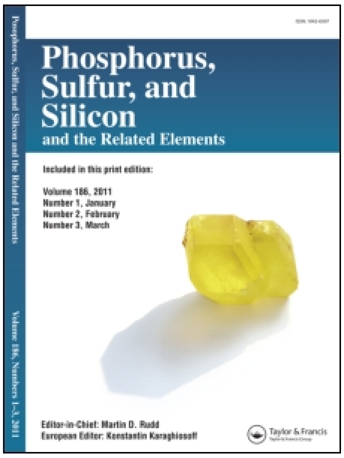

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POSITIVE ION LIQUID SECONDARY ION MASS SPECTRA OF AROMATIC SULFONIUM SALTS

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Organic sulfonium salts exist as pre-charged species in the matrices normally used for liquid secondary ionization mass spectrometry. Positive ion LSIMS mass spectra of the sulfonium salts therefore exhibit the intact cation (C^+) as the dominant ion species. Generally, the fragment ions are of 30–40% relative intensity and are formed through simple cleavages and rearrangements. Cluster ions such as CAC^+ and $C_3A_2{}^+$ are also present in the mass spectra (A is the counter ion of the salt). These cluster ions provided confirmation of the molecular weight. Adduct ions are formed between organic sulfonium salts and matrices used in LSIMS such as diethanolamine and triethanolamine. Beam-induced reactions are identified by comparison of mass spectra obtained with electrospray ionization, and by changes in ion products with changes in solvent matrix.

Keywords: Mass spectrometry; LSIMS; sulfonium salts; electrospray

INTRODUCTION

An organic sulfonium salt of the general structure $ABCS^+X^-$ contains a tricoordinate sulfur atom bearing a positive charge; A, B, and C are organic groups, and X is the counter ion associated with the cation. The sulfonium salts analyzed in this study consist exclusively of those salts in which all three bonds from the sulfur atom link to carbon. Sulfonium salts have been utilized as cationic photopolymerization agents, as intermediates in organic synthesis, and as agents in areas such as coating, inks and adhesives, photo polymers for the preparation of printing plates, fiber optic coatings, fiber-reinforced composites, and for electronic encapsulation. For these uses, aromatic sulfonium salts have been synthe-

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sized in a wide variety of synthetic forms suited to the specific applications. Since sulfonium salts are non-volatile, electron and chemical ionization are not appropriate for their mass spectrometric characterization. Fast atom bombardment (FAB) and liquid secondary ion mass spectrometry (LSIMS) sputter sample ions directly from a solution of sample, and have been used to produce high quality mass spectra from a number of "onium" salts. Duffin and Busch[1] examined several sulfonium salts with positive ion LSIMS, and found the mass spectra to be easily interpretable. The reported mass spectra contained a high intensity ion for the intact cation of the salt, designated as C^+, and fragment ions of 10–20% relative intensity that arise in simple cleavages and rearrangements from that cation. Of special interest was the observation of a beam-induced reaction between methyl- and ethyl diphenyl sulfonium salts and the triethanolamine support solvent used in the LSIMS experiment. The impact of the primary ion beam causes methylation or ethylation of the triethanolamine solvent, with the alkyl group originating in the sulfonium salt. The time dependence of this reaction could be followed by plotting the intensity of the ion signal as a function of time. Positive ion LSIMS mass spectra for a larger group of sulfonium salts were reported by Yin et al.[2]. The predominance of intact cations in the positive ion mass spectra was confirmed, and the presence of ions identified as CAC^+ and $C_3A_2{}^+$ (A is the anion of the salt) was repeatedly noted. Fragment ions were again identified as the products of simple cleavages and rearrangements from the intact cation.

In related work, the product ion MS/MS spectra of cations of sulfonium salts produced by fast atom bombardment were examined by Mestdagh et al.[3] The low energy collision-induced dissociation MS/MS spectra of several sulfonium cations contained a combination of simple cleavages, loss of alkyl radical groups, and rearrangements leading to loss of small neutral fragments, and in some cases, loss of R_2S from R_3S^+. A SIMS study by Groenewold et al.[4] has shown that sulfonium ion aggregates are stable on mineral surfaces. Such ion aggregates are used for monitoring decomposition products of mustard gas dispersed into the environment.

