

# The Analysis of Haloethylenes by an Electron Monochromator/ MS System

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## Overview

### Purpose

To determine electron capture energies for haloethylene compounds.

### Methods

Analysis of compounds by electron monochromator GC-MS system.

### Results

- Electron capture energies for halogenated ethylenes lie in the range 0.0 eV to 3.0 eV to produce molecular ions and other fragment ions.
- Loss of H and H<sub>2</sub> is facile at low electron capture resonance energies.
- At least 3 halogen atoms are required to have a detectable molecular ion.

## Introduction

Haloethylenes form a class of compounds that are known environmental contaminants<sup>1</sup>. These include trichloroethylene (TCE) and compounds used to model TFE and the associated environmental breakdown products. These compounds are particularly strong electron capture candidates because of the electronegativity of the halogen substituents. The relative position, number, and elemental composition of these halogen substituents result in differing electron capture energies.

## Methods

Samples were analyzed on a GC-EM-MS instrument described previously<sup>2</sup>. The system was calibrated using the hexafluorobenzene molecular ion resonance peak at 0.03 eV and the ion generated by the loss of a fluoride ion at 4.5 eV<sup>2</sup>. All samples were initially tested using a direct injection method to determine masses that produced peaks. Based upon data obtained during the initial experiments, masses were selected for analysis by GC introduction into the EM-MS. GC temperature conditions and injection port temperatures were varied to produce optimal peaks on a DB-5 column using He as a carrier gas. Ionization occurred with between 1\*10<sup>-8</sup> torr and 5\*10<sup>-6</sup> torr pressure in the ion source. Data were stored and later analyzed with peak fitting software to determine exact peaks values.

## Results

The electron capture molecular ion, the halogen loss, and the slow electron energies associated with the formation of ions for tetrachloroethylene, trichloroethylene, cis, trans, and geminal dichloroethylene, a cis and trans dibromoethylene mixture, and vinyl bromide were recorded. Data from each series of experiments were used to generate 3D plots of the data to show the electron capture energy and the relative intensities of the electron capture event (Figures 1-7).

The data that were generated from fitting the peaks were then used to determine electron capture energies for specific masses (Table 1).

From an examination of these data it is obvious that only highly substituted haloethylenes show molecular ions. The M-X species appear with higher electron capture energies when compared to the molecular ion, (M-H)- ion, and the lower X- ion species. The requirement for higher energy electrons suggests that there is some additional activation energy required to cause the carbon halogen bond to cleave.

The second result of interest is that loss of hydrogen atom occurs with approximately the same energy as the electron capture event to yield the molecular ion for TCE. This suggests that because the energies are indistinguishable from each other, there is a metastable decomposition of the molecular ion to form the (M-H)- ion.

The corresponding loss of a hydrogen atom, (M-X-H), and a hydrogen molecule, (M-X-H<sub>2</sub>), from the (M-X) ions occurs with the same resonance energy as the (M-X) ions for all compounds tested. This also suggests that there are metastable decompositions in all the compounds tested and for more than one ion in some compounds and, therefore, that the loss of H and H<sub>2</sub> are facile process assuming that an electron capture event can occur.

Thirdly, there is a reduction in the electron capture resonance in the cis and trans-dibromoethylene in comparison with the cis and trans-dichloroethylene. This reduction of ~0.35 eV for the (M-X) ion and ~0.75 eV for the lowest energy resonance of X- can be attributed directly to the change in halogen substituent.

Further comparison of the cis and trans-dichloroethylene with the geminal-dichloroethylene suggests that the presence of a halogen at the sight of anion formation in the ethylene does not provide charge stabilization as would be expected by the electron withdrawing nature of the chlorine. Extending this concept to the entire chloroethylene series indicates that at least one stabilizing electron withdrawing group α to the sight of anion formation causes a reduction in the energy of the (M-X)- resonance of ~1.5 eV and potentially reduces others resonance energies, such as X-.

Lastly it seems necessary for the presence of at least one halogen atom to make the (M-X) or any other species detectable with this instrumentation as no ions were detected for any compound that consisted solely of a hydrocarbon. Molecular ions appear to require at least 3 halogens atoms to not auto disassociate and to be detectable under these experimental conditions.

