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Ionic and neutral decomposition of gaseous bromochloromethanes

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The ionization potentials for CCl_4 , CCl_3Br , CBr_2Cl_2 , CBr_4 , CCl_3 , and CBr_3 have been measured using electron impact techniques. These numbers have been combined with previously published thermodynamic values in order to construct thermodynamic cycles for ionic and neutral decomposition of the bromochloromethanes. The n to σ^* , n to s , and n to p electronic transition energies have also been determined on the basis of photoabsorption spectra.

I. INTRODUCTION

Many halogenated methanes are used in reactive ion etching. These molecules are often easier to handle and safer than the pure halogen vapors. Understanding the decomposition mechanisms of these molecules is, therefore, important in developing models of how plasma composition is established in a reactive plasma.

In a plasma, positive ions are created from the ambient gas as a result of the impact of electrons into neutral gaseous species. A very similar process occurs in the ion source of a mass spectrometer. Electrons incident upon a stream of gaseous molecules will, if given sufficient kinetic energy, create positive ions, which may then be mass selected and detected. For this reason, a mass spectrometer can be used to investigate some of the processes which may occur in a plasma.

A number of mass spectroscopy investigations have been unable to identify or observe the CCl_4^+ parent ion,¹⁻⁴ while only very small relative amounts of CBr_4^+ parent ion have been detected.⁴⁻⁶ An explanation³ for the absence of CCl_4^+ in mass spectra postulates a repulsive excited state of neutral CCl_4 which would dissociate to CCl_3 and Cl . Subsequent ionization of the trichloromethyl species to CCl_3^+ would then explain the large amount of CCl_3^+ observed in the spectra. Alternatively, the CCl_4^+ ion¹ may be unstable and dissociate rapidly to $\text{CCl}_3^+ + \text{Cl}$. Ion pair production such as $\text{CCl}_4 \rightarrow \text{CCl}_3^+ + \text{Cl}^-$ has also been suggested.⁷ The CBr_4^+ ion however, is believed to be stable.⁴

Using mass spectral ionization efficiency measurements as well as previously published data we have constructed thermodynamic cycles for some of the bromochloromethanes. These results, as well as additional photoabsorption data probing excitations to the C-Br and C-Cl antibonding orbital, are presented in hopes of furthering the understanding of the chlorobromomethane decomposition process.

II. EXPERIMENTAL

Electron impact studies were carried out in a Hitachi RMU-6 single sector magnetic mass spectrometer differentially pumped by two diffusion pumps. The energy of the incident electrons in the ion source was varied in 0.1 eV steps

between 6 and 30 eV. The appropriate mass was selected by setting the current in the sector electromagnet and detected in an ion multiplier to obtain an ionization efficiency curve (IEC). The calibration of the electron energy scale was made from high purity argon, bromine, residual CO, and residual hydrogen.

Photoabsorption spectra were obtained at the Synchrotron Radiation Center of the University of Wisconsin-Madison (the storage ring Tantalus). The light was dispersed by a 1 m McPherson normal incident monochromator. The detector was a photomultiplier with a sodium salicylate phosphor. Since the monochromator and the gas vessel were separated by a LiF window, in practice, spectra could only be obtained between 2.5 and 10 eV photon energy. A steady gas flow through the cell was maintained to prevent buildup of fragments in the cell.

The vapor in equilibrium with the sample at room temperature was leaked into the photoabsorption cell and mass spectrometer at a steady rate so that a constant pressure was maintained in each chamber during an experimental run. Pressure could only be measured on a relative scale; no absolute pressures were known due to the problem of correcting for ionization gauge cross section and gauge failure due to the corrosive nature of the admitted gases. The pressures could be kept constant and known to within a factor of 4-5. Spectra were obtained in the range 0.1-10 mTorr for the photoadsorption studies and in the range between 10^{-7} - 10^{-5} Torr for the mass spectrometer ionization efficiency curves.

CBr_4 and CCl_4 were obtained from Aldrich Chemical Company, while CBrCl_3 was obtained from Koch Light Laboratories and CBr_2Cl_2 was obtained from Alfa Products.

