.

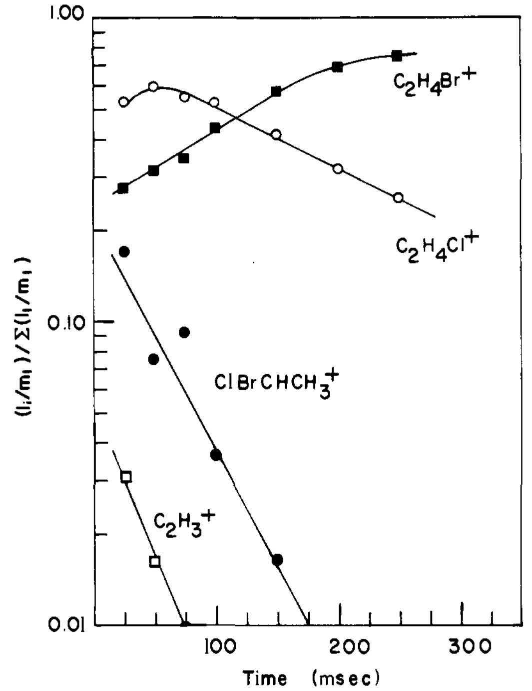


Figure 6. Variation of ion abundance with time following a 10-ms, 20.0-eV electron beam pulse in $ClBrCHCH_3$ at 3.0×10^{-7} Torr.

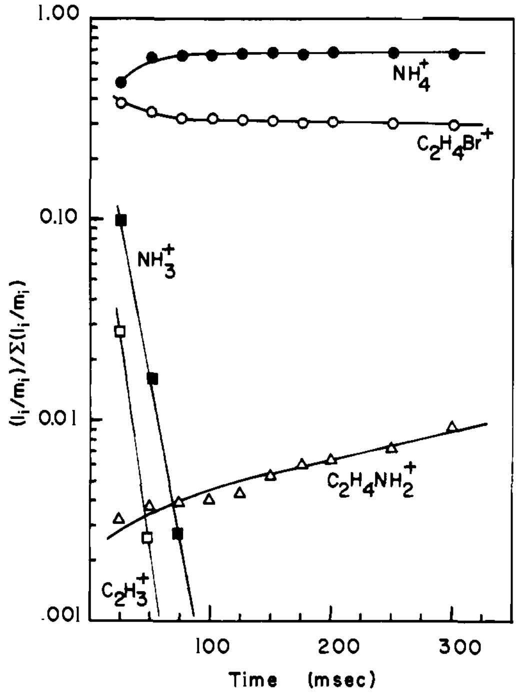
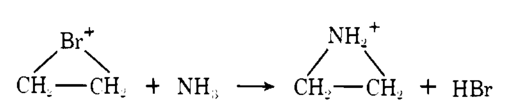


Figure 7. Variation of ion abundance with time following a 10-ms, 20.0-eV electron beam pulse in a 1:2 mixture of $BrCH_2CH_2Br$ and NH_3 at 1.5×10^{-6} Torr total pressure.

The gas phase ion chemistry of 1,2-dibromoethane has been reported previously.[7] With the exception of 1,2-dichloroethane,[28] the major species remaining at long times for dihaloethanes is the halonium $C_2H_4X^+$, with X = Br being more prevalent in the case of the bromochloroethanes. This facilitates the study of reactions of halonium ions in mixtures with other compounds.

Reactions in Mixtures of Dihaloethanes with NH_3. Processes observed in mixtures of dihaloethanes with NH_3 demonstrate differential reactivity for the two $C_2H_4X^+$ structural isomers I and II (X = Cl or Br). In addition, observed reactions include examples of the HX exchange processes generalized in eq 7 and 8.

The temporal variation of ion abundances observed in a 1:2 mixture of 1,2-dibromoethane and NH_3 upon ionization by 20-eV electrons is presented in Figure 7. As illustrated, the primary ions $C_2H_3^+$ and NH_3^+ react mainly to yield NH_4^+ Major ions remaining at long times are NH_4^+ and the bromonium ion $C_2H_4Br^+$. However, the species $C_2H_4NH_2^+$ is also observed, and double resonance indicates that it is formed from $C_2H_4Br^+$ via the slow reaction 13 ($k = 0.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). This process is a specific example of the HX exchange reaction generalized in eq 7. In a 2.7:1 mixture of 1,1-dibromoethane and NH_3 the same five ions are observed (Figure 8). It is evident from a comparison of Figures 7 and 8, however, that the reaction schemes differ. For the data shown in Figure 8, in addition to being formed from NH_3^+ and $C_2H_3^+$, the major product NH_4^+ is also formed in reaction 14 from $C_2H_4Br^+$. The product ion $C_2H_4NH_2^+$ is formed via reactions 15 and 16 in greater abundance than observed in Figure 7. Reaction 16, identified by double resonance, is too rapid to permit accurate measurement of the molecular ion abundance after production of this species has ceased. The initial abundance is approximately 10% of the total ionization, with the signal divided between three different isotopic species. The important conclusion drawn from these results relates to the reactions of $C_2H_4Br^+$ with NH_3, namely, that isomer I reacts by proton transfer (reaction 14) and isomer II reacts by HX exchange (reaction 13). Structural isomers of $C_2H_4Br^+$ can therefore be distinguished.



