

Absolute dissociative electron attachment cross-sections of chloro- and bromo-ethylenes

Yury V. Vasil'ev, Benjamin J. Figard, Valery G. Voinov, Douglas F. Barofsky, Max L. Deinzer
Department of Chemistry, Oregon State University, Corvallis, OR 97331

Overview

Purpose:

To develop a novel method for the measurements of cross-sections of gas-phase electron-capture reactions resulting in generation of temporary negative ions (resonances)

Method:

Resonant electron capture mass spectrometry was performed on an orthogonal acceleration reflectron time-of-flight mass spectrometer with a trochoidal electron monochromator and a gas chromatograph

Results:

Absolute dissociative electron attachment cross-sections for molecules of some chloro- and bromo-ethylenes were obtained

Introduction

The determination of the absolute cross-sections of ion-formation as a function of collision energy is important to fully understand the electron capture process. Lowering of the interaction energy leads to difficulties in understanding the theory and interpreting the experimental results. Theoreticians need to include quantum properties of the colliding particles and experimentalists must deal with the problem of stray electric and magnetic fields exceeding collision energies. These circumstances are always present when dealing with low-energy negative ion (NI) formation and therefore fast experiments are especially desirable for providing essentially unchanged experimental conditions. Using a recently described [1] gas chromatograph/resonant electron capture-TOF mass spectrometer (GC-REC-TOF-MS), a new method was developed for the determination of absolute NI formation cross-sections. Molecules of halo-ethylenes that are known to have atmospheric and environmental significance have been investigated using this technique.

Methods

A GC-REC-TOF-MS [1] incorporating a trochoidal electron monochromator as an electron gun with 40-200 meV, FWHM, energy in the range 0 to 12 eV was used in this study. Mixtures of a 1/100 v/v halo-ethylene and pentafluorane- $\text{C}_2\text{F}_5\text{CF}_3$ (1000:1) were injected (0.5 micro-liter) into the GC (DB-624 column). He at 3 mL/min, temperature program 4 °C/min from 30 to 160 °C), CO_2 , CHCl_3 , and low pressure (< 10⁻⁷ Torr SF_6 -gas were used for calibration of cross-sections, resonance energies and mass scales. All halo-ethylenes were purchased from Sigma-Aldrich. Molecular and fragmentation NIs were interpreted using semi-empirical PM3 level calculations and density-functional theory, i.e. B3LYP/6-31**+G basis set, except in the case of molecules with bromine atoms, in which case effective core potentials were used as defined in the LAV3P**+ B3LYP basis set calculations.

GC-REC-TOF Mass Spectrometer System

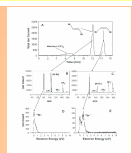
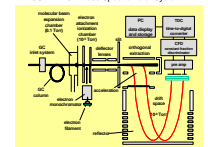


Fig. 1. (A) Total ion current chromatogram, mass spectra of GC peaks corresponding to (B) trans- and (C) cis- $\text{C}_2\text{H}_2\text{Br}_2$ introduced into the GC together with CO_2 . Effective yield curves of $^{\text{m}}\text{Br}^-$ from (D) trans- and (E) cis- $\text{C}_2\text{H}_2\text{Br}_2$.

Results

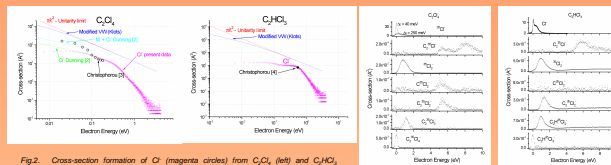


Fig. 2. Cross-section formation of Cl^- (magenta circles) from C_2Cl_4 (left) and C_2HCl_3 (right); theoretical limit of s-wave resonance electron attachment (red line); modified Klotz-Vogt-Warner cross-section (blue line); experimental data from Ref 2 (blue and green lines), Ref 3 (black open circles) and Ref 4 (black closed circles) for comparison.

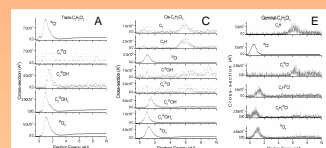


Fig. 4. Dissociative free electron capture cross-sections of trans- and cis- $\text{C}_2\text{H}_2\text{Br}_2$ (A and C) and trans- and cis- $\text{C}_2\text{H}_2\text{Br}_2$ (B and D) together with general $\text{C}_2\text{H}_2\text{Br}_2$ (E).

Fig. 3. Dissociative and nondissociative free electron capture cross-sections of C_2Cl_4 (left) and C_2HCl_3 (right).

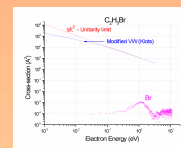


Fig. 5. Cross-section of Br^- formation (magenta circles) from $\text{C}_2\text{H}_2\text{Br}_2$; theoretical limit of s-wave resonance electron attachment (red line); modified Klotz-Vogt-Warner cross-section (blue line).

Conclusions

- A new method for absolute free electron capture cross-section measurements has been developed. Cross-sections for C_2Cl_4 and $\text{C}_2\text{H}_2\text{Cl}_2$ have been found to be in excellent agreement with earlier published data. Cross-sections for other compounds have been determined for the first time.
- Although earlier determined relative intensities of Cl_2^- and Br_2^- from trans and cis isomers of $\text{C}_2\text{H}_2\text{Cl}_2$ and $\text{C}_2\text{H}_2\text{Br}_2$, respectively, showed large differences, the experimental results from the present work show that cross-sections for the formation of these ions are practically identical. These facts can be interpreted as involving isomerization of the negative ion of the trans-isomers into the cis-counterpart before dissociation.
- $\text{C}_2\text{H}_2\text{Br}$ indicates small but quite measurable cross-section formation for Br^- at room temperature.

Acknowledgements

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References

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