Isomerization and Fragmentation Products of CH_2Cl_2 and Other Dihalomethanes in Rare-Gas Matrices: An Electron Bombardment Matrix-Isolation FTIR Spectroscopic Study[†]

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Isodihalomethanes have been isolated by electron bombardment of CH_2Cl_2, CD_2Cl_2, CH_2Br_2, or CH_2ClBr in argon, krypton, or xenon followed by condensation on a 15 K matrix-isolation window. Numerous neutral and ionized decomposition products of dihalomethane ionization were also observed. Irradiation with visible or UV light, isotopic substitution, and previous literature assignments of the matrix-isolated products allow definitive identification of most of the observed product bands in the infrared spectra recorded after electron bombardment matrix-isolation experiments (EBMI). Experiments involving substitution of argon with krypton or xenon gas, mixtures of CH_2Cl_2 and CH_2Br_2, rare-gas resonant emission irradiation, and thermodynamic considerations support the proposed mechanism for isomerization of the dihalomethane radical cation in the gas phase. This mechanism involves charge-exchange ionization of dihalomethane followed by gas-phase isomerization, isolation, and stabilization in the solid matrix and subsequent neutralization through electron capture. An upper limit to the barrier for $CH_2Cl_2^{\bullet+}$ to $CH_2ClCl^{\bullet+}$ isomerization of 43 kJ mol^{-1} is deduced following observation of the isodichloromethane product after EBMI of xenon/dichloromethane mixtures. Two isomers of the molecular cation, one resembling the distonic isomer of $CH_2Cl_2^{\bullet+}$ ($HClC^{\bullet+}{-}ClH$) and the other a complex between CH_2Cl^+ and a chlorine atom [$(CH_2Cl^+)Cl^\bullet$] have been distinguished based on their stability with respect to UV−visible light irradiation, their infrared spectra, and published ab initio calculations. Vibrational wavenumbers for isodichloromethane and various other products of dichloromethane EBMI experiments in krypton and xenon matrices are reported for the first time. We propose reasoning for the general observation that ions that have an electron affinity (EA) greater than ∼10.8 eV (the "5 eV rule") are not observed in argon matrices, but those with EAs less than 10.8 eV are observed.

1. Introduction

The fate of molecular ions following their formation has been one of the central foci of gas-phase ion chemistry and mass spectrometry. Recently, we have investigated fragmentation and isomerization processes that follow formation of molecular ions using a combination of gas-phase electron bombardment and matrix-isolation infrared spectroscopy. Application of this technique to the formation and characterization of 1-propen-2-ol,[1] to the mixed rare-gas cations[2] $(RgHRg')^+$ (Rg = rare gas and $Rg \neq Rg'$), and to the elucidation of some gas-phase ion processes pertaining to the oxalyl chloride radical cation[3] has recently been reported.

Physical, electronic, and spectroscopic properties of halomethane systems have been investigated extensively[4−14] through a variety of methods in both the gas and the condensed phases. The neutral and ionic decomposition products of photoionization and radiolysis of halogenated methanes were first investigated by Andrews et al.[9] using matrix-isolation infrared and ultraviolet spectroscopy. Other techniques, such as excimer-laser irradiation,[10,14] electron impact[12] (EI), and chemical ionization[15] have since been employed to generate and/or to characterize spectroscopically various chlorinated species.

Maier et al.[10] have reported IR and UV−visible spectroscopic studies of the photoisomerization of dihalomethanes (CH_2XY, X/Y = I/I, Br/I, Cl/I, F/I, Br/Br, Cl/Br, Cl/Cl) isolated in argon matrices. UV irradiation of dihalomethanes trapped in argon matrices at 12 K generated visible-light-absorbing species that decomposed on subsequent irradiation. These species were proposed to be isomers of dichloromethane having an unusual structure involving a CH_2X-Y linkage that was supported by both spectroscopic evidence and ab initio calculations. More recently, Lugez et al.[16] have observed the neutral tetrachloromethane isomer, Cl_2CCl-Cl, in a neon matrix by co-depositing Ne/CCl_4 mixtures with neon atoms that have been excited in a microwave discharge. In the present work, the relatively new technique of electron bombardment and subsequent matrix isolation was applied to Rg/dihalomethane mixtures (Rg = Ar, Kr, or Xe). Subsequently-recorded infrared spectra revealed that isodihalomethanes are produced in abundance.

To our knowledge, isodichloromethane and many of the other fragmentation products of ionized dichloromethane have not been observed previously in krypton or xenon matrices. Wavenumber positions of these species in both krypton and xenon are reported here, and spectroscopic assignments are supported by isotopic substitution and photochemical behavior. In addition, the mechanism for the formation of isodichloromethane via the

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dichloromethane radical cation and to that of other neutral and ionic fragmentation products is considered.

2. Experimental Section

The apparatus used in this work has been described in detail elsewhere.[3] Briefly, electrons were accelerated through 300 V between a negatively biased, resistively heated tungsten filament and a positively biased anode that doubled as a Faraday plate to monitor electron current. A premixed gas (1:400 mole ratio rare gas/dihalomethane) was introduced through the gas inlet line that pointed directly at the cold surface. The flow of the gas mixture was controlled by an MKS mass-flow controller, set to 1.6 cm^3/min. Immediately above the surface of the cold window, the gas sample flow was intersected perpendicularly by the electron beam. Ionization products, together with the neutral precursor and excess rare gas, were then co-condensed to form the matrix. Deposition times were typically 8 h.

The CsI substrate was cooled to 15 K by means of an APD Cryogenics Displex closed-cycle helium refrigeration system. Dichloromethane (distilled in glass, 99.8%, Caledon) and other dihalomethanes (99+%, Sigma/Aldrich) were degassed in a series of freeze−pump−thaw cycles. Rare-gas/dihalomethane mixtures were prepared in an all-metal, high-vacuum line. Research-grade argon (>99.9999%), krypton (>99.998%), or xenon gas (>99.995%) were purchased from Matheson Canada.

Fourier transform infrared absorption spectra were recorded at 1 cm^{-1} resolution with 500 scans averaged per spectrum using a Bomem-102 FTIR spectrometer. After the infrared spectrum of the initial deposition was collected, the matrix was exposed to the full (200−1000 nm) or filtered radiation from a xenon arc lamp (450 W) for various periods of time.

3. Results

3.1. CH_2Cl_2 or CD_2Cl_2 in Argon. The infrared spectrum obtained following exposure of CH_2Cl_2 in Ar (1:400) to electron bombardment with subsequent matrix isolation revealed that about 38% of the precursor was destroyed. Under these conditions, numerous new features were also observed (see Table 1 for a summary of assigned bands). When the ratio of CH_2Cl_2 to Ar was changed to 1:600, the decomposition of precursor increased to 46%. Products due to fragmentation of CH_2Cl_2 were relatively more abundant, while those considered as isomerization products and molecular ions of the precursor were relatively less abundant at this lower concentration of CH_2Cl_2.

Some of the most intense product absorptions were in excellent agreement with those previously assigned by Maier et al.[10] to isodichloromethane CH_2ClCl. All of these features decreased in intensity upon irradiation of the matrix with red light filtered from the xenon arc lamp ($\lambda > 550$ nm) for 5 min as can be seen in Figure 1. Similarly, when CD_2Cl_2 was used in place of its H-isotopomer, CD_2ClCl was observed, and it displayed the same behavior upon exposure to light of $\lambda > 550$ nm. Irradiation with light of $\lambda > 550$ nm in both the CH_2Cl_2 and the CD_2Cl_2 experiments produced a slight increase in intensity of the precursor bands that corresponds to back isomerization of isodichloromethane to dichloromethane.