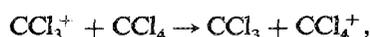
III. ELECTRON IMPACT STUDIES

A. CCl_4

From the equilibrium vaporization of CCl_4 liquid, the following parent and fragment species were identified in the mass spectrum: CCl_4^+ , CCl_3^+ , CCl_2^+ , Cl^+ , CCl^+ , and C^+ . The appearance potential for CCl_4^+ was 8.7 ± 0.1 eV, with higher appearance potentials at 11.5 ± 0.1 , and 14.8 ± 0.2

eV. The appearance potential of CCl_3^+ was also 8.7 ± 0.3 eV with a higher appearance potential at 11.6 ± 0.3 eV.

The appearance potential for CCl_4^+ at 11.5 ± 0.1 is the first ionization potential for CCl_4 corresponding to the ionization of the $2t_1$ molecular orbital. This was first observed by electron impact techniques to be at 11.0 ± 1.0 eV⁷ but Watanabe *et al.*⁸ were able to more accurately determine the value to be 11.47 ± 0.01 eV in agreement with our value. In addition, a number of photoelectron spectroscopy studies⁹⁻¹² have been undertaken and have found the binding energy of the CCl_4 $2t_1$ orbital as indicated in Table I. The 8.7 ± 0.1 eV appearance potential for CCl_4^+ is below the first ionization potential for CCl_4 , and may be a result of collisions with CCl_3^+ . A reaction of the form

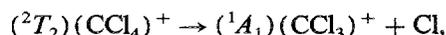


could result in CCl_4^+ sharing a common appearance potential with CCl_3^+ . This would not be surprising since the relative abundance of $\text{CCl}_3^+/\text{CCl}_4^+$ is approximately 10^3 .

The appearance potential of 8.7 ± 0.1 eV for CCl_3^+ we assign to the ionization potential of the CCl_3 methyl species. The CCl_3 is created in the vapor phase from neutralization of

CCl_3^+ , and fragmentation of CCl_4^+ and CCl_4 . Bews and Glidewell¹ have calculated the adiabatic ionization potential to be 8.69 eV (D_3h). Werner, Tsai, and Baer⁴ have measured the appearance potential of CCl_3^+ from the photoionization of CCl_4 to be 11.28 eV. If we subtract from this value of 11.28 eV, the bond dissociation energy $D(\text{CCl}_3-\text{Cl})$ which has been determined to be 3.05 eV,¹⁵ we may estimate the ionization potential of CCl_3 to be 8.2 eV in reasonable agreement with our measurements. The calculated bond dissociation energy $D(\text{CCl}_3-\text{Cl})$ of 2.4 eV¹ suggests an ionization potential of 8.9 eV.

The value of 11.28 eV for the $\text{CCl}_4 \rightarrow \text{CCl}_3^+ + \text{Cl}$ process also implies that the bond dissociation energy $D(\text{CCl}_3^+-\text{Cl})$ for the parent ion is exothermic with 0.2 eV energy released. Bews and Glidewell¹ have calculated the fragmentation pathway



to be exothermic by 0.24 eV in good agreement with this derived value. If we accept this bond dissociation energy for the ion CCl_4^+ , then the absence or low relative abundance of CCl_4^+ in the mass spectral fragmentation of CCl_4 is easily

TABLE I. Electronic transition energies for the bromochloromethanes. The heats of formation H_f (298 K), first ionization potential, and the n to σ^* , n to s , and n to p electronic transition energies are tabulated for the bromochloromethanes.

