

SECONDARY ION MASS SPECTRA FOR IODONIUM SALTS

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INTRODUCTION

Secondary ion mass spectrometry (SIMS) is ideal for measuring mass spectra for most nonvolatile organic onium salts. In SIMS, an energetic primary ion beam is directed at a sample surface. In liquid SIMS, the sample is dissolved in a vacuum-compatible liquid matrix. In these examples, the samples are dissolved in a glycerol matrix. Upon impacting the surface of the glycerol/analyte solution, the primary ion energy is transferred via a collision cascade to atoms and molecules at the surface lattice. The energy can eject neutral particles, ions, electrons, and photons into the vacuum. Ions are drawn away from the surface by an extraction potential, and mass is analyzed by a quadrupole mass analyzer.

Previous work has shown that SIMS produces good quality mass spectra for iodonium salts (Duffin and Busch, 1986), containing abundant signals for the intact cation and some degree of structurally informative fragmentation. The compounds of interest in this study are the diaryliodonium salts. These compounds are particularly useful as photocatalysts of cationic polymerizations (Crivello and Lam, 1977). Diaryliodonium salts possessing complex metal halide anions photoinitiate the cationic polymerizations of a wide variety of monomers, including olefins, cyclic ethers, cyclic sulfides, cyclic acetals, and lactones. The majority of the polymers produced by photocatalysis of a diaryliodonium salt with a monomer are used as coatings.

In addition to interpretation of the mass spectra themselves, this paper describes the results of some calculations of ion structures for these salts. Specifically, previous work had noted occurrence of fragment ions corresponding to loss of iodine from the intact cations of some iodonium salt. The purpose of this study was to establish the geometry of the iodonium cation to ascertain if such a loss was reasonable. The computational program utilized in the study of some of these salts is available from the Quantum Chemistry Program Exchange located at Indiana University. The program, MOPAC, is a general purpose semiempirical molecular orbital package for the study of chemical structures and reactions (Stewart and Seiler, no date). The software is itself a combination of programs. The semi-empirical Hamiltonian AM1 is used in the electronic portion of the calculations to obtain molecular orbitals, heats of formation, and its derivatives with respect to the molecular geometry. Using the results obtained, MOPAC will further calculate the vibronic spectra, thermodynamic quantities, isotopic substitution effects, and force constants for molecules, radicals, ions, and polymers. The quantities to be examined here are the bond lengths and angles for the iodonium cations.