Despite the ease with which LSIMS mass spectra for aromatic sulfonium salts can be measured, general rules that support the structural interpretation of the mass spectra for these salts are still based on the relatively small number of examples cited above. One purpose of the present work is to record the mass spectra for a group of structurally diverse sulfonium salts, and to further establish the ground rules for spectral interpretation. Further, since sulfonium salts react with some of the matrices used for sample preparation in LSIMS [1], we wished to further explore this reactive chemistry.

EXPERIMENTAL

Positive ion mass spectra were acquired on a VG 70-SEQ hybrid mass spectrometer of EBqQ geometry. The primary beam was produced from a thermionic cesium ion source operated at 35 kV. Ions from CsI were used for mass calibration. Mass resolution was determined at baseline as 1000. Nitrobenzyl alcohol (mNBA) was used as obtained from Aldrich Chemical Company as the solvent for preparation of sample solutions for LSIMS analysis. Sample concentrations were approximately 10 ug/uL. Samples of the sulfonium salts were available from synthetic programs within the School of Chemistry and Biochemistry and from J. Crivello of Rensselaer Polytechnic Institute. Proton NMR spectrometry was used to check salt structure as appropriate. No background subtraction was used to prepare data for figures, and the ratio of the sample-related signal to the background signal can be clearly assessed. The calculated ion structures were modeled on Siliscon Graphic computers using Biosym's Insight II program.

RESULTS AND DISCUSSION

Structures of the sulfonium salts examined in this study are given in Figure 1, along with the numbering system used to make the following discussion tractable. Spectra are summarized in Table I. A few figures document the quality of the data obtained. Figure 2 is the positive ion LSIMS mass spectrum for sulfonium salt I. The strong signal at m/z 275 corresponds to the intact cation of the sulfonium salt. The isotope peak at $(C + 2)^+$ represents the isotope of the sulfur atom. The fragment ion at m/z 197 (20% relative intensity) corresponds to a loss of 78 Daltons from the intact cation, attributed to the loss of neutral benzene. Simple cleavage by loss of a phenyl group would lead to an odd-electron ion. Instead, hydrogen transfer to the phenyl group occurs (presumably from the bridging methylene), and loss of a neutral benzene molecule preserves the even-electron character of the fragment ion. Mestdagh et al. postulated that loss of 78 Da (neutral benzene) from the intact cation of a dialkylphenyl sulfonium salt was due to a secondary fragmentation rather than a direct loss from the cation. Usually, losses of both 77 and 78 Da were observed in their collision-induced dissociation MS/MS spectra. Since this is not the case here, we suggest simply that the hydrogen transfer required for loss of 78 Da is particularly easy in this case. Loss of 32 Da from the fragment ion at m/z 197 to form the fragment ion at m/z 165 (not labeled) corresponds to loss of a sulfur atom. The signal at m/z

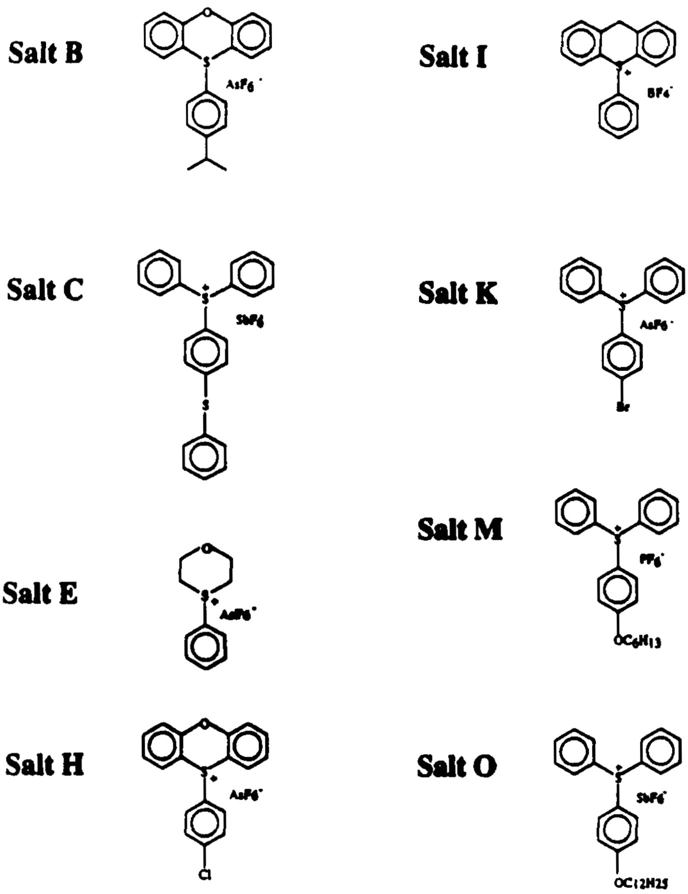

FIGURE 1 Structures of the sulfonium salts examined in this study.