Molecule	Ionization potential (eV)	H_f (298 K) (kcal/mol)	$n-\sigma^*$ (eV)	$n-s$ (eV)	$n-s$ (eV)	$n-p$ (eV)
CCl_4	11.5 ± 0.1^a	-22.4^o	7.1^a	8.0^a	8.67^y	8.9^y
	11.0 ± 1.0^b	-22.9^p	7.097^y			8.8^{cc}
	11.47 ± 0.01^c	-24.61^q	7.09^z			
	11.69^d	-25.2^r	6.5^{aa}			
	11.60^e	-26.0^s	7.1^{bb}			
	11.69^f	-24.5^h	7.13^{cc}			
	11.7^g					
	11.32^h					
	11.63^i					
	11.56^j					
	CBrCl_3	10.8 ± 0.1^a	-10.0^o	6.6^a	7.6^a	
11.05 ± 0.02^k		-9.3^p	6.4^z			
		-10.23^q				
		-9.4^r				
CBr_2Cl_2	10.5 ± 0.2^a	2.22^p	6.25^a	7.35^a		
		-0.86^q				
CBr_3Cl		6^r				
		11.65^p				
		10.17^q				
CBr_4	10.3 ± 0.2^a	19.0^p	5.5^a	6.8^a	7.65^a	8.3^a
	10.54^d	20.2^q	5.56^{dd}		7.69^{dd}	8.42^{dd}
	10.40^e	38^r				
	10.39^f	24^i				
	10.34^j	19.0^q				
	10.8 ± 0.3^i	19.0^v				
	10.31^m	19.0^w				
11.0 ± 0.5^n	12.0^s					

^a Indicates a measurement derived or reported in this work. ^b Reference 7. ^c Reference 8. ^d Reference 9. ^e Reference 10. ^f Reference 11. ^g Reference 12. ^h Reference 1. ⁱ Reference 13. ^j Reference 14. ^k Reference 31. ^l Reference 20. ^m Reference 4. ⁿ Reference 6. ^o Reference 15. ^p Reference 16. ^q Reference 17. ^r Reference 18. ^s Reference 23. ^t Reference 20. ^u Reference 24. ^v Reference 28. ^w Reference 29. ^x Reference 30. ^y Reference 33. ^z Reference 34. ^{aa} Reference 31. ^{bb} Reference 36. ^{cc} Reference 37. ^{dd} Reference 35.

understood. Dissociation of CCl_4 prior to ionization is no longer necessary for an explanation of CCl_4 mass spectra.¹

B. CBrCl_3

The CBrCl_3^+ parent and CCl_3^+ , CBrCl_2^+ , CCl_2^+ , CBrCl^+ , CCl^+ , CBr^+ , Cl_2^+ , Cl^+ , Br^+ , and C^+ fragmentations were observed in the mass spectra of CBrCl_3 . The appearance potential for CBrCl_3^+ was 8.7 ± 0.3 eV with a higher appearance potential at 10.8 ± 0.1 eV. The appearance potentials for the CBrCl_2^+ fragment were at 8.9 ± 0.2 , and 10.8 ± 0.2 while the appearance potentials for CCl_3^+ were at 8.7 ± 0.2 , 10.8 ± 0.1 , 12.6 ± 0.3 , and 15.0 ± 0.2 eV.

The appearance potential of CBrCl_3 at 10.8 eV may be assigned to the first ionization potential for CBrCl_3 corresponding to the ionization of the $2e$ molecular orbital. Photoionization methods²¹ have placed the ionization potential at 11.05 ± 0.02 eV in good agreement with our measurement.

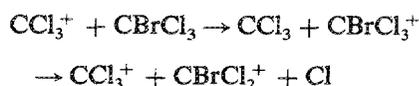
As with the electron impact studies of CCl_4 , we assign the 8.7 eV appearance potential of CBrCl_3^+ to be a result of ion-molecular collisions with CCl_3^+ , i.e.,



resulting in CBrCl_3^+ sharing a common appearance potential with CCl_3^+ . Again this is unsurprising since the relative abundance of CCl_3^+ to CBrCl_3^+ is quite high ($\sim 10^3$). The appearance potential of 8.7 eV for both CCl_3^+ and CBrCl_3^+ is therefore the first ionization potential of CCl_3 , in agreement with our results for CCl_4 .

The appearance potential of 8.9 ± 0.2 eV for the CBrCl_2^+ fragment ion of CBrCl_3 may either be a result of the decom-

position of CBrCl_3^+ following an ion molecular collision with CCl_3^+ , i.e.,



or as a result of a collision of a CBrCl_2 fragment with CCl_3^+ . Both reactions are likely since the relative abundance of $\text{CCl}_3^+/\text{CBrCl}_2^+$ is greater than 10.