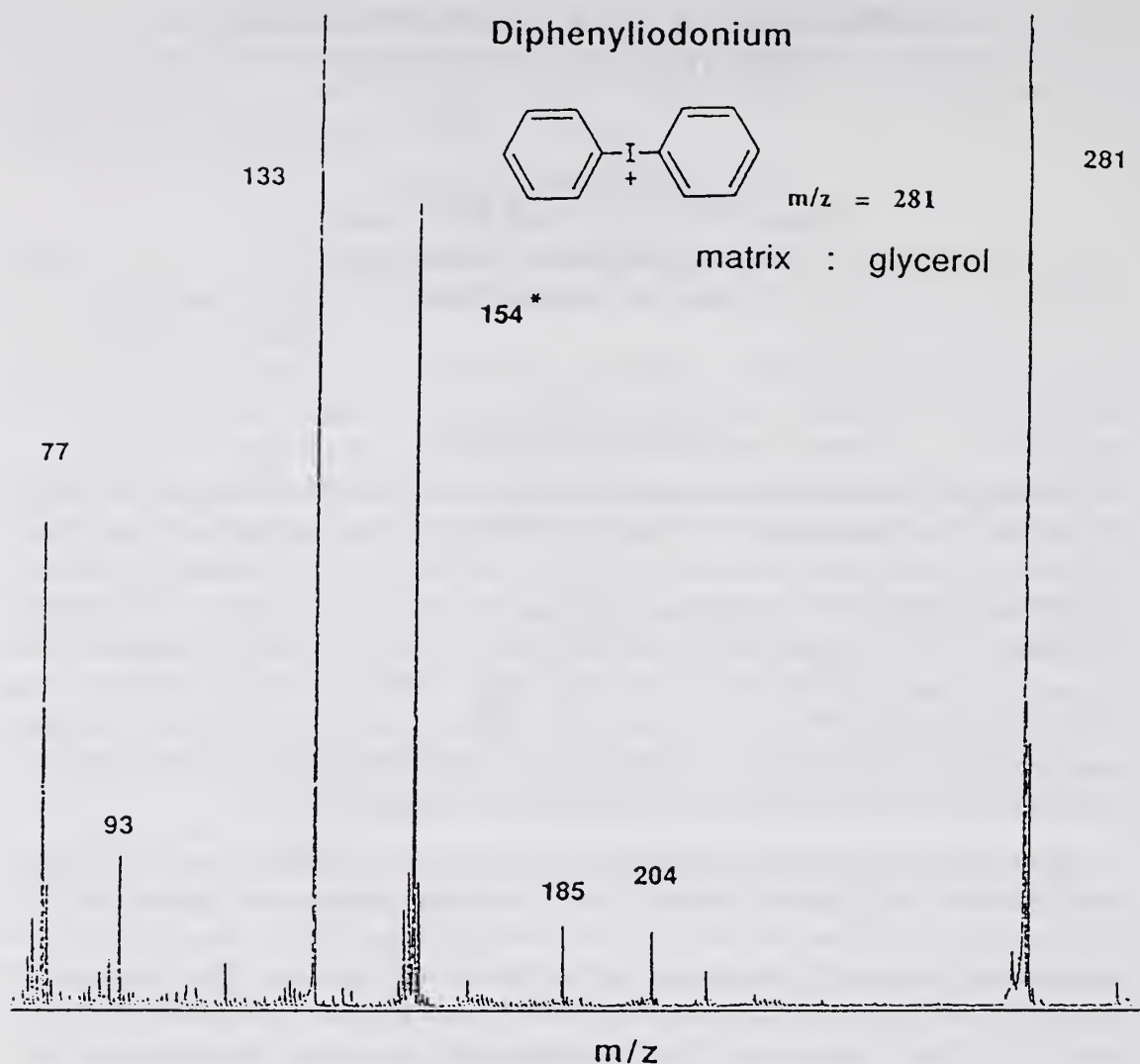


FIGURE 1. SIMS spectrum of diphenyliodonium arsenic hexafluoride.

EXPERIMENTAL

Samples were prepared by dissolution of 1-10 micrograms of each iodonium salt into 10 to 20 microliters of glycerol. The spectra were acquired on a modified Extrel C-50 quadrupole secondary ion mass analyzer (Fiola, *et al.*, 1986). A thermionic cesium source was used for production of the primary cesium ions at a potential of 8 keV. Pressure in the chamber was maintained at approximately 10^{-5} torr. The symmetrical salts studied were diphenyliodonium, 4,4'-dimethyldiphenyliodonium, 2,3,2',3'-tetramethyldiphenyliodonium, and 4,4'-ditertbutyldiphenyliodonium salts. The asymmetrical salts studied were 4-methoxydiphenyliodonium, 4-propanoic-2-oxyphenyl (phenyl) iodonium, and hexadecyloxyphenyl (phenyl) iodonium salts. Counter ions varied with the salt but were typically arsenic hexafluoride, phosphorous hexafluoride, and the tosylate ion.

Calculations of the iodonium salts were performed with MOPAC, a molecular mechanics program run on a VAX computer. Comparisons of the lengths of the carbon to iodine bonds, the bond angles between the substituted phenyl rings and the iodine, and also the charge of the iodine were initially considered in the calculations.