637 (note the multiplication factor) corresponds to the CAC^+ cation, written in that manner to reflect the clustering of two cations (C) and a single anion (A). The ion at m/z 471 corresponds to a loss of 166 Da from the CAC^+ cation, configured as loss of methyl biphenylene. The ion at m/z 999 corresponds to the $C_3A_2{}^+$ cation. Other ions in the mass spectrum (unlabeled) are due to the mNBA matrix. The presence of both C^+ and CAC^+ provides a double check on the molecular mass of the cation, and identifies the anion by mass as well. The structure of the ion CAC^+ is still in question. Although it is simple to write $C^+A^-C^+$ as shown, this may not necessarily correspond to the most stable

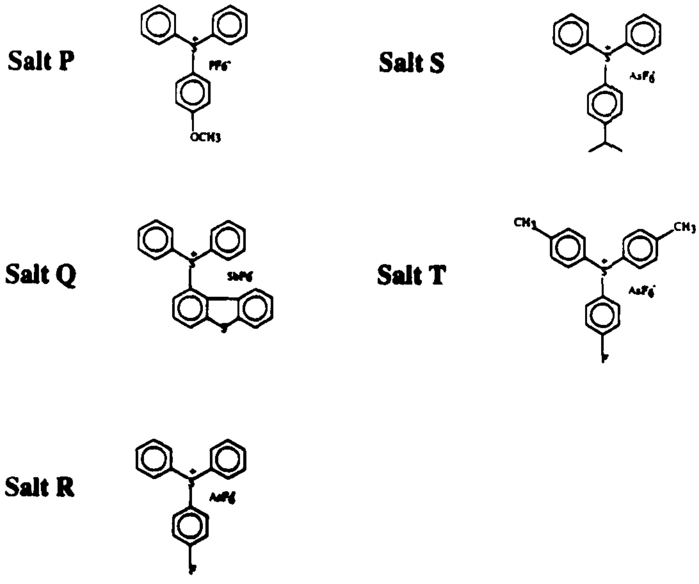

FIGURE 1a

structure for this cluster ion. In particular, the loss of methyl biphenylene as a neutral molecule from CAC$^+$, and not from C$^+$) indicates a structure in which the two cations may act in a concerted fashion to cause fragmentation.

Figure 3a is the positive ion LSIMS mass spectrum of sulfonium salt E. Again, the ions up to approximately m/z 160 are due to the mNBA matrix. The strong signal at m/z 181 corresponds to the intact cation of this sulfonium salt. The fragment ion at m/z 165 is formed by loss of 16 Da (atomic oxygen) from the intact cation. The signal at m/z 551 corresponds to the CAC$^+$ cation, and the peak at m/z 921 (magnified in intensity by a factor of 10) corresponds to $C_3A_2{}^+$. The signal at m/z 1291 corresponds to the $C_4A_3{}^+$ cation (magnified in intensity by a factor of 25).

Cluster ions are readily observed in the positive and negative ion LSIMS mass spectra of inorganic solids such as the alkali halides. Such cluster ions are, in fact, used for calibration of the mass scale of the mass spectrometer. Cluster ions as large as $C_4A_3{}^+$ have not been previously reported for organic compounds such as the sulfonium salts. Figure 3b is a possible structure of the $C_4A_3{}^+$ cation, based on the calculated ion structure output of the Insight II program. The possibility that positive and negative charges can be aligned in such a cluster ion, as shown, is analogous to structures proposed for molecular wires [5]. However, the exact structure of these ions remain to be determined.