A triplet at 1195, 1193, and 1190 cm^{-1} is assigned to $CCl_2^{\bullet+}$ in excellent agreement with previous studies;[11,17] however, after irradiation for approximately 1 h with $\lambda > 550$ nm, an intensity decrease was observed within this triplet (see Figure 2). The maximum decrease was centered at 1193 cm^{-1}. Following this irradiation, the remaining triplet had a 9:6:1 intensity ratio (Figure 2) characteristic of the dichlorinated species, $CCl_2^{\bullet+}$, and was unresponsive to irradiation with $\lambda > 200$ nm. The band at 1193 cm^{-1} agrees well with that assigned previously to the parent ion $CH_2Cl_2^{\bullet+}$,[11] suggesting a convolution of the feature with the triplet due to $CCl_2^{\bullet+}$.

In the CD_2Cl_2 experiments, the same triplet due to $CCl_2^{\bullet+}$ is observed along with a higher energy absorption at 1197 cm^{-1}. The disappearance of this high-energy band and a decrease in intensity at 1195 cm^{-1} after 1 h irradiation with $\lambda > 550$ nm revealed a 9:6:1 intensity ratio of the 1195, 1193, and 1190 cm^{-1} bands associated with $CCl_2^{\bullet+}$ as in the CH_2Cl_2 experiments. The absence of intensity depletion at 1193 cm^{-1} indicates that this absorption which overlapped with the $CCl_2^{\bullet+}$ absorption in the CH_2Cl_2 experiment has been shifted upon deuteration. A red-light-sensitive band was observed at 897 cm^{-1} in the CD_2Cl_2 experiment and is assigned to the parent cation, which is shifted isotopically from 1193 cm^{-1} in the CH_2Cl_2 experiment. We cannot assign structures to either the 1197 or the 1195 cm^{-1} features, but according to their intensity ratios, they are likely to be due to a species containing one chlorine atom.

Upon destruction of the features associated with isodihalomethane, a feature at 956 cm^{-1} was observed. This band is assigned to the $\nu_1 + \nu_3$ combination band of the bichloride anion $ClHCl^-$.[18] The ν_3 band was also observed at 696 cm^{-1}. The corresponding ν_3 band of $ClDCl^-$ was observed at 464 cm^{-1} in the deuterium experiments.

The bands assigned to $CHCl_2^\bullet$ [9,19] were not affected by irradiation using any of the filters but did increase slightly upon exposure to the full output from the xenon arc lamp. Those assigned to $CHCl_2^+$ [11,21] approximately doubled in intensity upon exposure to 30 min of $\lambda > 300$ nm. Bands assigned previously[11,21] to $CDCl_2^+$ were also observed in the CD_2Cl_2 experiments. We could not assign with certainty any features to the deuterated counterpart[20,21] of the neutral species $CHCl_2^\bullet$.

Bands assigned to $CCl^\bullet$ [22,23] were observed in both the CH_2Cl_2 and the CD_2Cl_2 experiments; bands assigned to HCCl[24] and to the corresponding cation were also observed; however, the deuterated isotopomers were not identified in the CD_2Cl_2 experiments.

In the CD_2Cl_2 experiments, an intense band was observed at 644 cm^{-1} corresponding to Ar_2D^+,[25] yet in the CH_2Cl_2 experiments, no Ar_2H^+ was observed even though it is an expected product, especially given the intensity of the absorption due to the deuterium isotopomer. Precursor bands do, however, interfere with the observation of products in this region of the spectrum.

In the CH_2Cl_2 experiments, two sets of features were observed, one appearing at 2882 and 3108 cm^{-1} and the other appearing at 2903 and 3130 cm^{-1}. The first set diminished in intensity after 30 min irradiation with $\lambda > 300$ nm light and were almost completely destroyed upon irradiation for 30 min with the full output from the lamp (see Figure 3). The second set of features increased slightly in intensity after the $\lambda > 300$ nm irradiation. In the CD_2Cl_2 experiments, a set of features was observed at 2129 and 2061 cm^{-1} corresponding to the 2882 and 3108 cm^{-1} features described above. The CD_2Cl_2 features displayed the same behavior upon irradiation with $\lambda > 300$ nm and the full lamp; in each case, the absorption intensities decreased. These bands have *all* been previously assigned to the complex $(CH_2Cl^+)Cl^\bullet$ or its deuterated isotopomer;[11] however, we question these assignments, and we present an argument below in favor of two different isomers of the molecular cation.

TABLE 1: Species Observed by FTIR following Electron Bombardment and Subsequent Matrix Isolation of CH_2Cl_2 (or CD_2Cl_2) in Ar, Kr, and Xe (1:400)

identity	CH_2Cl_2 in Ar (cm^{-1})	CH_2Cl_2 in Kr[l] (cm^{-1})	CH_2Cl_2 in Xe[l] (cm^{-1})	identity	CD_2Cl_2 in Ar (cm^{-1})	CD_2Cl_2 in Kr[l] (cm^{-1})	CD_2Cl_2 in Xe[l] (cm^{-1})
CH_2Cl-Cl[a]	3144			CD_2Cl-Cl[a]			
	3031				2226		
	3023	3019			2221	2220	2212
	1703						
	1696						
	1561				1224		
	1545	1566			1212		
	1408				1087		
	1405	1405	1402		1084		1082
	967				891		
	958	965			886		
	953				880		
					875		
	772	775	776		610		613
	763				604		
$CH_2Cl_2^{\bullet+}$	1193			$CD_2Cl_2^{\bullet+}$[b]	897		
HClC-Cl-$H^{\bullet+}$[b]	3108			DClC-Cl-$D^{\bullet+}$[b]	2129		
	2882				2061		
$(CH_2Cl^+)Cl^{\bullet}$[b]	3130	3129					
	2903	2912					
$CHCl_2^+$[c,d]	3033			$CDCl_2^+$[d]			
	1291	1283			1127		
					1126		
					1124		
	1050						
	1048						
	1045	1038			865		
	1042	1035					
	1039						
	845						
	841						
	838						
$CHCl_2^{\bullet}$[e]	1225	1222					
	1219						
	901						
	898	NR[m]					
	897	896					
$CCl_2^{\bullet+}$[c]	1195	1197		$CCl_2^{\bullet+}$[c]	1195		
	1193	1194			1193		
	1190	1190			1190		
CCl_2[e,f]	NR	755		CCl_2[e,f]	746	756	
		741				741	
	720				NR		
	718						
$CH_2Cl^{\bullet}$[g,h]	1390			$CD_2Cl^{\bullet}$[g,h]	1046		
	826	827	829		788	791	793
	820	820	824		782	784	786
	396	395	389				
	395	392					
$HCCl^{\bullet+}$	1078						
	1070						
HCCl[f]	1201	1201					
	815	817					
HCl_2^-[i]	956			DCl_2^-[i]	464	438	
	696	664					
$CCl^{\bullet}$[j]	871	866	860	$CCl^{\bullet}$[j]	870	866	860
	865	860	853		865	860	853
Rg_2H^+[k]			1064	Rg_2D^+[k]			
		1009	954			938	752
	NR	854	844			772	635
			732		644	607	517

[a] Ref 10. [b] This work. [c] Ref 11. [d] Ref 21. [e] Ref 19. [f] Ref 24. [g] Ref 22. [h] Ref 26. [i] Ref 18. [j] Ref 23. [k] Ref 25. [l] Wavenumber values for species in Kr and Xe matrices are from this work except for the proton bound dimers of Cl^- (see ref 18) and the proton bound dimers of the rare gases (see ref 25). [m] NR, not resolvable due to interference from precursor.