Ratio of Ion Intensities vs. Symmetric Salt

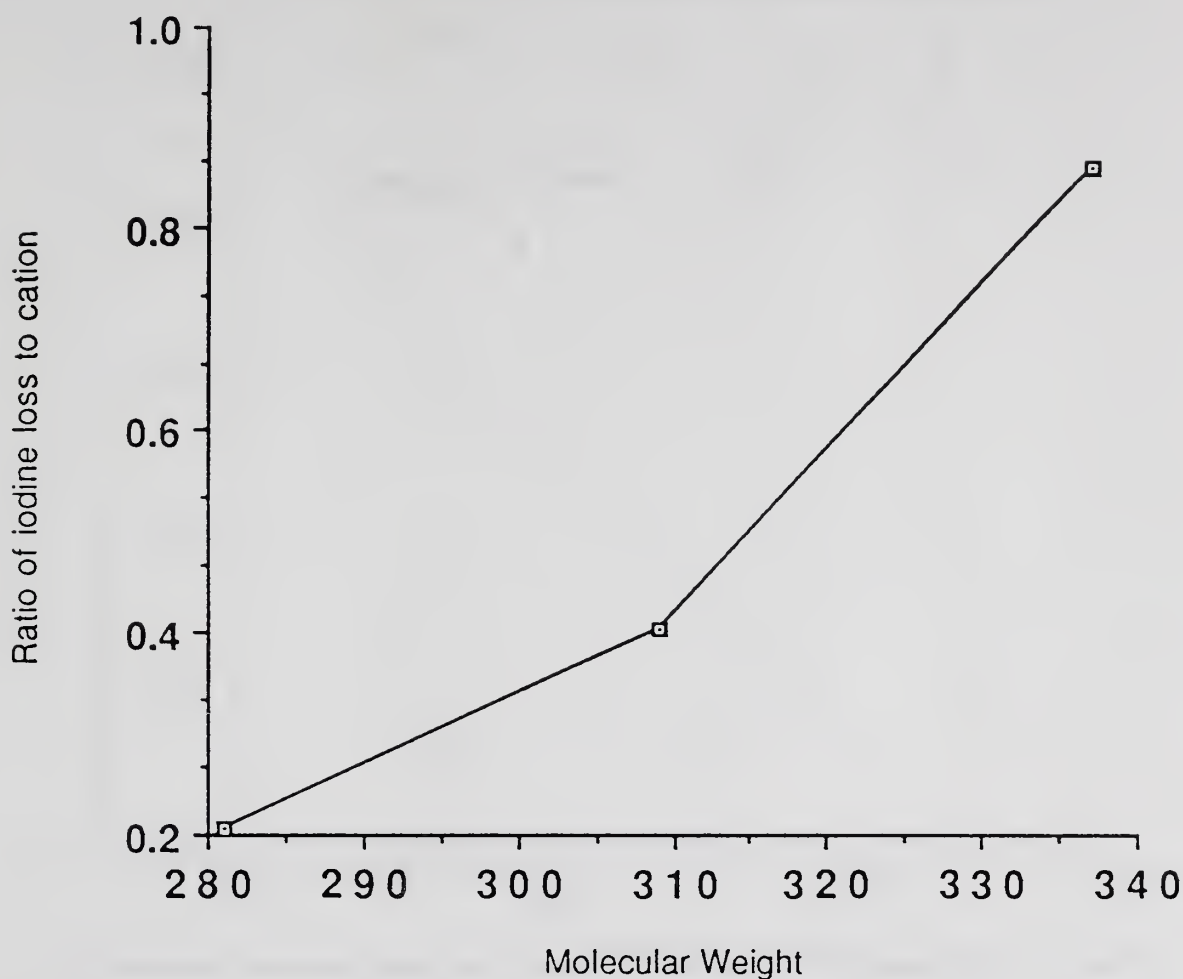


FIGURE 2. Plot of the ratio of ion intensities versus the molecular weight of symmetric iodonium salts.

RESULTS AND DISCUSSION

The positive ion SIMS mass spectrum of diphenyliodonium arsenic hexafluoride is representative of the symmetrical iodonium salts (Figure 1). The base peak corresponds to the intact cation for the salt at m/z 281. The loss of atomic iodine is evident by formation of the fragment ion at m/z 154. Additional fragmentation of the cation includes loss of a phenyl group to yield an ion at m/z 204. Conversely, a peak at m/z 77 is identified as the phenyl group. The glycerol ions ($M + H^+$) and ($2M + H^+$) are seen at m/z 93 and m/z 185, respectively. The large peak at m/z 133 is Cs^+ from the primary beam. The mass spectra of the other symmetrical iodonium salts studied also show an intense peak for the intact cation. Loss of atomic iodine from the intact cation is seen in all of the mass spectra, with the exception of 4,4'-di-*tert*-butyldiphenyliodonium tosylate. If the ratio of the peak intensity for the fragment ion resulting from the loss of iodine to the peak intensity of the cation is plotted versus the molecular weight of the salt, a general increase of the ratio with increasing molecular weight is noted (Figure 2). Calculations with MOPAC indicate an increase in the bond length as well as the bond angle between the two phenyl carbons and the iodine with increasing molecular weight. It is suspected that this increase in bond angle and length can facilitate bond formation at the ortho positions of the two phenyl groups