TABLE I Summary of positive ion LSIMS of organic sulfonium salts (ND = not detected)

Salt Designation	*Cation Mass m/z (RI)*	*Fragment Ions m/z (RI)*	*CAC⁺ Cluster Ion m/z (RI)*	*Other Cluster Ions m/z (RI)*
Sulfonium Salt B	319 (100)	200 (13%)	827 (2.6%)	1335 (0.004%)
Sulfonium Salt C	371 (100)	294 (13%)	977 (1.2%)	ND
Sulfonium Salt E	181 (100)	165 (15%)	551 (14%)	921 (0.76%) 1291 (0.4%)
Sulfonium Salt H	311 (100)	NONE	811 (3.5%)	1311 (0.27%)
Sulfonium Salt I	275 (100)	197 (26%) 165 (3%)	637 (4%)	999 (1%)
Sulfonium Salt K	341 (100)	263 (7%)	873 (3.3%)	1434 (0.005%)
Sulfonium Salt M	363 (100)	291 (4%) 286 (3%) 279 (4%) 202 (11%)	871 (1.2%)	1379 (0.004%)
Sulfonium Salt O	465 (100)	Charge-Remote Fragmentation	ND	ND
Sulfonium Salt P	293 (100)	216 (12%)	731 (3.2%)	1169 (0.6%)
Sulfonium Salt Q	369 (100)	292 (14%) 215 (2%)	ND	ND
Sulfonium Salt R	281 (100)	204 (8%) 186 (4%)	751 (7%)	1221 (1%)
Sulfonium Salt S	305 (100)	228 (3%) 213 (8.5%) 186 (2%) 109 (2%)	799 (35%)	1293 (0.08%)
Sulfonium Salt T	309 (100)	NONE	807 (9%)	1300 (0.85%)

Figure 4 is the positive ion LSIMS mass spectrum for sulfonium salt M. The strong signal at m/z 363 corresponds to the intact cation, and the fragment ion at m/z 291 is the loss of 72 Da from the intact cation, originating as loss of neutral C_5H_{12} from the long-chain hydrocarbon chain. The fragment ion at m/z 286 represents the loss of 77 Da (a phenyl group) from the intact cation. In this case, hydrogen transfer must not be as facile as in salt I. The signal at m/z 871 represents the CAC^+ cation. The signal at m/z 1379 corresponds to $C_3A_2{}^+$ CAC^+ cation.

Figure 5 is the positive ion LSIMS mass spectrum for sulfonium salt O. The strong signal at m/z 465 corresponds to the intact cation. The ion at m/z 649 corresponds to the beam-induced addition of a $OC_{12}H_{25}$ fragment to the intact cation. The positive ion electrospray ionization mass spectra of the same sample showed no ion at m/z 649, discounting the possibility that there was an impurity at this mass in the original sample. The peak at m/z 649 is also present when both triethanolamine, as well as nitrobenzylalcohol, were used as the solvent, and so the direct involvement of the solvent can also be excluded. In contrast to

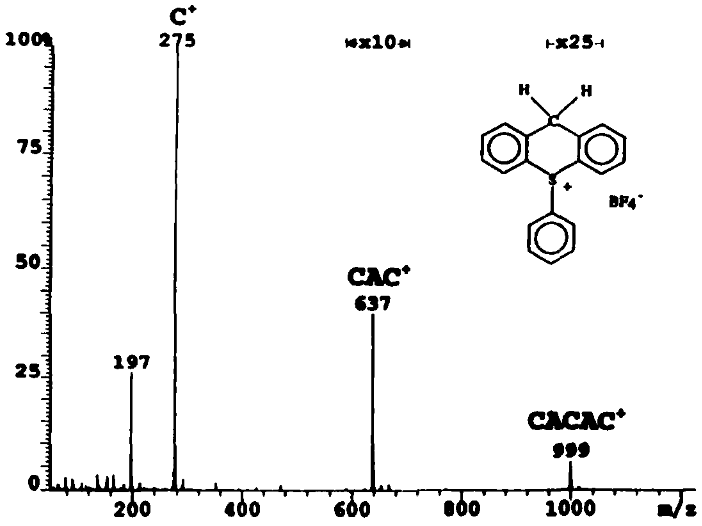

FIGURE 2 Positive ion LSIMS mass spectrum for sulfonium salt I.

what might be expected [11], there is no increase in intensity of the m/z 649 ion with time (see Figure 6). The addition of a second alkyl chain to the sulfonium salts generates a strongly surface-active species. Since this new compound