$$\overset{Br^+}{CH_2\text{—}CH_2} + NH_3 \longrightarrow \overset{NH_2^+}{CH_2\text{—}CH_2} + HBr \qquad (13)$$

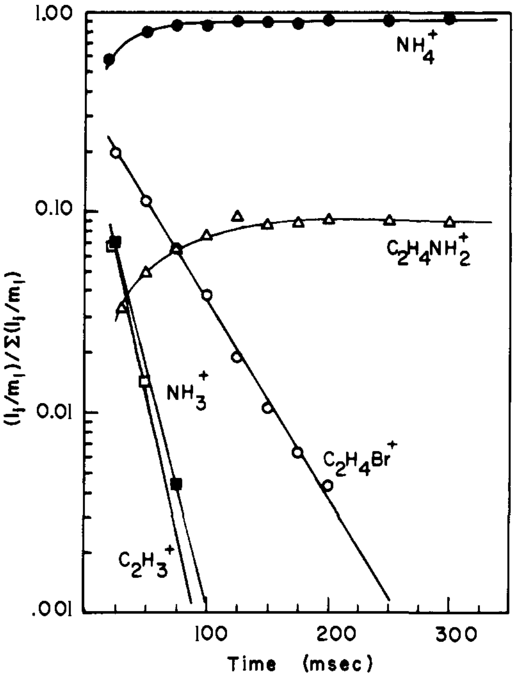


Figure 8. Variation of ion abundance with time following a 10-ms, 20.0-eV electron beam pulse in a 2.7:1 mixture of Br_2CHCH_3 and NH_3 at 9.1 × 10^{-7} Torr total pressure.

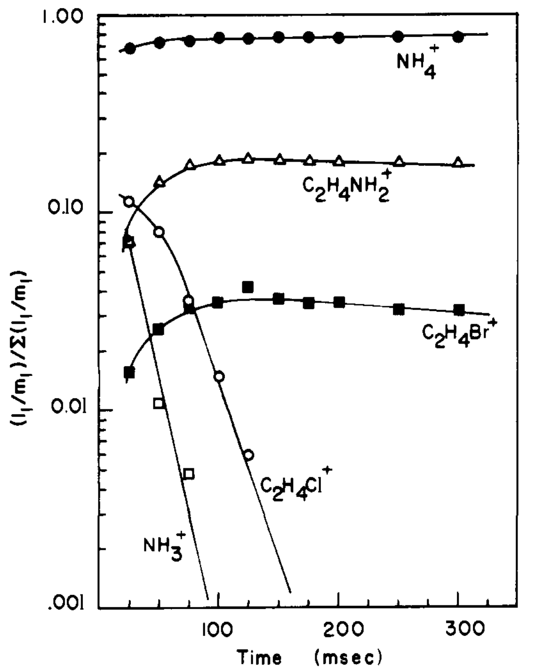


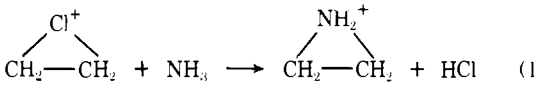
Figure 9. Variation of ion abundance with time following a 10-ms, 20.0-eV electron beam pulse in a 1:7 mixture of $BrCH_2CH_2Cl$ and NH_3 at 2.7 × 10^{-6} Torr total pressure.

$$CH_3CHBr^+ + NH_3 \rightarrow NH_4^+ + C_2H_3Br \quad (14)$$

$$NH_3^+ + Br_2CHCH_3 \rightarrow C_2H_4NH_2^+ + Br + HBr \quad (15)$$

$$NH_3 + Br_2CHCH_3^+ \rightarrow C_2H_4NH_2^+ + Br + HBr \quad (16)$$

The species $C_2H_4Cl^+$ is an abundant ion at short times in a 1:7 mixture of 1,2-bromochloroethane and NH_3 upon ionization by 20-eV electrons (Figure 9). This species reacts rapidly with excess NH_3 to yield $C_2H_4NH_2^+$ (reaction 17) and



(17)

does not contribute to NH_4^+ NH_4^+ is formed mainly from NH_3^+, NH_2^+, and $C_2H_3^+$ (the latter two ions are not included in Figure 9). The species $C_2H_4Br^+$ is generated both by electron impact and in reaction 12 observed in $BrCH_2CH_2Cl$ alone. As is the case in the mixture of $BrCH_2CH_2Br$ and NH_3 discussed above, this species reacts slowly to yield $C_2H_4NH_2^+$ at long times (reaction 13).