3.2. CH_2Cl_2 or CD_2Cl_2 in Krypton. In Table 1 are listed the new features observed after EBMI of 1:400 mixtures of CH_2Cl_2 or CD_2Cl_2 in krypton. Five absorption bands corresponding to isodichloromethane were observed, although with lower intensity than in the argon experiments. These bands displayed the same behavior as those in the argon experiments on exposure to $\lambda > 550$ nm in that they were unstable.

As is shown in Table 1, it was possible to assign features to many of the same species as were observed in the argon experiments. As in the argon experiments, a set of features was

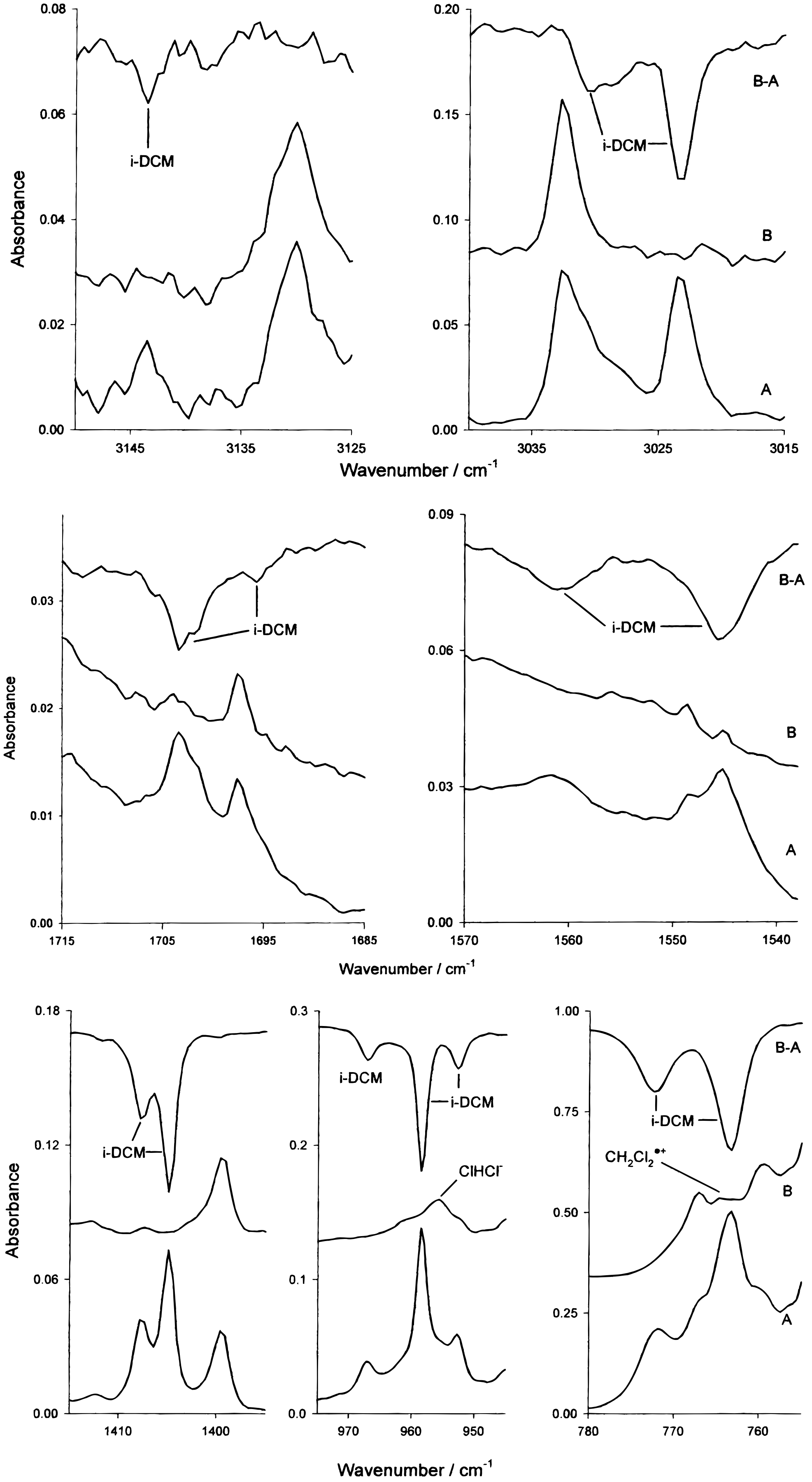


Figure 1. Portions of the infrared spectra recorded (A) after 8 h electron bombardment and subsequent matrix isolation of a 1:400 mixture of CH_2Cl_2:Ar and (B) following 5 min irradiation with red light $\lambda > 550$ nm. The top trace (B−A) is the difference spectrum obtained by subtraction of the EBMI spectrum (A) from the irradiation spectrum (B).

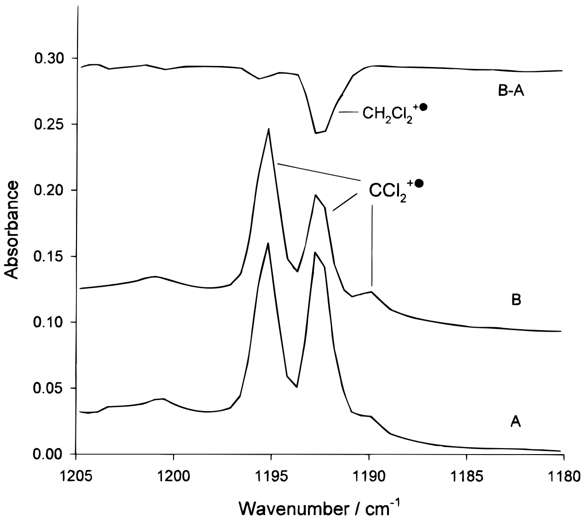


Figure 2. Portion of the infrared spectrum in the region of the $CCl_2^{•+}$ asymmetric stretch showing a red-light-sensitive band at 1193 cm^{-1}. Trace A was recorded following 8 h EBMI of a 1:400 mixture of CH_2Cl_2:Ar, trace B was recorded after 55 min irradiation with light $\lambda > 550$ nm, and the top trace is the difference spectrum (B−A).

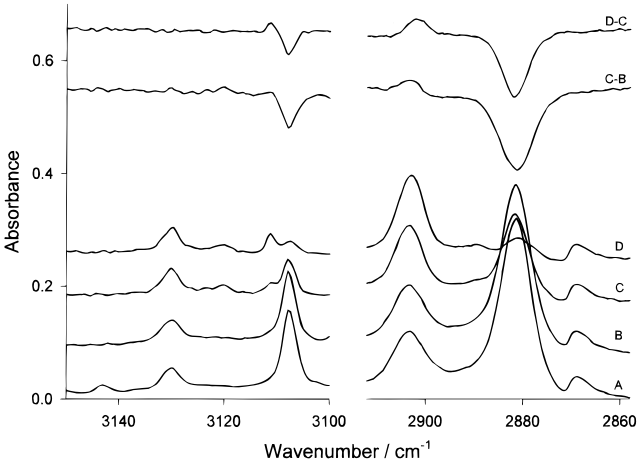


Figure 3. Portions of the infrared spectrum taken in the 3150−2850 cm^{-1} region recorded (A) after 8 h electron bombardment and subsequent matrix isolation of a 1:400 mixture of CH_2Cl_2:Ar, (B) after 55 min irradiation with light $\lambda > 550$ nm, (C) after 30 min irradiation with light $\lambda > 300$, and (D) after 30 min irradiation with the full output of the lamp ($\lambda > 200$ nm). Also shown are the difference spectra (D−C) and (C−B).

observed at 3129 and 2912 cm^{-1} when CH_2Cl_2 was the precursor. These bands correspond well with one of the sets of features previously assigned to $(CH_2Cl^+)Cl^•$; however, these bands were unstable to exposure with $\lambda > 300$ and 200 nm, and no growth of features was observed. No corresponding features could be identified in the CD_2Cl_2 experiments.