Figure 1: Electron Capture negative ion resonances for trichloroethylene

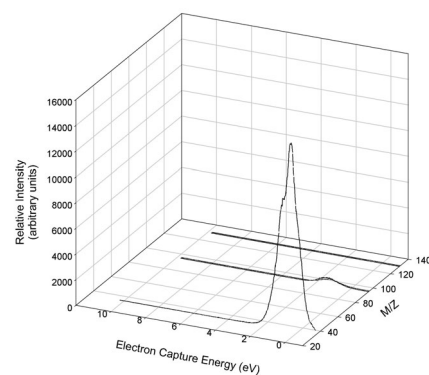


Figure 2: Electron capture negative ion resonances for tetrachloroethylene

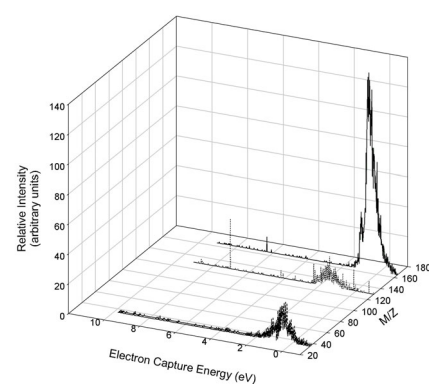


Figure 3: Electron capture negative resonances for trans-dichloroethylene

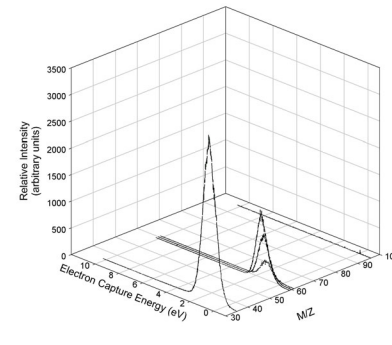


Figure 4: Electron capture negative ion resonances for cis-dichloroethylene

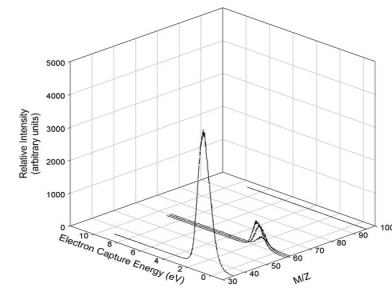


Figure 5: Electron capture negative ion resonances for geminal-dichloroethylene

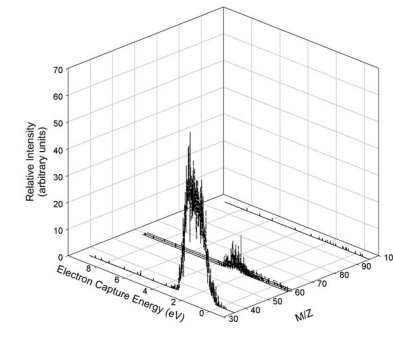


Figure 6: Electron capture negative ion resonances for cis/trans-dibromoethylene

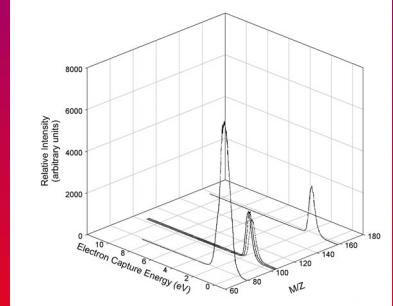
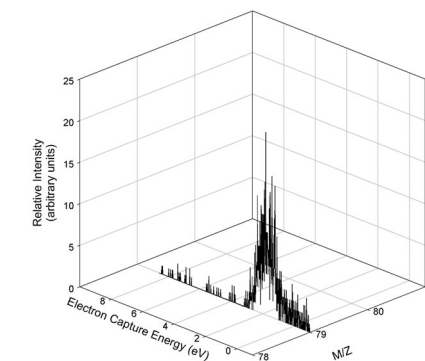


Figure 7: Electron capture negative ion resonances for vinyl bromide



## Conclusions

- Negative ion resonances for haloethylenes are in the range of 0.0 eV to 3.0 eV for molecular ions and other fragment ions.
- Loss of H and H<sub>2</sub> appears to be facile at low energy negative ion resonances.
- Halogenation α to the site of anion formation lowers negative ion resonances. Positional isomers of haloethylenes affects negative ion resonances.
- At least 3 halogen atoms are required to have a detectable molecular ion.

## References

- Hageman, K. J., Istok, J. D., Fields, J. A., Buscheck, T. E., Semprini, L., *Environ. Sci. Technol.* **2001**, 35, 1729-1735
- Laramée, J. A., Kocher, C.A., Deinzer, M.L., *Anal. Chem* **1992** *64*, 2316-2322

## Acknowledgements

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Table 1 : Negative Ion Resonances for Halogenated Ethylenes (all values in eV)

Compound	M-	(M-H)-	X-	(M-X)-	Other
Tetrachloroethylene	0.394, 0.218		0.457, 0.397	1.352	
Trichloroethylene	0.314	0.257	0.698, 1.470	1.152	1.217 (M-X-H)-
Trans-Dichloroethylene			1.126	1.137	1.151 (M-X-H)-, 1.149 (M-X-H <sub>2</sub> )-
Cis-Dichloroethylene			1.364	1.195	1.198 (M-X-H)-, 1.207 (M-X-H <sub>2</sub> )-
Gem-Dichloroethylene			1.479, 1.449	2.824	2.616 (M-X-H)-, 2.760 (M-X-H <sub>2</sub> )-
Cis/Trans-Dibromoethylene			0.505, 1.337	0.788	0.937 (M-X-H)-, 0.948 (M-X-H <sub>2</sub> )-
					1.106(X <sub>2</sub> )-, 1.774 (X <sub>2</sub> )-
Vinyl Bromide			0.535, 1.449		