The temporal variation of ion abundances observed in a 1:1.5 mixture of 1,1-bromochloroethane and NH_3 is shown in Figure 10. In this system double resonance indicates that $C_2H_4Cl^+$ reacts only by proton transfer with NH_3, yielding NH_4^+ (reaction 18), while processes analogous to reactions 15 and 16 lead to formation of $C_2H_4NH_2^+$ The important conclusion drawn from these results relates to the reactions of $C_2H_4Cl^+$ with NH_3, namely, that isomer I reacts by proton transfer (reaction 18) and isomer II reacts by HX exchange (reaction 17).

$$CH_3CHCl^+ + NH_3 \rightarrow NH_4 + C_2H_3Cl \quad (18)$$

Reactions of a Wider Range of Onium Ions. In addition to studies of the dihaloethanes, reactions of onium ions generated from oxirane, acetaldehyde, thiirane, and aziridine were also investigated using ion cyclotron resonance spectroscopy. In mixtures containing the parent species and HX (X = Cl, Br, OH, SH, NH_2, and PH_2), the preferred direction of HX exchange (eq 7 and 8) was determined by trapped ion experiments as discussed above. Competing reactions were also studied. For example, the temporal variation of ion abundance in a mixture of $BrClCHCH_3$ and H_2S is presented in Figure 11. At long times only $C_2H_4SH^+$ persists, produced by HX exchange from both $C_2H_4Cl^+$ and $C_2H_4Br^+$ (reactions 19 and 20) and by reactions 21, 22, and 23 from the minor ions $BrClCHCH_3^+$, H_2S^+, and H_3S^+

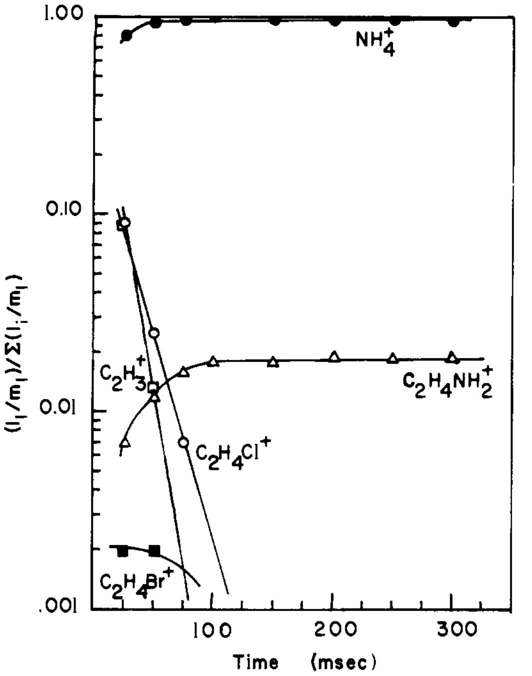
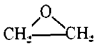
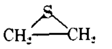
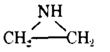


Figure 10. Variation of ion abundance with time following a 10-ms, 20.0-eV electron beam pulse in a 1:1.5 mixture of $BrClCHCH_3$ and NH_3 at 1.7 × 10^{-6} Torr total pressure.