3.3. CH_2Cl_2 or CD_2Cl_2 in Xenon. Because of the behavior of CH_2Cl_2 or CD_2Cl_2 on exposure of the matrix to irradiation with red light, it was possible to assign a few bands to both isotopomers of isodichloromethane in a Xe matrix (Table 1). The only other bands identifiable in the matrix were those corresponding to $CH_2Cl^•$,[26] $CCl^•$,[23] and Xe_2H^+ (Xe_2D^+ when CD_2Cl_2 was the precursor).[25]

3.4. CH_2ClBr in Argon. In Table 2 are listed the products formed by electron bombardment of CH_2ClBr (Ar/CH_2ClBr = 400/1). The red light photosensitivity of the absorbing group composed of 1390, 1380, 931, 923, 725, and 714 cm^{-1} and the excellent agreement with those bands assigned previously by Maier et al.[10] allow the assignment of these bands to isobromochloromethane, CH_2Cl-Br, with confidence. The identification of each of $CHClBr^+$, $CHClBr^•$, $CClBr^{•+}$, and CClBr was made based upon the results of previous work.[11,27]

TABLE 2: Infrared Absorption of Matrix-Isolated Products of Electron Bombardment of CH_2ClBr in Ar

identity	wavenumber (cm^{-1})
CH_2Cl-Br[a]	1389
	1380
	931
	923
	725
	714
$(CH_2Cl^+)Br^•$ or $(CH_2Br^+)Cl^•$ [b]	3119
	2930
	2928
	2915
	2912
$CHClBr^+$ [c]	993
	988
$CHClBr^•$ [d]	1195
	866
$CClBr^{•+}$ [e]	1121
	1111
CClBr[c]	744
	612

[a] Ref 10. [b] Ref 9. [c] Ref 9. [d] Ref 19. [e] Ref 11.

CH_2Cl^+ is a prominent fragment cation common to the mass spectra of CH_2Cl_2 and CH_2ClBr. Therefore, a search for new absorption features common with the spectrum of CH_2Cl_2 was carried out in the C−H and C−Cl stretching region of CH_2Cl^+. However, following irradiation with red light, no new photosensitive bands were detected except for those corresponding to common products such as $CCl^•$. Further irradiation with 220−1000 nm for 30 min revealed one shared and unassigned feature at 2869 cm^{-1}, which was reduced to 70% of its original intensity. This feature remains unassigned.

Other features of interest in the C−H stretching region are the 3119 cm^{-1} band, a doublet at 2930 and 2928 cm^{-1}, and a doublet at 2915 and 2912 cm^{-1}, all of which showed sensitivity to irradiation with $\lambda > 300$ nm. These bands have been proposed to be absorptions due to $(H_2CCl^+)Br^•$ or $(H_2CBr^+)Cl^•$.[9]

3.5. Mixtures of CH_2Cl_2 and CH_2Br_2 in Argon. Intermolecular halogen exchange processes are possible mechanisms for the formation of isodihalomethanes in these experiments. Therefore, we tested for the presence of such processes by bombarding three mixtures of CH_2Cl_2 and CH_2Br_2 that were prepared with different mole ratios initially (CH_2Cl_2:CH_2Br_2 = 1:1, 1:2, or 2:1) and diluted with Ar to achieve a molar ratio of R:Ar = 1:400 (R = CH_2Cl_2 + CH_2Br_2). The composition of each IR spectrum obtained following electron bombardment was very similar to that of a synthesized spectrum obtained by simple addition of the individual spectra of pure CH_2Cl_2 and pure CH_2Br_2 in Ar. The absorption features corresponding to isodichloromethane and isodibromomethane as well as to the conventional fragment ions, such as $CHCl_2^+$, $CCl_2^{•+}$ or $CHBr_2^+$, and $CBr_2^{•+}$, were easily identified on the basis of previous work. No absorption bands could be assigned to isobromochloromethane, CH_2ClBr, or CH_2BrCl, that is, to scrambled products of the mixture of CH_2Cl_2 and CH_2Br_2 (see Figure 4).

3.6. EBMI of Pure Rare Gases above Dichloromethane-Doped Matrices. Isomerization of dihalomethanes by vacuum−UV (V−UV) light is now a well-known process.[10] Given that electron bombardment of rare gases may give rise to V−UV emission, the contribution of such V−UV irradiation to the

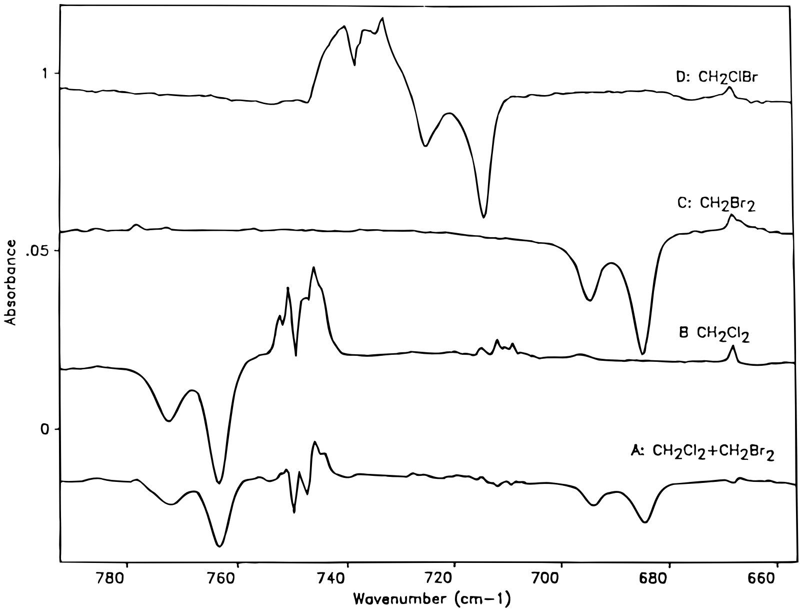


Figure 4. Portion of the infrared spectra recorded in the CH_2 wag region of isodihalomethanes of the matrices formed after electron bombardment matrix isolation of 1:400 mixtures of various dihalomethanes in argon. Each IR spectrum shown is the net difference spectrum obtained by subtracting the initial spectrum from that recorded after red light irradiation. (A) mixture of CH_2Cl_2 and CH_2Br_2, (B) CH_2Cl_2, (C) CH_2Br_2, and (D) CH_2ClBr (bromochloromethane).

isomerization process under the present ionization conditions was investigated.

An Ar/CH_2Cl_2 matrix was prepared as in the previous experiments, except without the electron source, and an infrared spectrum of the resulting matrix was recorded. Following electron bombardment of pure krypton, originating from a separate bulb directly above the Ar/CH_2Cl_2 matrix, a second infrared spectrum was obtained that revealed no products or destruction of dichloromethane. The same null result was observed when pure argon was submitted to electron bombardment above a Kr/CH_2Cl_2 matrix. These results show conclusively that irradiation by resonant emission from excited rare-gas atoms is not significant in either the destruction of dichloromethane or the production of isodichloromethane.