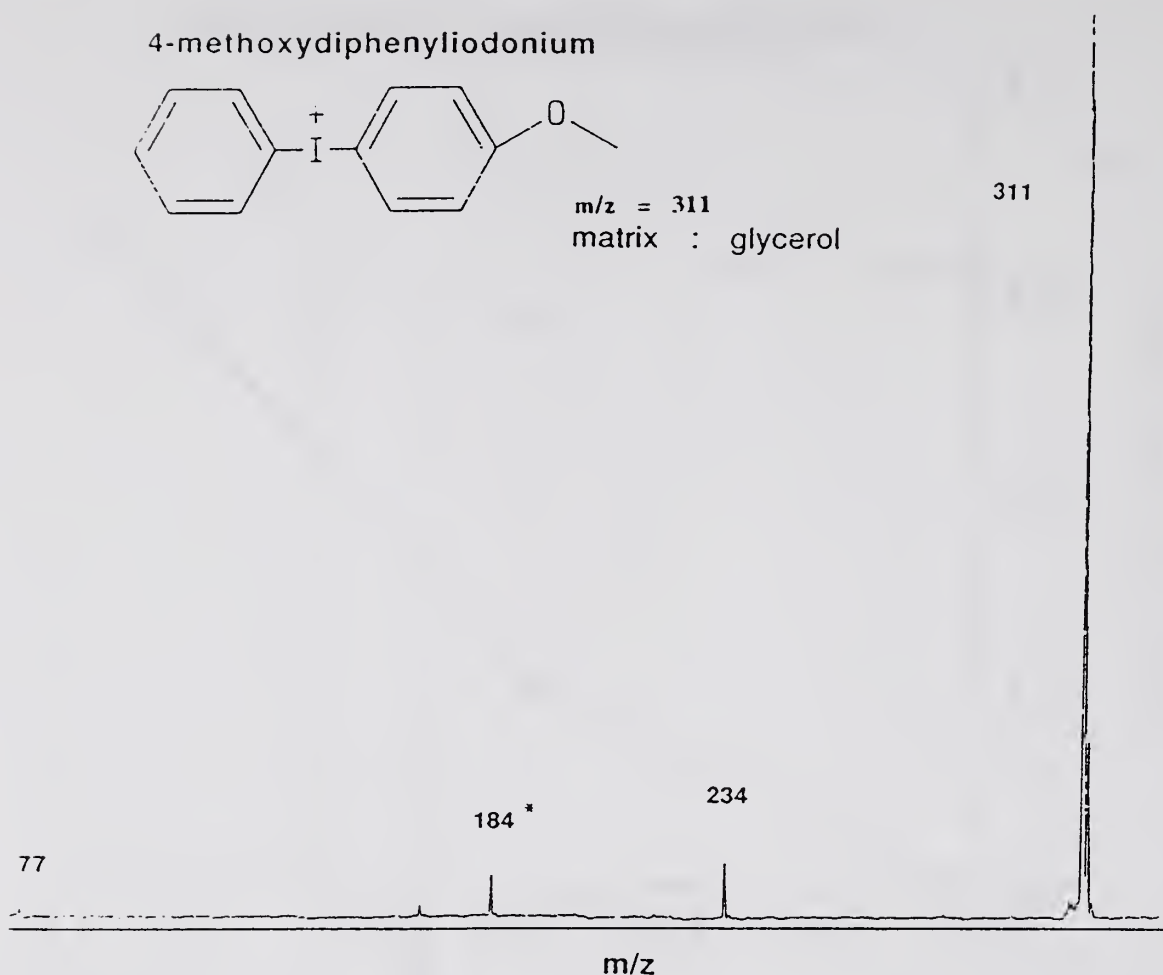


FIGURE 3. SIMS spectrum of 4-methoxydiphenyliodonium phosphorous hexafluoride.

simultaneously with bond breakage between the iodine and the two phenyl groups. This results in an ejection of the iodine from the molecule to produce the "biphenyl" ion seen in the spectra.

The loss of iodine is not evident in the positive ion SIMS mass spectrum of 4,4'-di-*tert*-butyldiphenyliodonium tosylate. The lack of this fragment ion can be explained by steric hindrance of the *t*-butyl groups present in the position para to the iodine bond. According to MOPAC calculations, there is now a decrease in the bond lengths but an increase in the bond angles. This makes it more difficult for the phenyl groups to come close enough for bond formation at the ortho position.