$$H_2S + CH_3CHCl^+ \rightarrow CH_3CHSH^+ + HCl \quad (19)$$

$$H_2S + CH_3CHBr^+ \rightarrow CH_3CHSH^+ + HBr \quad (20)$$

Table IV. Summary of ICR Data for Gaseous Mixtures Investigated

onium ion precursor	hydride	reactant ion	product ion
$ClCH_2CH_2Cl$[a]		II (X = ^{35}Cl)	II (X = ^{37}Cl)[b]
	HBr	II (X = Cl)	II (X = Br)
$BrCH_2CH_2Br$		II (X = ^{79}Br)	II (X = ^{81}Br)[c]
	HCl		none obsd
	HOH		none obsd
	HSH	II (X = Br)	II (X = SH)
	HNH_2	II (X = Br)	II (X = NH_2)
	HPH_2	II (X = Br)	II (X = PH_2)
$ClCH_2CH_2Br$		II (X = Cl)	II (X = Br)
	HOH		none obsd
	HSH	II (X = Cl)	II (X = SH)
	HNH_2	II (X = Cl, Br)	II (X = NH_2)
	HPH_2	II (X = Cl, Br)	II (X = PH_2)
Cl_2CHCH_3			
	HOH	H_2O^+, H_3O^+ I (X = Cl)[d]	I (X = OH)
	HNH_2	I (X = Cl)	NH_4^+
		NH_3^+, $Cl_2CHCH_3^+$	I (X = NH_2)
Br_2CHCH_3		I (X = ^{79}Br)	I (X = ^{81}Br)[b]
	HCl		none obsd
	HOH	H_2O^+, H_3O^+	I (X = OH)
	HNH_2	I (X = Br)	NH_4^+
		NH_3^+, $Br_2CHCH_3^+$	I (X = NH_2)
$BrClCHCH_3$		I (X = Cl)	I (X = Br)
	HSH	I (X = Cl, Br), H_2S^+, H_3S^+	I (X = SH)
	HNH_2	I (X = Cl, Br)	NH_4^+
		NH_3^+, $BrClCHCH_3^+$	I (X = NH_2)
	HPH_2	I (X = Cl, Br), PH_3^+	I (X = PH_2)
	HCl	II (X = OH), HCl^+, H_2Cl^+	II (X = Cl)
	HSH[f]	II (X = OH),[e,f] H_3S^+[f]	II (X = SH)[f]
	HNH_2	I (X = OH)	NH_4^+
	HPH_2[f]	II (X = OH),[e,f] H_3P^+[f]	II (X = PH_2)[f]
	HNH_2	I (X = SH)	NH_4^+
	HSH		none obsd
	HPH_2		none obsd
CH_3CHO	HSH[f]		none obsd[f]
	HNH_2	I (X = OH)	NH_4^+
	HPH_2		none obsd[f]

[a] II (X = Cl) is a minor ion in the mass spectrum $ClCH_2CH_2Cl$; see Figure 2 and discussion in text. [b] The thermoneutral transfer reaction is observed in both directions. [c] The thermoneutral transfer reaction is observed in both directions, ref 7. [d] The reaction I (X = Cl) + $H_2O \rightarrow$ I (X = OH) + HCl exhibits positive double resonance but does not appear to go thermally. [e] Reference 39. [f] Reference 42.

$$H_2S + BrClCHCH_3^+ \rightarrow CH_3CHSH^+ + HCl + Br \quad (21)$$

$$H_2S^+ + BrClCHCH_3 \rightarrow CH_3CHSH^+ + HCl + Br \quad (22)$$

$$H_3S^+ + BrClCHCH_3 \rightarrow CH_3CHSH^+ + HCl + HBr \quad (23)$$

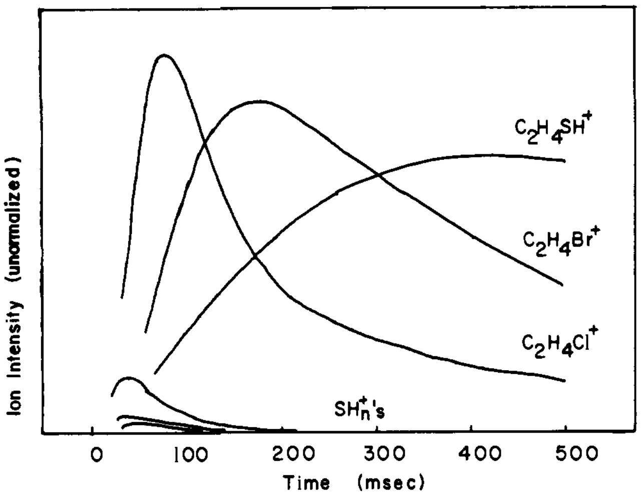


Figure 11. Variation of ion abundance with time following a 10-ms, 20.0-eV electron beam pulse in a 1:1 mixture of $ClBrCHCH_3$ and H_2S at 1.2×10^{-6} Torr total pressure.