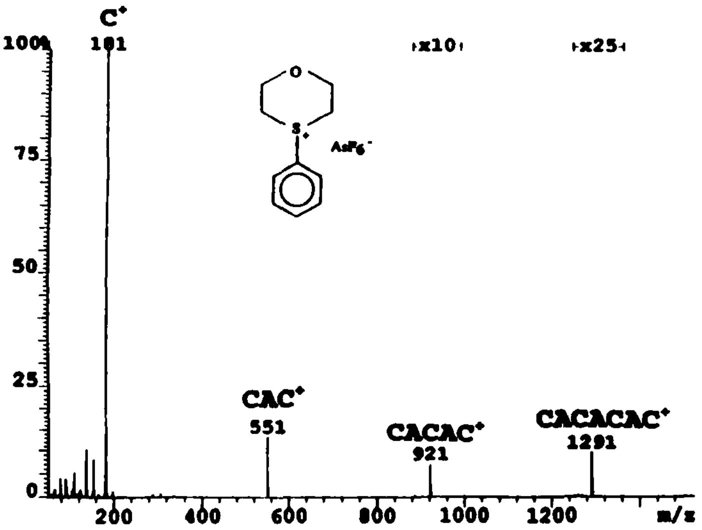

FIGURE 3A Positive ion LSIMS mass spectrum of sulfonium salt E.

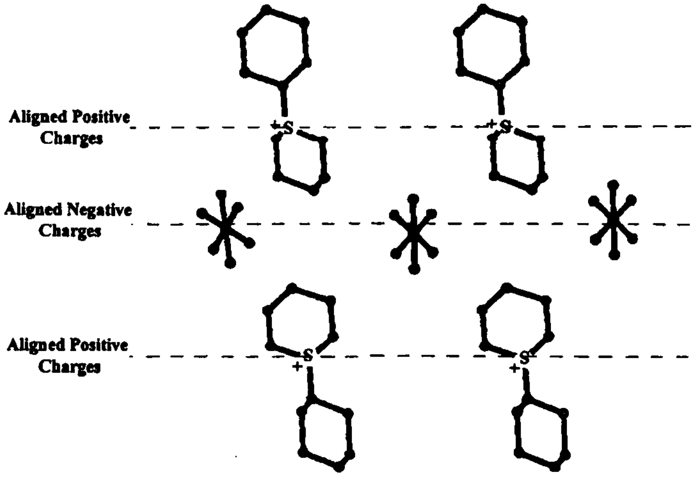

FIGURE 3b Possible structure of $C_4A_3^+$ cluster for sulfonium salt E.

should preferentially reside at the matrix surface, it is immediately sputtered away after its formation. Therefore, since the new compound is not present in the bulk of the sample solution, no increase in intensity with time is observed.

Charge-remote fragmentation is a dissociation process that was first observed in the product ion MS/MS spectra of charge-localized parent ions [6]. Recently, it was observed in the mass spectra of carbocyanine dyes that contain a localized

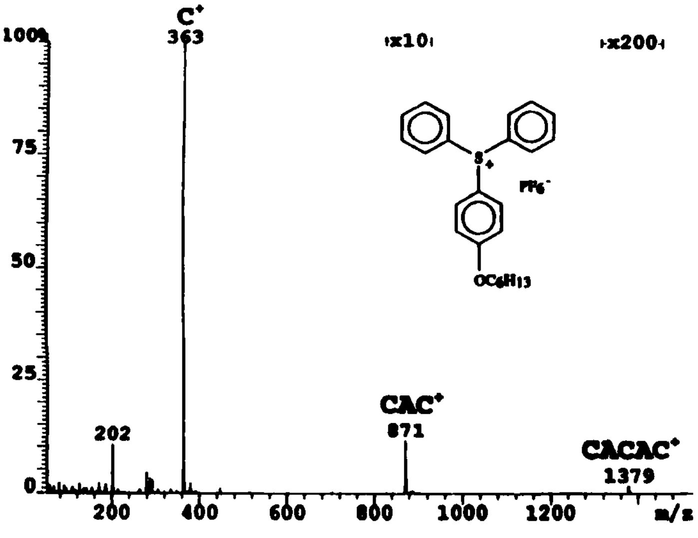

FIGURE 4 Positive ion LSIMS mass spectrum for sulfonium salt M.