When pure argon was ionized directly above an Ar/CH_2Cl_2 matrix, a small amount of isodichloromethane was observed. The intensities of the 772 and 763 cm^{-1} absorptions of isodichloromethane were less than 3% of the same features observed by conventional EBMI of dichloromethane/Ar mixtures as described in section 3.1. No other absorptions were observed. The small amount of isodichloromethane observed is likely due to argon cations impinging on the dichloromethane-doped matrix. It is expected that the charge would be easily transferred to an argon host atom where dichloromethane could be ionized and subsequently undergo isomerization. The ion would then be subsequently neutralized by recombination with a low-energy electron or by some other process. The insignificant destruction of dichloromethane precursor in these experiments is evidence that the condensed-phase chemistry is not very important.

4. Discussion

The results of the present study offer some interesting insights into the processes that accompany electron bombardment of dihalomethane/rare-gas mixtures and illustrate the general utility of matrix-isolation techniques in complementing gas-phase ion chemistry studies. Various fragment ion products such as $CHCl_2^+$ and $CCl_2^{\bullet+}$ are observed, as expected, from mass spectrometric studies. In addition, several neutral products such as $CHCl_2^\bullet$ and CCl_2 are observed and whose presence has largely been inferred in previous mass spectrometric work.

4.1. Ionization. There has been some discussion as to whether the products observed in these EBMI experiments are due either to isomerization or to decomposition of an electronically excited neutral precursor. This excited neutral could be the product of collisions between metastable rare-gas atoms Rg* (which have lifetimes of ∼1 s in the gas phase[28]) and the ground-state neutral precursor. The fact that many ions are observed in the dichloromethane experiments indicates that ion chemistry is an important contributor in these experiments. Furthermore, the fact that the current measured at the anode increases by 2 orders of magnitude when the gas flow begins also suggests that ionization is occurring. Rare-gas cations formed by EI have infinite lifetimes in the absence of a molecule with a lower ionization potential than that of the rare gas, whereas the excited states of neutral rare-gas atoms are relatively short-lived. As well, the observation of some isomeric species such as 1-propen-2-ol[1] and various isotopomers of decomposition products of CD_3OH[2] are best explained by neutral base-catalyzed hydrogen shifts of the corresponding radical cation.[29]

The most compelling evidence that the observed chemistry occurs on an ionic potential energy surface is obtained by comparing the results of the EBMI experiments conducted with each of the three diluent rare-gas systems, CH_2Cl_2 in Ar, Kr, or Xe. The magnitude of the ionization potential of CH_2Cl_2 (11.32 eV) lies between the excitation energies of the first excited states of neutral Ar (11.72 and 11.55 eV) and those of neutral Kr (10.56 and 9.92 eV). Collisions with neutral Ar metastables would result in ionization of dichloromethane; however, collisions with Kr or Xe (9.54 and 8.32 eV for Xe) metastables would not produce ions. Since similar products are observed after EBMI of Ar/CH_2Cl_2, Kr/CH_2Cl_2, or Xe/CH_2Cl_2, it can only be concluded that the chemistry observed results from charge-exchange collisions between $Rg^{\bullet+}$ and CH_2Cl_2. Although excited neutral chemistry cannot be ruled out, it is safe to say that, on the basis of the indirect evidence provided above, the initial step in the process is only consistent with charge-transfer ionization of the neutral precursor.

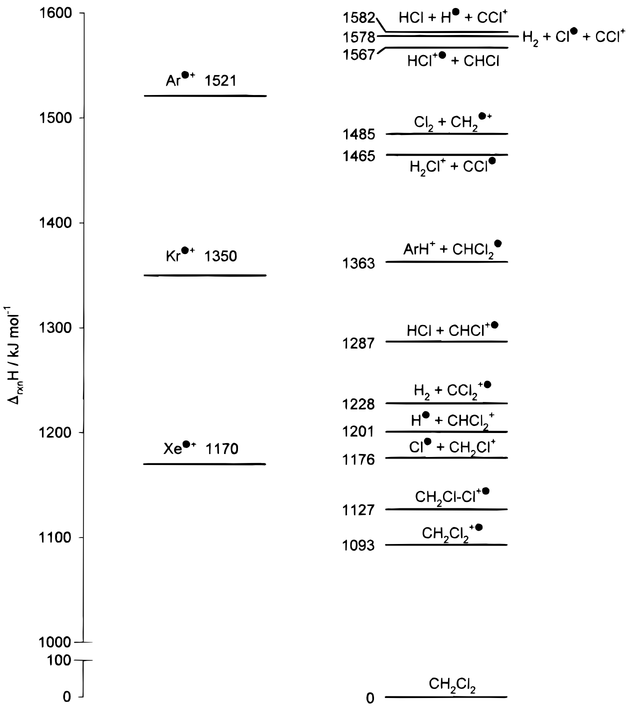


Figure 5. Schematic energy level diagram showing the ionization energy of the rare gases as well as the energy of relevant isomerization and decomposition products of the dichloromethane radical cation. All energies are relative to neutral dichloromethane, and all thermodynamic quantities were taken from refs 36 and 37 except that for which was taken from ref 30.

The presence of excess rare gases in the gas mixtures makes the charge-exchange reaction of CH_2Cl_2 with $Rg^{\bullet+}$ the most likely route to CH_2Cl_2 ionization, rather than direct EI ionization of CH_2Cl_2. Following ionization of CH_2Cl_2 by this route, the accessible decomposition pathways are limited by the difference between the ionization energy (IE) of CH_2Cl_2 and the $Rg^{\bullet+}$ cation−electron recombination energy. In Figure 5 are displayed the relevant thermochemical relationships for the CE reaction of the rare-gas cations and dichloromethane. It is clear that with $Ar^{\bullet+}$ as the charge-exchange agent most of the decomposition pathways of $CH_2Cl_2^{\bullet+}$ are accessible. However, with $Kr^{\bullet+}$ and $Xe^{\bullet+}$ as the charge-exchange agents, the range of decomposition pathways should be reduced progressively, as is apparent from Figure 5; this conclusion is supported by the experimental observations listed in Table 1.

The presence of HCCl in the argon and krypton experiments can only be explained if one considers neutralization of $HCCl^{\bullet+}$ in the argon or krypton matrix since there is insufficient energy available to produce the neutral by loss of $HCl^{\bullet+}$ when the parent cation is formed by charge exchange with $Ar^{\bullet+}$ or $Kr^{\bullet+}$. As expected, neither the neutral nor the cation is observed in the xenon experiments. This is consistent with charge exchange between $Xe^{\bullet+}$ and CH_2Cl_2 as the ionization step in the mechanism as there would be not enough energy for the parent cation to decompose forming $HCCl^{\bullet+}$.

$CH_2Cl^{\bullet}$ is not expected in any of the experiments, but evidence for its presence is observed in all three rare-gas systems. The cation is expected since it is the major product observed in mass spectrometry experiments. The observed neutral may be a product of CH_2Cl^{+} or $(CH_2Cl^{+})Cl^{\bullet}$ neutralization in the matrix. The absence of spectral features assignable to the cation is puzzling, but its infrared spectrum has never been observed in matrix experiments or in the gas phase. Considering that this cation is a major product of dichloromethane radical cation decomposition, its absence is either due to its extremely weak infrared absorptions or to the very efficient neutralization of this species in rare-gas matrices. On the basis of only arguments in section 4.7, the former explanation is consistent. However, the fact that the neutral counterpart is observed is more likely due to the adiabatic electron affinity of CH_2Cl^{+} being considerably higher than the accepted adiabatic ionization potential of the corresponding neutral, resulting in an exothermic neutralization of CH_2Cl^{+} in the argon matrix (see section 4.7).