Table V. Summary of HX Exchange Experiments[a]

		Y in cyclic reactant ions II: c-$C_2H_4Y^+$					
A.	HX	OH	Cl	Br	HS	H_2P	H_2N
	H_2O		−	−	0	0	0
	HCl	+		−	0	0	0
	HBr	0	+		0	0	0
	H_2S	+	+	+		?	−
	H_3P	+	+	+	?		−
	H_3N	PT	+	+	PT	0	

		Y in acyclic reactant ions I: CH_3CHY^+					
B.	HX	Cl	Br	SH	PH_2	OH	NH_2
	HCl		−	0	0	0	0
	HBr	0		0	0	0	0
	H_2S	+	+		?	−	0
	PH_3	+	+	?		−	0
	H_2O	endo	−	0	0		0
	NH_3	PT	PT	0	0	PT	

[a] Notation in tables is as follows: + indicates reaction observed; − indicates reaction not observed; PT indicates reaction not observed, proton transfer observed instead; ? indicates reactant and product ion have same mass; 0 indicates mixture not investigated; and endo indicates positive double resonance with indication that the reaction does not occur at thermal energies.

Experiments and results involving all onium ions investigated are presented in Table IV. Table II summarizes known thermochemical data for these species. Using the thermochemical data in Table II, the predicted order in which the different nucleophiles HX will replace one another[29] is HX = $NH_3 > H_2S >$ HBr > HCl $\simeq H_2O >$ HF for the cyclic onium ions II and HX = $NH_3 > H_2O > H_2S >$ HBr > HCl > HF for the isomeric species I. Not all predicted reactions are observed, however. As noted above in the examination of mixtures of NH_3 with dihaloethanes, proton transfer is often observed exclusive of the displacement process. This process is observed in other mixtures as well and is not surprising since NH_3 is the most basic of the nucleophiles examined. A digested form of the data in Table IV is given in Table V, which indicates the mixtures examined, the occurrence or nonoccurrence of exchange reactions in the mixture, and competing reactions when they were identified. All observed reactions agree with the predicted order.

Discussion

Existence and Thermochemistry of Isomeric Halonium Ions. For the halonium ions $C_2H_4X^+$ (X = Cl, Br), two structurally unique isomers can be distinguished in gaseous mixtures containing dihaloethanes and NH_3. The species which reacts with NH_3 by HX exchange (eq 13 and 17) is assumed to be the cyclic isomer II. The species which reacts with NH_3 by proton transfer (eq 14 and 18) to yield NH_4^+ is assumed to be the

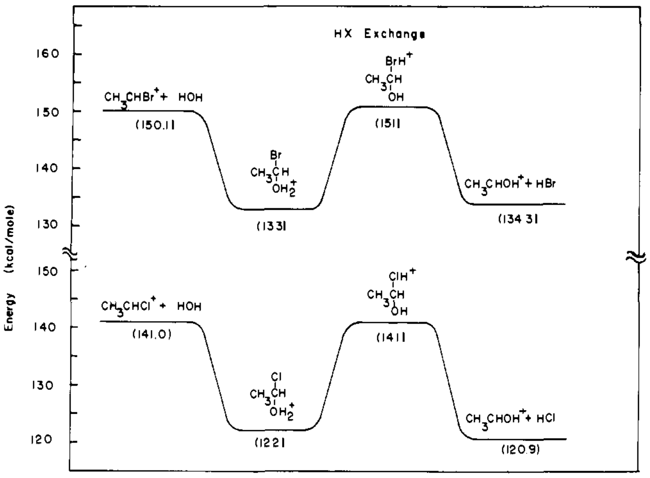
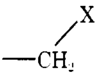


Figure 12. Energetics of probable intermediates in the exchange reaction between $C_2H_4Br^+$ and H_2O (a), and $C_2H_4Cl^+$ and H_2O (b). Enthalpies for intermediate structures are approximated from proton affinities of related monofunctional neutrals from ref 43.

acyclic isomer I. Theoretical calculations[14,15] indicate that the open chloroethyl cation III is 15 kcal/mol less stable than the cyclic ion II and has no barrier to ring closure. For this reason the species III is not assumed to be present.



III

Compared to I[4,30-34] observations of the cyclic chloronium ion II in solution are relatively recent,[30] implying that the acyclic species is energetically favored. PIMS results for X = Cl indicate that the acyclic structure I has a heat of formation 5.6 kcal/mol less than the cyclic form II. This confirms the evidence from condensed phase studies. Gas-phase investigations of bromonium ions indicate that the cyclic species II is favored by 1.4 kcal/mol over the isomeric structure I. This concurs with solution-phase work where only the cyclic ion has been observed.[4,31-33,35,36] Because of the uncertainties in the thermochemistry of the neutrals involved, it is difficult to provide estimates of the actual errors in the determined heats of formation. Probable errors of ±2 kcal/mol are reasonable, however, and the small differences in the measured heats of formation are thus not sufficient evidence for the existence of unique and distinguishable structural isomers. The present results still indicate, however, that the halonium ion isomers I and II (X = Cl or Br) retain their structural integrity and can easily be distinguished by differences in their chemical behavior.