The bond dissociation energy $D(\text{CCl}_3\text{-Br})$ of the neutral parent has been measured to be 2.42 eV.¹⁵ This implies that the bond dissociation energy of the parent ion $D(\text{CCl}_3\text{-Br})^+$ is approximately 0.3 eV, employing the measured ionization potential of CCl_3 (8.7 eV) and CBrCl_3 (10.8 eV). The parent ion CBrCl_3^+ may therefore be slightly more stable than the CCl_4^+ parent ion.

Ionization of CCl_4 of T_d symmetry to the $2e$, $2t_2$, and $2t_1$ states of CCl_4^+ will lead to a Jahn-Teller distortion reducing the stability of the ion.¹ The C_{2v} and C_{3v} geometries of CCl_4^+ are the most stable, and are the lowest energy distortions for CCl_4^+ . The CBrCl_3^+ ion is C_{3v} , not T_d as a result of the bromine substitution thus reducing the Jahn-Teller distortion. As a result, one would expect the CBrCl_3^+ ion to be more stable than the CCl_4^+ ion.

C. CBr_2Cl_2

The $\text{CBr}_2\text{Cl}_2^+$, CBr_2Cl^+ , CBrCl_2^+ , CBr_2^+ , CCl_2^+ , CBrCl^+ , CBr^+ , Cl_2^+ , Cl^+ , Br^+ , CCl^+ , and C^+ ions were observed in the mass spectral fragmentation pattern of CBr_2Cl_2 . The appearance potentials for $\text{CBr}_2\text{Cl}_2^+$ were observed at 7.5 ± 0.3 and 10.5 ± 0.1 eV. We assign the 10.5 ± 0.1 eV appearance potential to the first ionization potential of $\text{CBr}_2\text{Cl}_2^+$.

TABLE II. Thermodynamic energies for the methyl radicals. The ionization potentials and the heats of formation are tabulated for CCl_3 and CBr_3 . The bond dissociation energies $D(\text{CCl}_3\text{-Cl})$, $D(\text{CCl}_3\text{-Br})$, $D(\text{CBr}_3\text{-Br})$, and $D(\text{CBr}_3\text{-Cl})$ are also listed.

Molecule	Ionization potential (eV)	H_f (298 K) (kcal/mol)	Bond dissociation energy (eV) $D(\text{CX}_3 - \text{X})$	Bond dissociation energy (eV) $D(\text{CX}_3 - \text{Y})$
CCl_3	8.7 ± 0.1^a	18.6 ^f	3.05 ^c	2.42 ^c
	8.69 ^b	19.0 ^g	3.08 ^k	
	8.2 ^c	2.15 ^b	3.12 ^l	
	8.78 ± 0.05^d	14 ^h		
		19 ⁱ		
CBr_3	7.5 ± 0.2^a	44 ^j	2.44 ^m	2.8 ± 0.2^q
	9.3 ^c	52 ^d	2.65 ⁿ	
			<2.2 ^o	
			2.29 ^p	
			2.16 ^l	

^a Indicates a measurement reported from this work. ^b Reference 1. ^c Reference 15. ^d Reference 22. ^e Reference 6. ^f Reference 27. ^g Reference 19. ^h Reference 25. ⁱ Reference 26. ^j Reference 20. ^k Reference 37. ^l Reference 41. ^m Reference 28. ⁿ Reference 38. ^o Reference 39. ^p Reference 5. ^q Was derived using average thermodynamic measurements reported in Refs. 22 and 24 and Table I.

D. CBr_4

In the fragmentation mass spectra of CBr_4 , the CBr_4^+ , CBr_3^+ , CBr_2^+ , CBr^+ , Br_2^+ , Br^+ , and C^+ ions were observed. The appearance potentials for CBr_4^+ were observed at 10.3 ± 0.2 and 13.5 ± 0.3 eV. There are some ionization efficiency curves that show an appearance potential at 7.5 ± 0.3 eV for CBr_4^+ but this was not consistently observed. The appearance potentials for CBr_3^+ were observed at 7.5 ± 0.2 and 10.5 ± 0.3 eV. The relative abundance of CBr_3^+ to CBr_4^+ was about 10^2 .