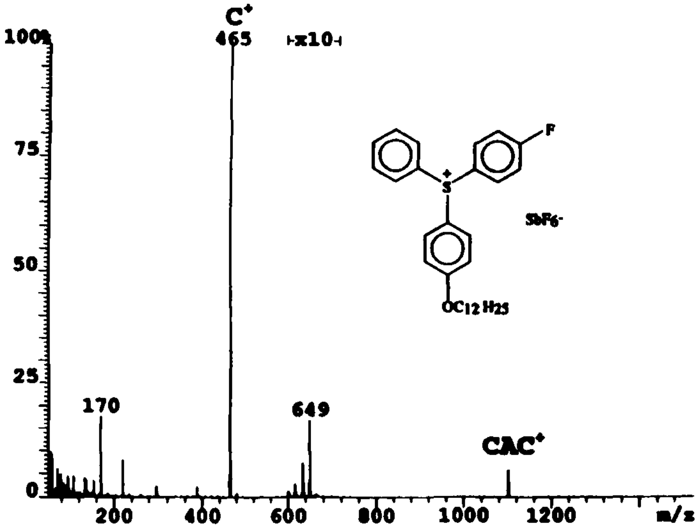

FIGURE 5B Positive ion LSIMS mass spectrum for sulfonium salt O showing charge-remote fragmentation.

charge site proximate to a long alkyl chain [7]. For salt O, charge-remote fragmentation is also observed as successive losses of methylene groups along the long alkyl chain, providing another example of such a process in an LSIMS mass spectrum.

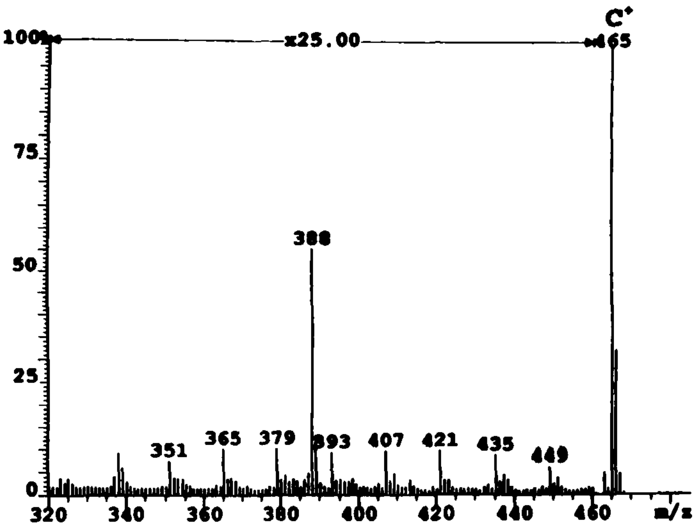

FIGURE 5A Positive ion LSIMS mass spectrum for sulfonium salt O.

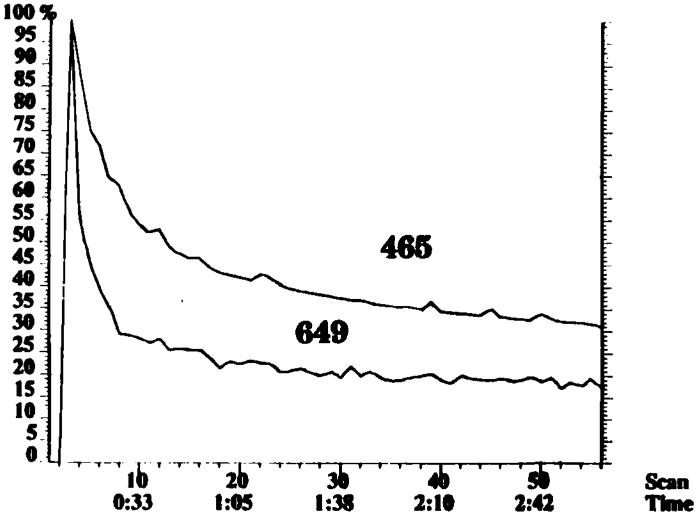

FIGURE 6 Time dependence for ion intensities in the mass spectrum of salt O

An instance of reactive chemistry involving a sulfonium salt and the matrix used is evident in the analysis of sulfonium salt T. When mNBA was used as a matrix, the spectra generated followed the same pattern previously discussed, with the intact cation as the base peak in the mass spectrum. However, when TEA (triethanolamine) was used as a matrix, the spectra generated was different and the most intense sample-related ion in the mass spectrum corresponds to an