The presence of $CCl^{\bullet}$ in the xenon experiments is difficult to explain except perhaps due to some direct EI ionization of dichloromethane. In the case of 300 eV EI ionization, the $CCl^{\bullet}$ fragment could be expected on thermodynamic grounds.

4.2. Isodichloromethane, CH_2Cl-Cl. The intense absorptions assigned to isodichloromethane, formed through electron bombardment of CH_2Cl_2 in Ar, have wavenumbers in excellent agreement with the fundamental absorptions of the same species obtained through photoionization of matrix-isolated dichloromethane.[10] The known instability of this species upon exposure to radiation with wavelengths corresponding to one of its UV−visible absorptions at 620 nm was verified in that the IR absorption bands were completely removed by irradiation with light of $\lambda > 590$ nm. Evidence for the back-isomerization reaction is provided by the modest increase in intensity of CH_2Cl_2 absorption. The deuterium isotope experiments confirmed the assignments made to isodichloromethane. Identification of isodibromomethane and isobromochloromethane was also made based on their photochemical behavior and previous assignments.[10]

Wavenumbers of several of the absorptions due to both isotopomers of isodichloromethane in Kr or Xe matrices (Table 1) have also been determined. The wavenumbers of these absorptions show differing shifts depending upon the mode of vibration. For example, the absorptions due to the CH_2 wag and the CCl stretch all show blue shifts on switching the matrix medium from Ar to Kr to Xe. The symmetric CH stretch shows a normal slight red shift over the same medium series. The CH_2 scissors mode, however, shows a blue shift on going from Ar to Kr but shows a red shift in Xe. The differences observed in the CH_2 scissors mode may be due to different trapping environments within the different matrices.

It should be noted that most of the bands due to isodichloromethane observed in argon and reported in Table 1 are due to site splitting. The absence of many of these bands in the krypton experiments may be a result of fewer trapping sites in the krypton matrix.

In experiments in which both CH_2Cl_2 and CH_2Br_2 were used as precursors and diluted in the same argon mixture, no features were observed that were attributable to the mixed isodihalomethane species (Figure 4), even though they are well-characterized products of CH_2ClBr V−UV photolysis[10] and of our electron bombardment matrix-isolation experiments using CH_2ClBr as the precursor. The absence of halogen scrambling in the electron bombardment of mixtures of dichloro- and dibromomethane clearly shows that the isomerization process is intramolecular. Such observations are incompatible with a mechanism involving dissociation of a halogen atom from the parent ion, followed by recombination with a $CH_2X^{\bullet}$ fragment, either neutral or cationic.

The formation of the isodihalomethanes, therefore, is most certainly via isomerization of either the cation $CH_2X_2^{\bullet+}$ or of the neutral CH_2X_2. Isomerization of the neutral would require significant energy input, either from nonionizing EI, collisions with rare-gas metastables, or electron−$CH_2Cl_2^{\bullet+}$ recombination. These processes, however, would initially produce an excited neutral with a minimum of some 6 eV excess energy above the isomerization barrier[30] that would, in the gas phase, result in rapid dissociation rather than isomerization. Photoinduced isomerization of the matrix-isolated precursor by resonant emission of rare-gas metastables is ruled out for reasons outlined in section 3.6. That the isodichloromethane absorptions arose in experiments involving electron bombardment of Ar as well as of Kr and Xe suggests that the formation of the dichloromethane cation via a charge-exchange collision between the rare-gas cation and the dichloromethane is a prerequisite for the formation of neutral isodichloromethane.

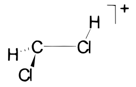
It has been observed that when the amount of precursor in the initial gas mixture was decreased, there is a relative increase in fragmentation products, a relative decrease in isodichloromethane, and a decrease in the amount of precursor. Following charge exchange with $Ar^{\bullet+}$, the newly formed isomer would have approximately 4.5 eV of excess energy. Collisions with other precursor molecules would effectively quench internal energy. Quenching processes in these gas-phase electron bombardment matrix-isolation experiments have been examined in a recent communication[3] and are consistent with such a process being active in this work.

The observation of neutral isodichloromethane in the context of isomerization of the radical cation requires a subsequent neutralization of the latter. It is reasonable to propose that the neutralization step should occur following isolation of the isomerized cation in the solid matrix. This is because the energy that would be associated with electron capture of a free electron in the gas phase would be close in magnitude to the ionization energy of CH_2Cl_2. The barrier to back isomerization or decomposition of neutral isodichloromethane is not likely to be nearly as large as this, such that gas-phase neutralization would be expected to result in rapid and highly exothermic dissociation of the newly born neutral molecule. Neutralization in the cryogenic matrix solid would give the greatest probability of effective electron−cation recombination and stabilization of neutrals formed in this way. Such a series of steps, ionization−isomerization−isolation−neutralization −stabilization, has also been proposed for the isomerization of acetone to 1-propen-2-ol.[1]

4.3. Barrier for $CH_2Cl_2^{\bullet+}$ to $CH_2ClCl^{\bullet+}$ Isomerization. The positions of $CH_2Cl_2^{\bullet+}$ and $CH_2Cl\text{-}Cl^{\bullet+}$ in the energy level diagram shown in Figure 5 and the fact that isodichloromethane is observed in xenon, allows one to put an upper limit on the barrier for $CH_2Cl_2^{\bullet+}$ to $CH_2ClCl^{\bullet+}$ isomerization of about 78 kJ mol^{-1} and an upper limit on the reverse barrier of 43 kJ mol^{-1}. This follows since the maximum internal energy available to $CH_2Cl_2^{\bullet+}$ is determined by the electron affinity of $Xe^{\bullet+}$. This barrier has not been determined experimentally, and theoretical attempts to estimate its value[30] have been unsuccessful.

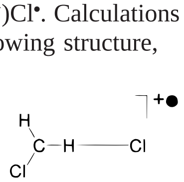
4.4. Isomers of the Molecular Cation. The presence of an absorbing species other than $CCl_2^{\bullet+}$ responsible for overlapping the band at 1193 cm^{-1} was easily confirmed due to the restoration upon irradiation with red light of the natural isotopic abundance ratio of the triplet at 1195 cm^{-1} associated with $CCl_2^{\bullet+}$. (The maximum depletion was centered at 1193 cm^{-1}.) The absence of depletion at 1193 cm^{-1} when CD_2Cl_2 was employed confirms that the absorption is associated with a vibrational mode involving hydrogen nuclei motion. The band in question observed at 1193 cm^{-1} was first assigned to CH_2 wag of the parent cation $CH_2Cl_2^{\bullet+}$ by Andrews et al.[9] since it was essentially destroyed by irradiation with $\lambda > 550$ nm, which is the typical but not distinctive photochemical behavior of trapped ionic species. Andrews et al. also assigned an absorption near 763.4 cm^{-1} to $CH_2Cl_2^{\bullet+}$;[9,11] however, this band is in excellent agreement with that assigned and confirmed by deuterium experiments and ab initio calculations to be due to isodichloromethane.[10] In accord with this reassignment, the relative intensity of the 764 and 1193 cm^{-1} absorptions was found in the present work to vary significantly with gaseous sample flow rate, indicating that they are indeed associated with different carriers. The band at 897 cm^{-1} in the CD_2Cl_2 experiments, tentatively assigned to $CD_2Cl_2^{\bullet+}$, also displays the same instability toward exposure to red light. Our DFT calculations predict features at 1195.3 cm^{-1} for $CH_2Cl_2^{\bullet+}$ and at 862.0 cm^{-1} for $CD_2Cl_2^{+}$ in fairly close agreement to the observed bands. It is interesting and important to note that the intense absorptions observed in early photolysis studies of matrix-isolated methylene halides[9,11] at 764 cm^{-1} and both 605 and 611 cm^{-1} and assigned to $CH_2Cl_2^{\bullet+}$ and $CD_2Cl_2^{\bullet+}$, respectively, have been reassigned to isodichloromethane.[10]