The appearance potential for CBr_4^+ at 7.5 ± 0.2 eV may be assigned to the ionization potential of CBr_3 . The CBr_3 (as with CCl_3 resulting from CCl_4 or CBrCl_3) is created in the vapor phase from neutralization of CBr_3^+ and/or fragmentation of CBr_4^+ and CBr_4 . From published spectra of Werner, Tsai, and Baer,⁴ the appearance potential of CBr_3^+ from photoionization is approximately 10.27 eV. Using the value of 2.44 eV for the bond dissociation energy²⁸ $D(\text{CBr}_3-\text{Br})$ we derive an ionization potential of 7.83 eV in good agreement with our measured value.

This value of 10.27 for the process $\text{CBr}_4 \rightarrow \text{CBr}_3^+ + \text{Br}$ implies that the bond dissociation energy $D(\text{CBr}_3^+-\text{Br})$ for the parent ion is approximately 0; Kaposi *et al.*²⁰ have estimated the bond dissociation energy of the ion to be 0.78 eV.

E. Thermodynamic cycles

The ionization potentials for CCl_4 , CCl_3Br , CBr_2Br_2 , and CBr_4 show a trend towards lower energies. Using these ionization potentials, the ionization potentials of CCl_3 and CBr_3 and previously measured thermodynamic bond strengths we can construct thermodynamic cycles shown in Fig. 1.

Our evidence suggests the ionic bond dissociation energy $D(\text{CX}_3^+-\text{X})$ for CBr_4^+ is not as exothermic as for the CCl_4^+ parent ion (~ 0.2 eV for CCl_4^+ and ~ 0 for CBr_4^+). This is reflected in a lower relative abundance of $\text{CX}_3^+/\text{CX}_4^+$ observed for CBr_4 than for CCl_4 (approximately 10^2 as compared to 10^3). Using the ion-molecular collision fragmentation pathway invoked to explain the appearance potentials below the first ionization potential for CCl_4 , we would not expect to dominate as seriously the decomposition of CBr_4 in the mass spectrometer.

The relative stabilities of the chlorofluoromethane and fluorobromomethane ions have been studied by photolysis and it was observed that the trend for stability went as $\text{CF}_2\text{Cl}_2^+ > \text{CF}_3\text{Cl}^+ > \text{CFCl}_3^+ > \text{CCl}_4^+$ and $\text{CF}_2\text{Br}_2^+ > \text{CF}_3\text{Br}^+ > \text{CFBr}_3^+ > \text{CBr}_4^+$.⁴⁰ Thus, it may not be unreasonable to expect $\text{CBr}_2\text{Cl}_2^+$ and CBrCl_3^+ to be more stable than CCl_4^+ or CBr_4^+ .

F. Photoabsorption

The photoabsorption spectra have been observed for CCl_4 , CBrCl_3 , CBr_2Cl_2 , and CBr_4 as shown in Fig. 2. The first major absorption features for CCl_4 may be assigned to the n to σ^* transition (halogen lone pair to carbon halogen antibonding orbital excitation). The energy for this excitation is in agreement with most previously measured values.³⁴ The second major feature in the photoabsorption spectra we

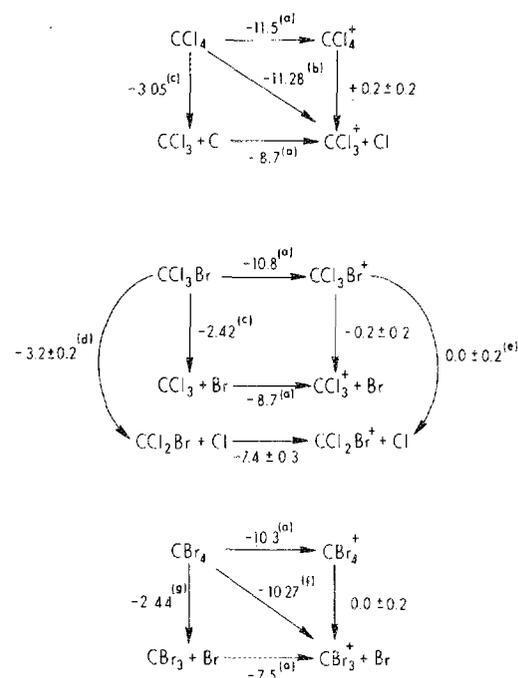


FIG. 1. Ionic and neutral fragmentation energies. Bromochloromethanes are shown in the form of thermodynamic cycles. The sources for the energies are (a) this work, (b) Ref. 4, (c) Ref. 15, (d) from the photoadsorption onset, (e) assuming an ion-molecular collision this is the difference between the 8.7 ± 0.2 and 8.9 ± 0.2 eV appearance potentials for CCl_3^+ and CBrCl_2^+ , (f) inferred from published spectra in Ref. 4, and (g) Ref. 28. All numbers are shown in units of eV.