Periodic Trends in the Stability of Onium Ion Structural Isomers. For X = NH_2 the acyclic isomer I is 19 kcal/mol more stable than II.[37] Similarly, protonated acetaldehyde, I (X = OH), is energetically favored by 26 kcal/mol when compared to protonated oxirane, II (X = OH).[38] Each of these pairs of structural isomers can be distinguished by their gas phase ion chemistry. In contrast, the cyclic fluoronium ion II (X = F) has not been observed in either gas phase or solution.[31] Jolly[39] has estimated a heat of formation for this species of 201 kcal/mol to be compared with the acyclic ion I (X = F) for which ΔH°_f = 165.9 kcal/mol has been determined in recent PIMS studies.[27] Thus, the acyclic structure is more stable than the ring form for ions containing first-row heteroatoms. This differential stability appears to increase as the heteroatom is varied in proceeding from left to right in the periodic table, implying that enhanced relative stability of the acyclic ion correlates with increased electronegativity and contraction of the heteroatom bonding orbits (principally the 2p).[40] This relation is further confirmed by trends within any family, or column, of the periodic table. For example, electronegativity diminishes and p-orbital size expands for progressively heavier halogen congeners. This is coupled with a corresponding increase in the stability of the ring II isomer relative to the acyclic species I for ions containing halogen heteroatoms. These trends are such that in the case of Br it is found that the cyclic isomer is more stable than the acyclic form. As another illustration, in contrast to oxonium ions (X = OH),[38] the cyclic species II is 3 kcal/mol more stable than I for the sulfur analogues (X = SH).[41]

Table VI. Hydride and Halide Affinities for Several Onium Ions and Carbonium Ions[a]

ion	A_{Cl^-}	A_{Br^-}	$\Delta(A_{Cl^-} - A_{Br^-})$	A_{H^-}
H^+	334.9	325.1	9.8	400.4
CH_3^+	227.2	219.3	7.9	312.1
CH_2Br^+				303.3
$C_6H_5^+$	218.4	209.0	9.4	298.4
$C_2H_3^+$	203.0	196.5	6.5	286.6
CH_2Cl^+	195.6			280.8
$C_2H_5^+$	188.8	181.5	7.3	270.5
$CHCl_2^+$	182.2			268.2
II (X = Cl)[b]	181.2	169.3	11.9	263.7
I (X = F)				262.1[c]
II (X = OH)				258.4
I (X = Cl)[b]	175.0	165.1	9.9	258.1
n-$C_3H_7^+$	176.6	169.7	6.9	258.0
I (X = Br)[b]	170.6	164.1	6.5	256.3
CCl_3^+	168.8			255.8
II (X = Br)[b]	167.8	165.3	2.5	254.9
$C_3H_5^+$				253.8
sec-$C_3H_7^+$	170.9	164.4	6.5	249.7
I (X = SH)				241.2
II (X = SH)				238.2
I (X = OH)				232.4
$C_6H_5CH_2^+$	152.1	143.3	8.8	232.2
t-$C_4H_9^+$	152.8	144.6	8.2	229.1
II (X = NH_2)				217.6
I (X = NH_2)				198.8

[a] All data in kcal/mol, based on information in Table VII. [b] Derived from this work. [c] Reference 27.

Reactions of Onium Ions with Nucleophiles. Reactions 7 and 8 are probably initiated by nucleophilic attack of HY at an electropositive carbon of the onium ion. Presumably, the energetically favored form of the resulting intermediate would be either one with the proton on the more basic site, or one where the proton bridges the two substituents. If sufficient internal energy for intramolecular proton transfer is provided by formation of the intermediate, then loss of HX may be the favored decomposition pathway, provided that the overall reaction is exothermic. However, if internal proton transfer is energetically precluded, it may be possible that the intermediate can decompose only by loss of HY to regenerate the reactants. The latter situation may apply in mixtures containing 1,1-dihaloethanes and H_2O. Although there are obvious uncertainties in estimating the stability of reaction intermediates, the examples presented in Figure 12 do suggest that energetically unfavorable intermediates prevent the expected HX exchange between I (X = Cl or Br) and H_2O from occurring.