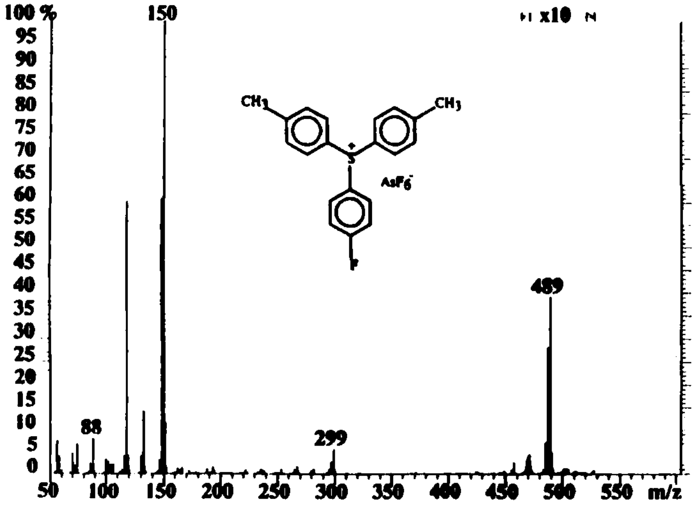

FIGURE 7 Positive ion LSIMS mass spectrum for sulfonium salt T.

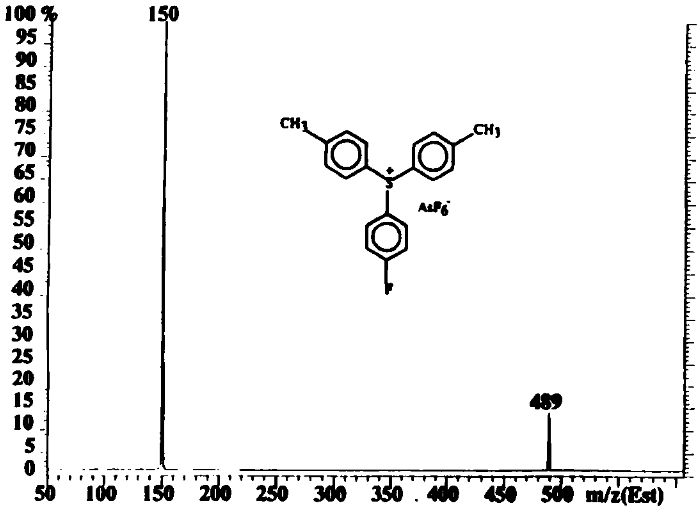

FIGURE 8 Product ion MS/MS spectra of the cation/solvent adduct ion for sulfonium salt T.

adduct, formally (C^+ + TEA + OCH_2) (See Figure 7). The intact cation at m/z 309 is not observed at all when TEA is used as the matrix. Figure 8 is the product ion MS/MS spectra of the cation/solvent adduct ion. The presence of protonated TEA as a product ion suggests that the TEA does not induce rearrangement of the salt, but rather forms a simple adduct to the ion derived from the cation.

CONCLUSIONS

The ground rules for spectral interpretation of the positive ion LSIMS mass spectra of sulfonium salts are established here. The intact cation of sulfonium salts is a dominant ion in the mass spectrum and only a minimal amount of fragmentation occurs. Clustering of the cation and anion is manifest in the appearance of the CAC^+ peak, the $C_3A_2{}^+$ peak and, for some salts, the $C_4A_3{}^+$ cluster ion. Most fragment ions observed as dissociations of the cation appear to be cleavages. Rearrangement ions are observed only in salt E and I, and represent losses from within the aromatic ring. Higher mass ions in the mass spectra represent fragmentation from the cluster cations, and the cluster ions themselves. These fragmentations often mirror those that occur from the cation itself, but in at least one instance, a concerted dissociation process that requires the involvement of both cations in CAC^+ was observed. We have documented a beam-induced alkoxylation reaction for one of the sulfonium salts analyzed, and a reaction of a sulfonium salt with triethanolamine is described. Sulfonium salts can be included in the short list of compounds that exhibit charge remote fragmentation in the LSIMS spectrum, provided that the structure of the salt contains at least one long alkyl chain proximate to the charged sulfonium atom. LSIMS produces easily interpretable positive ion mass spectra for sulfonium salts in general with dissociation processes directly related to structure. A similar ability to deduce cationic mass exists with electrospray ionization, but the fragment ions are much reduced in intensity.

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