tentatively assign to an n to s transition. The higher energy transitions at 8.67 and 8.9 eV for CCl_4 and 7.69 and 8.42 eV for CBr_4 have been assigned^{33,35} to the n to s (t_2 ion state) and n to p (t_1 ion state), respectively. Thus for CBr_4 and CCl_4 a transition at 6.8 and 8.0 eV, respectively, may be assigned the n to s transition (t_1 ion state). The assignment of the observed electron transitions is shown in Table I.

The absorption threshold for these bromochloromethane molecules appears to be at an energy much smaller than the 5 eV suggested by earlier measurements.³⁶ The sharp absorption onset of CCl_4 , CBrCl_3 , and CBr_2Cl_2 between 3 and 3.5 eV photon energy may be a result of the bond dissociation of chlorine from the parent molecule. This assignment would be consistent with the thermodynamic cycles shown in Fig. 1 derived from previously published literature and our ionization efficiency curves.

The decreasing energy of the n to σ^* transition (shown in Fig. 2) with increasing bromine substitutions in the bromochloromethanes suggests that the neutral parent molecule stability decreases as well. Certain excitations into the antibonding orbital require less energy with increasing bromine substitution. The $D(\text{CCl}_3-\text{Cl})$ and $D(\text{CBr}_3-\text{Br})$ bond dissociation energies of 3.05¹⁵ and 2.44,²⁸ respectively, are consistent with this observation.

IV. CONCLUSION

In summary, we have determined the n to σ^* and n to s electron transition energies as well as the first ionization po-

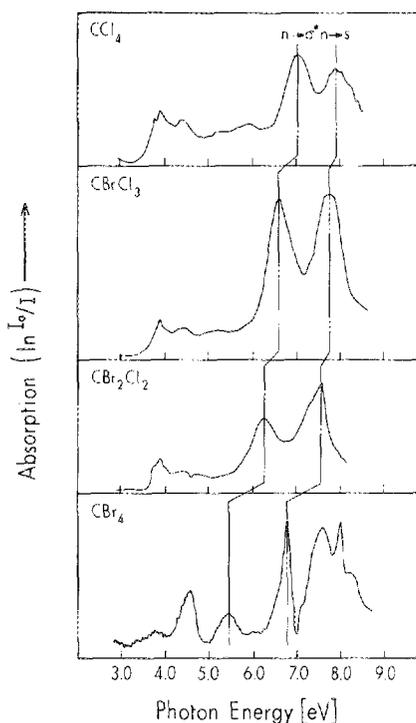


FIG. 2. Photoabsorption spectra for CCl_4 , CBrCl_3 , CBr_2Cl_2 , and CBr_4 . Absorption is plotted as $\ln(I_0/I)$, where I_0 is the transmitted light intensity of the empty cell and I is the transmitted intensity of the filled cell at a halocarbon pressure about 10 mTorr.

tentials of CCl_4 , CBrCl_3 , CBr_2Cl_2 , and CBr_4 as shown in Table I. There are strong indications that the CCl_4^+ parent ion is quite unstable and dissociates exothermically. The CBr_4^+ ion is more stable than the CCl_4^+ ion. For the neutral molecules, on the other hand, a decreasing stability with an increasing number of bromine atoms is indicated (see Table II).

Ion-molecular collisions appear to be necessary to explain the observed electron impact ionization data. The ion-molecular collisions, which occur readily for the halogenated methanes, in the ionization source of the mass spectrometer may explain why the parent ions of CCl_4^+ and CBr_4^+ can be observed only with considerable difficulty.

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