In several instances, proton transfer is observed rather than the predicted exchange reaction. These cases involve the most basic nucleophile NH_3 reacting with onium ions containing heteroatoms bearing labile protons (X = SH and OH), or with acyclic isomers of the halonium ions where deprotonation of I (X = Cl or Br) yields the corresponding vinyl halide directly

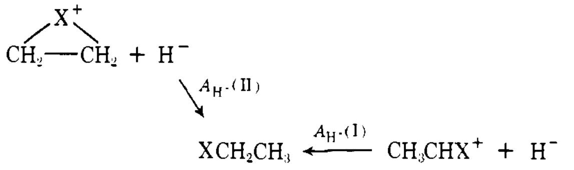
Table VII. Relevant Thermochemical Data (kcal/mol)

species	$\Delta H°_f$	species	$\Delta H°_f$	species	$\Delta H°_f$	species	$\Delta H°_f$
H^+	367.2[a]	t-$C_4H_9^+$	163.5[d]	H^-	33.2[a]	c-C_2H_4O	−12.58[i]
CH_3^+	261.0[b]	$C_6H_5^+$	285.9[c]	F^-	−61.1[a]	c-C_2H_4S	19.69[i]
$C_2H_3^+$	266.0[c]	$C_6H_5CH_2^+$	211.0[d]	Cl^-	−54.4[h]	c-C_2H_5N	30.24[i]
$C_2H_5^+$	217.1[d]	CH_2Cl^+	227.0[e]	Br^-	−50.81[h]	CH_3CHO	−39.73[i]
$C_3H_5^+$	225.5[d]	CH_2Br^+	261.0[f]	H	52.1[a]	C_2H_3Cl	8.6[i]
sec-$C_3H_7^+$	191.7[b]	$CHCl_2^+$	212.0[e]	Cl	28.92[a]	C_2H_3Br	18.71[i]
n-$C_3H_7^+$	200.0[b]	CCl_3^+	198.0[g]	Br	26.74[a]	C_2H_5F	−62.9[j]

[a] "JANAF Thermochemical Tables", 2nd ed., NSRDS-NBS 37 (1971). [b] From ionization potentials of radicals, ref 12, $\Delta H°_f$ of radicals, ref 28, and W. Tsang, *J. Phys. Chem.*, **76**, 143 (1972). [c] F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971). [d] F. A. Houle, private communications. [e] F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81**, 125 (1972). [f] F. P. Lossing, P. Kebarle, and J. B. Defonsa, *Adv. Mass Spectrom.*, **1**, 431 (1959). [g] S. G. Lias and P. Ausloos, *Int. J. Mass Spectrom. Ion Phys.*, **23**, 273 (1977). [h] Based on EA(Cl) = 3.613 eV, EA(Br) = 3.363 eV: R. S. Berry and C. W. Reinmann, *J. Chem. Phys.*, **38**, 1540 (1963). [i] J. D. Cox and E. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. [j] S. S. Chen, A. S. Rodgers, J. Chao, R. S. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **4**, 441 (1975).

with minimal structural rearrangement. This pathway is not available for the cyclic species II (X = Cl or Br) even though proton transfer to NH_3 is calculated to be exothermic for these isomers as well. By the same argument, if III (X = Cl or Br) were present, it might be expected to react by proton transfer with species such as NH_3.

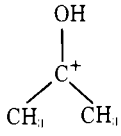
Hydride and Halide Affinities. Hydride and halide affinities for a variety of species including the onium ions considered in this study are listed in Table VI. These values are based on thermochemical data summarized in Table VII. Hydride affinities reflect differences in enthalpies of formation, providing a method for directly comparing relative stabilities of the structural isomers for each onium ion by associating both structures with a common intermediate, eq 24.



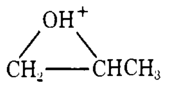
(24)

It is interesting to note from Table VI that the acyclic structures of halosubstituted methyl ions have affinities roughly equivalent to those of corresponding alkyl cations where a methyl group replaces the halogen. Thus, halogens are approximately as effective as methyl groups in stabilizing a positive charge.

Substitution Effects on the Relative Stability of Isomeric Onium Ions. The data in Table II indicate that protonated acetaldehyde I is 26 kcal/mol more stable than protonated oxirane. This differential stability increases by 4 kcal/mol in comparing protonated acetone (α-methylacetaldehyde, IV) to protonated propylene oxide (methyloxirane, V).[38,42] Thus,

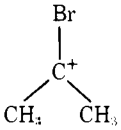


IV

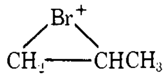


V

methyl group inductive stabilization is more effective at the α carbon of an acyclic onium ion than at a ring carbon of the corresponding cyclic isomer.[29] Similar effects have been observed among bromonium ion isomers.[7] In this case, the cyclic ion is favored over the acyclic structure for the unsubstituted species. Because this difference is small, however, inductive effects are sufficient to cause the acyclic ion to be stabilized with respect to the ring isomer upon methyl substitution. Hence, VI is more stable than its cyclic analogue VII.