The previous assignments of bands observed in this work at 3108 and 2882 cm^{-1} (which we denote bands A) in the CH_2Cl_2 experiments and 2129 and 2061 cm^{-1} (denoted bands B) in the CD_2Cl_2 experiments to a complex between $Cl^{\bullet}$ and CH_2Cl^{+}, $(CH_2Cl^{+})Cl^{\bullet}$, are questionable since the second band in each pair above resembles closely the fundamental infrared absorptions of HCl and DCl at 2888.0 and 2089.0 cm^{-1}, respectively, in argon matrices.[31] The species responsible for the bands is most likely HCl complexed with another matrix-isolated species. It will now be argued that the species to which HCl is complexed is $CClH^{\bullet+}$ and that the bands in question are due to an isomer of the molecular cation with the following structure that resembles a distonic isomer of the dichloromethane radical cation in which one of the resonance structures would formally have the charge on Cl (of the HCl moiety) and carbon would be the radical center. This species is denoted $HClC^{\bullet+}$−ClH in the text.



Note that in the proposed structure, it is the chlorine of HCl that is connected to the carbon of $CClH^{\bullet+}$.

The two sets of bands A and B are reduced in intensity on irradiation with light of $\lambda > 300$ nm and are completely destroyed on irradiation with light of $\lambda > 200$ nm. In the CH_2Cl_2 experiments, the depletion of the A bands on 300 nm irradiation may be correlated with an increase in intensity of bands at 2903 and 3130 cm^{-1}, which have also been previously assigned[11] to $(CH_2Cl^{+})Cl^{\bullet}$. Calculations by Lewars[30] on $(CH_2Cl^{+})Cl^{\bullet}$, with the following structure,



predict the two most intense absorptions to be at 2984 and 3125 cm^{-1}, in good agreement with the observed wavenumber positions. The observed photochemistry and the fact that the A bands do not lose any intensity under conditions in which there is an increase in the intensity of the 2903 and 3130 cm^{-1} bands in annealing experiments suggest that the two species are isomeric rather than the same species in different matrix sites.

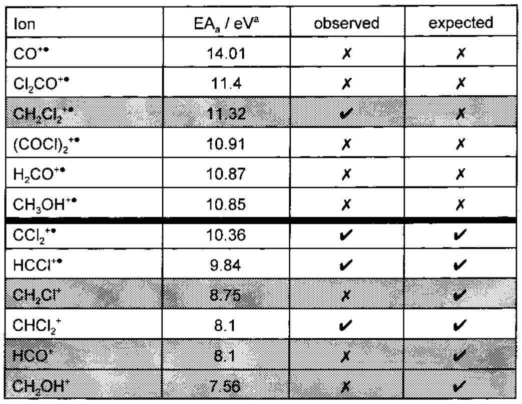
We are fairly confident that the isomer of the molecular cation responsible for the A bands is neutral HCl complexed with $CClH^{\bullet+}$ rather than the charge being on HCl, since the ionization energy of HCl is much higher than CClH and since the H−Cl stretch of $HCl^{\bullet+}$ occurs at a much lower wavenumber value (2543.8 cm^{-1} in a neon matrix[32]). In studies in which HCl was complexed with neutral nonpolar species such as Ar, H_2, and N_2,[33] the HCl stretch was found to be red shifted by 2.9, 2.4, and 12.3 cm^{-1} from the band center in solid neon. These are fairly large shifts compared to the 1.8-cm^{-1} shift observed for HCl complexed with O_2.[33] The difference is because Ar, H_2, and N_2 are attached to HCl through hydrogen, whereas O_2 is "bound" to chlorine. When a mildly polar molecule such as NO[34] and a very polar molecule such as H_2O[33] are bound to the hydrogen of HCl, the shift in the H−Cl stretch increases dramatically, 56.7 and 195.7 cm^{-1} red shifts, respectively, in solid neon. As the bands observed in this work are shifted only slightly from the noncomplexed HCl stretch in solid argon, we conclude that, if HCl is complexed to a charged species, it is bonded via chlorine and not via hydrogen. On the basis of these arguments and the observation leading to the conclusion that the species responsible for the A bands is an isomer of the molecular cation (see above), we propose that the structure of the absorber responsible for the A bands is a cation with the structure $HClC^{\bullet+}-$ ClH and that the B bands in the CD_2Cl_2 experiments are due to its deuterated isotopomer.

The calculations by Lewars[30] predict such a species resembling HCl bound to $CClH^{\bullet+}$ on the $CH_2Cl_2^{\bullet+}$ potential energy hypersurface. However, the MP2(FC)/6-31G*-computed infrared spectrum predicts an intense absorption assigned to the H−Cl stretch at 2689 cm^{-1}, almost 200 cm^{-1} lower than the observed band, while the C−H stretch, observed at 3108 cm^{-1}, is predicted to absorb at 3107 cm^{-1}. Calculations performed by us at the B3LYP/6-31G** level and basis set closely agree with these calculations. We suggest, however, that the calculations overestimate the C−Cl bond strength or that the matrix-isolated species is perturbed somewhat, resulting in a longer C−Cl bond.

The fragment ion CH_2X^+ is the dominant decomposition product in both conventional EI or CE reaction mass spectrometric studies, as discussed above. However, in earlier photoionization experiments of dichloromethane isolated in Ar matrices, the species CH_2Cl^+ was not observed; rather, the ion complex $(CH_2Cl^+)Cl^\bullet$ was observed. This latter species was thought to be produced from a matrix-induced recombination process in which both CH_2Cl^+ and $Cl^\bullet$ are trapped in the same matrix site due to the inability of chlorine atom to migrate appreciably in the rigid cryogenic matrix. In the present work, only the complex is observed. No new feature growing on destruction of this complex could be assigned to CH_2Cl^+, likely for reasons discussed below.

4.5. $CHCl_2^+$ and $CHCl_2^\bullet$. The absorptions due to the $CHCl_2^+$ daughter ion were first identified in $CHCl_3$ matrix photoionization experiments.[21] Andrews et al.[35] later showed those absorptions to be due to the $(CHCl_2^+)Cl^\bullet$ complex, which gave absorptions shifted to slightly lower wavenumber than those of the isolated $CHCl_2^+$ cation prepared from $CHCl_2^\bullet$.[9] The EBMI experiments presented here produced quite a large yield of $CHCl_2^+$, likely due to $H^\bullet$ loss from its precursor through the CE reaction with $Ar^{\bullet+}$. The increase in intensity of the bands associated with this cation on exposure to $\lambda > 300$ nm radiation correlates well with the decrease in intensity of the bands at 3108 and 2882 cm^{-1}, which also supports the assignment of these bands to the complex $HClC^{\bullet+}-ClH$ if the photochemical behavior is thought of as loss of hydrogen atom to produce $CHCl_2^+$.