As in the mass spectra of the symmetrical salts, loss of atomic iodine is also seen in the mass spectra of the asymmetrical salts. As an example, the mass spectrum of 4-methoxydiphenyliodonium phosphorous hexafluoride (Figure 3) gives an intense peak corresponding to the intact cation at m/z 311. The loss of iodine produces the fragment ion at m/z 184; the abundance of this ion is rather small. Loss of a phenyl group produces the fragment ion at m/z 234, and the phenyl ion itself is detected at m/z 77. The asymmetrical salts seem to exhibit a trend for iodine loss opposite to that measured for the symmetrical salts. When the ratio of ion abundances for the ion generated by iodine loss to the cation abundances is plotted against the molecular weight, a **decrease** in the degree of

Ratio of Ion Intensities vs. Asymmetric Salt

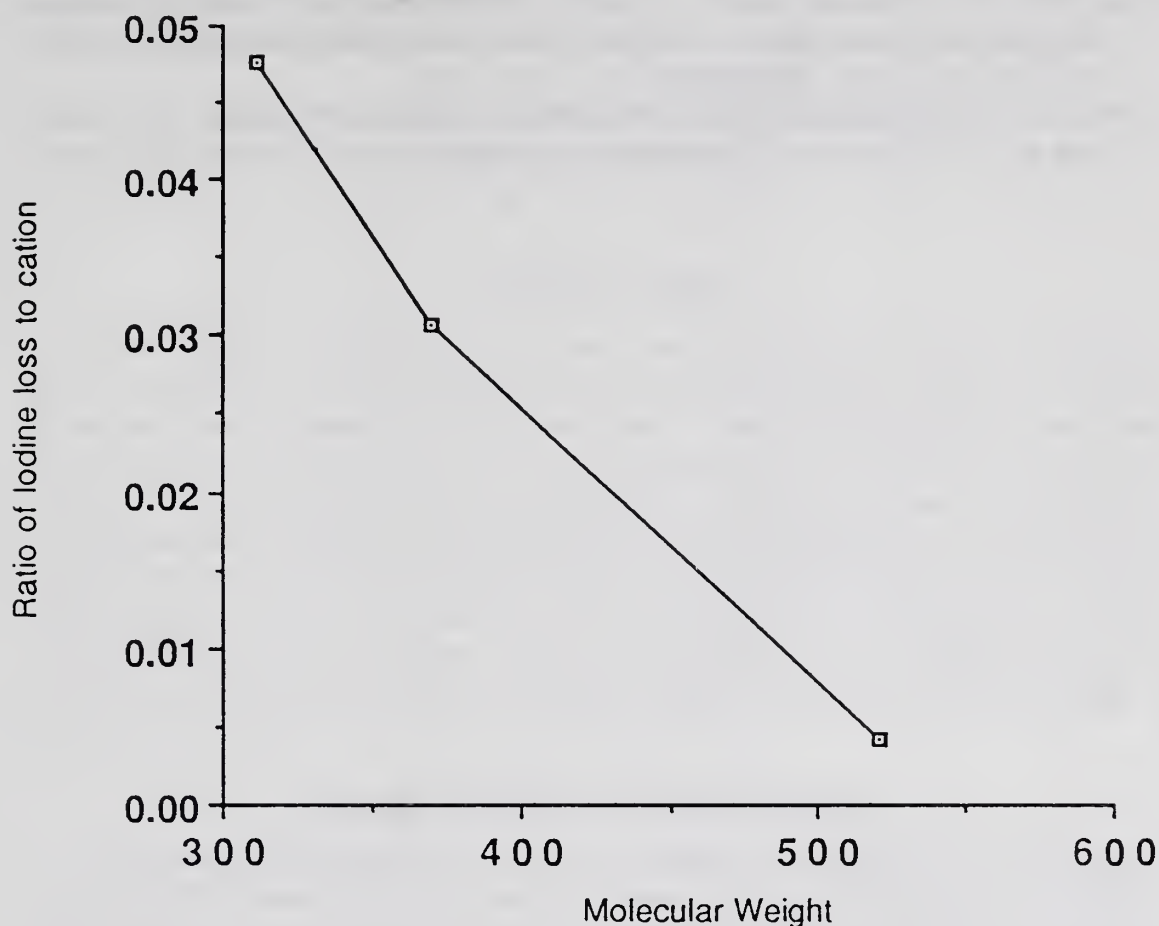


FIGURE 4. Plot of the ratio of ion intensities versus the molecular weight of the asymmetric salts.

fragmentation is seen (Figure 4). Increased molecular weight correlates with increased complexity in structure, preventing the bending of the ion necessary for iodine loss. Further calculations and examples are being studied to determine the generality of this conclusion.

CONCLUSIONS

The mass spectra of iodonium salts are easily measured with secondary ion mass spectrometry. Loss of atomic iodine is characteristic in many of the spectra. Calculations performed with molecular mechanics programs suggest that a bent structure for the ion leads most easily to this loss.

ACKNOWLEDGMENTS

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