VI



VII

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(29) In processes where reactant and product species have similar structures entropy changes are negligible. Hence, the enthalpy difference associated with the HX exchange should reasonably reflect the free-energy change for such reactions. However, when cyclic and acyclic onium ions are compared, the entropy change associated with ring formation is generally in the neighborhood of 10 eu. This will cause ΔG° to favor the acyclic structure by 3 kcal/mol over ΔH° at 298 K.
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Matrix Laser Fluorescence Spectra of Several Fluorobenzene Radical Cations

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Abstract: Several fluorobenzene radical cations were generated by vacuum UV photolysis of the parent fluorobenzenes in solid Ar matrix, and their laser fluorescence excitation spectra were studied. Their spectra show a well-resolved vibronic structure, which appears to be essentially unperturbed by the solid. Vibrational analysis provides strong evidence for the occurrence of a Jahn-Teller distortion in the degenerate $^2E_{1g}$ ground state of $C_6F_6^+$

1. Introduction

Until fairly recently, the number of spectroscopic studies of polyatomic ions was rather restricted.[1-3] In the last few years there has been a surge of activity in this field.[4-8] Most of the reported ions were generated either in discharges or by electron impact and identified by analysis of their emission spectra. Although immensely useful, studies of this nature have several limitations. In the first place, the emission spectra provide mostly information about the ground electronic state, and only limited data are generally obtained about the vibrational structure of the excited electronic state. Furthermore, particularly in larger molecules, the dense rotational structure and the large number of levels populated at high or even ambient temperatures usually result in poorly resolved spectra with broad and overlapping bands and make the interpretation difficult.

The first limitation can be overcome by the study of laser fluorescence excitation spectra, which can provide extensive information about the excited electronic states. Very recently we have indeed reported such a study of the $C_6H_3F_3^+$ cation.[9] The difficulties inherent in the complexity of the spectra can be eliminated by reducing the sample temperature. A convenient means for the study of low temperature spectra is provided by the matrix isolation technique.

Numerous studies of the matrix spectra of a variety of polyatomic anions and cations have appeared in the last few years, most of them employing infrared spectroscopy. Jacox and Milligan[10] have observed the matrix spectrum of CCl_3^+. Since then a number of other halogenated methylene and methyl radical ions have been reported,[11-13] mainly by Jacox and by Andrews and co-workers. Also a variety of other small inorganic ions have been observed.[14-16]

In contrast to the large number of infrared studies, very little is known about the electronic spectra of matrix isolated ions, and only the diatomic C_2^- was studied in some detail.[17,18] Studies of electronic spectra would clearly be desirable because of the inherent, much higher sensitivity. Furthermore, if vibrationally resolved electronic spectra can be obtained, they should provide mainly the symmetric vibrational modes and thus complement conveniently the infrared spectroscopy.

In the present manuscript we report the observation of vibrationally resolved emission and laser excitation spectra of several fluorobenzene radical cations. In a preliminary communication[19] we have already reported the matrix spectrum of $C_6F_6^+$. Such studies are desirable for two reasons. In the first place, the low-temperature spectra with their well-resolved vibrational structure should provide useful information about these interesting species or, when available, assist in the interpretation of the more congested gas-phase spectra.[20] In the second place, they provide the possibility of comparison of the molecular constants of these ionic species with their gas-phase values and give an indication of the extent to which the ions are perturbed by the solvent. This is of particular value, since, for most of the ions whose matrix IR spectra have been reported, such comparisons are not available.

2. Experimental Section

The parent fluorobenzenes (Aldrich) were purified by several freeze-pump-thaw cycles and mixed with Ar. Typically dilutions of 1:2000 to 1:5000 were employed. The samples were then deposited on a sapphire substrate at ≈5 K, mostly with simultaneous photolysis. In several experiments the samples were deposited without photolysis and subsequently photolyzed in situ. The photolysis was accomplished using an atomic resonance lamp excited by a microwave discharge. The hydrogen Lyman α 1216-Å line was usually employed, although the Xe 1470-Å radiation was used in several experiments.

The sample fluorescence was excited using a tunable dye laser pumped by an N_2 laser. To avoid saturating the individual vibronic transitions in the matrix isolated molecules, the laser power was typically attenuated by inserting an O.D. 2-3 neutral density filter into the laser beam. The sample emission was resolved in a SPEX 14018 monochromator. The PMT signal was time resolved and averaged in a Nicolet signal averager. The data acquisition as well as the scanning of the laser and the monochromator were controlled by a minicomputer.

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