TABLE 3: Ions That May Be Expected To Be Present in Argon Matrices on Decomposition of Oxalyl Chloride Radical Cation, Dichloromethane Radical Cation, and Methanol Radical Cation following Electron Bombardment



Ion	EA_a / eV[a]	observed	expected
$CO^{+\bullet}$	14.01	✗	✗
$Cl_2CO^{+\bullet}$	11.4	✗	✗
$CH_2Cl_2^{+\bullet}$	11.32	✔	✗
$(COCl)_2^{+\bullet}$	10.91	✗	✗
$H_2CO^{+\bullet}$	10.87	✗	✗
$CH_3OH^{+\bullet}$	10.85	✗	✗
$CCl_2^{+\bullet}$	10.36	✔	✔
$HCCl^{+\bullet}$	9.84	✔	✔
CH_2Cl^+	8.75	✗	✔
$CHCl_2^+$	8.1	✔	✔
HCO^+	8.1	✗	✔
CH_2OH^+	7.56	✗	✔

[a] Refs 36 and 37, the EA_a values are taken to be the same as the IP_a of the corresponding neutral, which may be in error if the IP_a values are actually vertical and may explain the absence of CH_2Cl^+, HCO^+, and CH_2OH^+. [b] Shaded rows indicate species that do not follow the "5 eV rule" (see text).

The neutral species $CHCl_2^\bullet$ was characterized by both its strong absorption in the C−Cl antisymmetric stretching region, which occurred at 901, 898, and 897 cm^{-1}, and its CHCl deformation at 1225 and 1219 cm^{-1}. The growth of the bands due to the neutral after irradiation with the full output of the xenon arc and the depletion of the bands associated with $HClC-Cl-H^{\bullet+}$ may be related by loss of H^+ or, more likely, loss of H *and* subsequent photochemically induced charge transfer from the matrix or impurity to produce the neutral radical.

Although the neutral deuterated isotopomer was not observed, the $CDCl_2^+$ cation was observed. The relationships between the bands associated with $CDCl_2^+$ and $DClC-Cl-D^{\bullet+}$ similar to that described above for the hydrogen isotopomers were observed.

4.6. Anions. In the experiment with CH_2Cl_2, absorptions due to only one negatively charged species was observed, $ClHCl^-$. However, because of the number and intensity of bands associated with cationic species, it is expected that there may be other anions present such as Cl^- to maintain charge neutrality within the matrix.

4.7. Why Are Some Ions Trapped in Ar Matrices and Not Others? Presented in Table 3 are the adiabatic electron affinities of the various cations that may be expected from the decomposition of the dichloromethane, oxalyl chloride, and methanol radical cations. These adiabatic electron affinities are based on the adiabatic ionization potentials given in Lias et al.[36,37]

Knight et al.[38] have observed that any attempts to isolate cations were unsuccessful when there was less than ~5 eV difference between the ionization potential of the matrix substrate atom and the electron affinity of the cation in question. Utilizing the observed 5 eV difference, ions with an electron affinity greater than ~10.8 eV (IP(Ar) = 15.76 eV) are not expected to be observed in an argon matrix, but those with electron affinities less than ~10.8 eV would be expected. On this basis, those ions that are expected to be observed in the argon matrix are so noted in the last column of Table 3. In the second last column, whether these cations were observed in these experiments or in experiments performed in this laboratory and reported in earlier communications[2,3] is noted.

At this point, before discussing the exceptions indicated in Table 3, it may be quite beneficial to provide an explanation for the "5 eV rule" since to our knowledge none has been offered previously.

Consider the charge-exchange reaction between an isolated cation (C^+) and the argon matrix, denoted Ar_n,

$$C^+ + Ar_n \rightarrow C + Ar_n^{\ +} \qquad (1)$$

The enthalpy change for this reaction can be written in terms of the heats of formation of the species

$$\Delta_r H = [\Delta_f H(C) - \Delta_f H(C^+)] + [\Delta_f H(Ar_n^{\ +}) - \Delta_f H(Ar_n)] \qquad (2)$$

The first set of brackets represents the negative of the adiabatic electron affinity of the cation $EA_a(C^+)$ (the adiabatic electron gain energy), while the second set of brackets represents the adiabatic ionization potential of the solid argon matrix $IP_a(Ar_n)$. Equation 2 can therefore be rewritten as follows:

$$\Delta_r H = IP_a(Ar_n) - EA_a(C^+) \qquad (3)$$

For the charge-transfer reaction denoted by eq 1 to be thermodynamically possible and recognizing that only cations with adiabatic electron affinities of roughly 10.8 eV are observed, the ionization potential of the host argon matrix would need to be roughly 10.8 eV. In fact, the onset of the photoemission from pure solid argon is 13.9 eV.[39] The charge-exchange reaction denoted by eq 1 would still be endothermic by approximately 3.1 eV for cations with electron affinities of about 10.8 eV. However, note that the matrix in which the cations are embedded is not composed of pure argon but is doped with various organic neutrals, anions, and cations with (except for the latter) ionization potentials lower than that of argon atoms. The effect of these dopants would be to decrease the effective ionization potential of the matrix or, in other words, to decrease $IP(Ar_n)$ such that cations with electron affinities of ∼10.8 eV (rather than 13.9 eV) may be neutralized in the matrix. The effect of dopants on band gaps and photelectron emissions of rare-gas solids has been studied in detail. Because of the substantially higher polarizability of the dopant, doping argon solids with 1% Kr or 0.3% Xe results in a decrease of the photoemission onset to 12.2 and 10.2 eV, respectively.[40,41] Similarly, a matrix doped with small amounts of benzene was shown to begin emitting electrons when photons corresponding to 8.4 eV radiated on the solid.[40] Thus, it can be seen that cations of high electron affinity may not be stabilized readily in rare-gas solids such as argon containing impurity molecules due to charge exchange with the matrix.

The cations that are not observed to conform to the “5 eV rule” are highlighted in Table 3. $CH_2Cl_2^{\bullet+}$ is not expected since it has a relatively large electron affinity. The bands assigned to this cation may be misassigned, or more likely the EA_a’s based on IP_a’s compiled in refs 36 and 37 are in error and the adiabatic electron affinity of $CH_2Cl_2^{\bullet+}$ is too high. CH_2Cl^+, HCO^+, and CH_2OH^+ are expected but are not observed. The only firm spectroscopic characterization of the formyl cation comes from NMR[42] and ESR spectra.[38] A very broad and extremely weak infrared absorption has been assigned to the formyl cation[42] at about 2100 cm^{-1}, but the species cannot be described as a free cation since it was observed in the presence of approximately 28 atm of CO and the strongest known superacid, HF-SbF_5. Similarly elusive in the infrared has been CH_2Cl^+ despite numerous attempts under ionizing conditions and despite it being the lowest-energy decomposition product of the dichloromethane radical cation. It can only be concluded, therefore, that these species are present but in quantities that are not observable by the relatively insensitive infrared spectroscopy or that the EA_a’s for these species which are based on IP_a’s compiled in refs 36 and 37 are too low.

5. Conclusions

We have shown here that among the products isolated in cryogenic matrices formed on gas-phase electron bombardment of dihalomethane/rare-gas mixtures are the neutral isodihalaomethanes. These isomers are believed to be formed by an initial charge-exchange ionization reaction between rare-gas cations and dihalomethane followed by intramolecular isomerization and neutralization. All processes are believed to occur in the gas phase except the neutralization step, which most likely occurs following matrix isolation. Similarly, bands associated with two different isomers of the dichloromethane radical cation, $HClC^{\bullet+}{-}ClH$ and $(CH_2Cl^+)Cl^\bullet$, have been assigned. The observation of both cationic and neutral forms of decomposition products when different diluent gases are utilized in this work illustrates the power of the electron bombardment/matrix-isolation technique for interpretation of gas-phase ion isomerization and decomposition processes.

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