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MASS SPECTROMETRY STUDIES OF THE IONIZATION OF ORGANIC MOLECULES BY SLOW POSITRONS

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Keywords: mass spectrometry, organic molecules, positronium ionization, sub-positronium ionization, dissociative ionization

ABSTRACT: The dissociative ionization of organic molecules, induced by positrons having energies below positronium thresholds (0.5-3 eV), has been studied. The ionization-fragmentation yields increase as positron energies decrease. The energies required for dissociative ionization are supplied by the annihilation processes. Fragmentation occurs by breakage of C-C single bonds in preference to double or triple bonds.

The establishment of an understanding of the interactions of molecules with positrons having kinetic energies below the positronium (Ps) thresholds (0.5-3 eV) is highly desirable; These are the energies at which positrons interact with the surrounding atoms and/or molecules of condensed matter and at surfaces. We have reported previously [1,2] that extensive fragmentation of organic molecules is observed with positrons having kinetic energies less than 1 eV. Energies of the order of 12 eV are required to ionize organic molecules and to fragment the resulting molecular ion. If the kinetic energy of the interacting positron is less than 1 eV, the only source of the necessary energy is through the annihilation process. These processes have been termed 'sub-positronium' ionizations. In this work, we present more studies of dissociative ionization processes that occur in the sub-positronium energy region.

Descriptions of the experimental setup have been given in previous publications [3]. The ORELA (Oak Ridge Electron Linear Accelerator) slow positron source delivered a 4 keV pulsed positron beam to a 100 nm tungsten foil, located immediately in front of

the input grid of a Penning trap. The Penning trap is 10 cm long and bounded at both ends by electrostatic grids. A one-kilogauss magnetic field was imposed along its axis. The positrons were thermalized in the foil and re-emitted from the backside with energies in the range of 2-3 eV. The energy of the positrons injected into the Penning trap was varied by biasing the moderator foil. The potential of the input grid was pulsed to ground to allow the re-moderated positrons to enter the Penning trap. The positrons were reflected from the output grid at the other end of the trap, but before they returned to the entrance grid its potential was restored. The trapped positrons were retained for times varying from 400 to 1800 microseconds.

The Penning trap served as the source of a time-of-flight mass spectrometer that was specially designed for this work. During the positron-molecule interaction period the walls of the Penning trap were at ground potential. To measure the masses of the ions produced, a potential gradient was applied from entrance to exit along the trap, accelerating the ions past the exit grid and toward the microchannel plate detector. As explained in ref. 7, the

acceleration potential was continuous, from the entrance of the Penning trap to the detector, proportional to the square of the distance from the detector. This caused the ions to move according to Hooke's law, such that their times of flight were independent of their starting positions in the Penning trap. The ORELA pulse served as the start signal, and the stop signal came from the microchannel plate pulse. Times of flight spectra for the ions were recorded by a time-to-digital converter, interfaced through a CAMAC unit to a personal computer.

Figures 1(a), 1(b), and 1(c) show mass spectra of 1-dodecene ionized by positrons

Figure 1. Time-of-flight mass spectra of 1-dodecene produced by (a) 1.0 eV, (b) 3.5 eV, and (c) 9.5 eV positrons.

having energies of 1.0, 3.5, and 9.5 eV respectively. The mass spectrum in Figure 1(a), produced by positrons of 1.0 eV, which is below the positronium threshold (2.6 eV, measured by Ps formation ionization), shows only fragment ions. The C₁₂ molecular ion could not be measured above background. It is seen that the mass distribution in this spectrum reflects more extensive fragmentation than that seen in Fig. 1(c), produced by the higher energy positrons. The mass spectrum in Figure 1(b) was produced by positrons having an energy of 3.5 eV, which is 0.9 eV above the positronium formation threshold. Note that the molecular ion is of the highest

Figure 2. Time-of-flight mass spectra of (a) butylbenzene, (b) 2-methyl-1-phenyl-1-propene, and (c) 1-phenyl-1-butyne.

intensity. Note also that the C_2 fragment ions are not produced under the higher-energy conditions of Figure 1(b) and 1(c), but they are produced by the 1 eV positrons (Fig. 1(a)). As shown in Figure 2(a), the $C_6H_5CH_2^+$ fragment peak dominates the spectrum when 1 eV positrons interact with butylbenzene. The broken bond responsible for the fragment is a σ bond that links the propyl group. Figure 2(b) compares the 1 eV fragmentation spectrum of 2-methyl-1-phenyl-1-propene which has nearly the same molecular weight as butylbenzene, and a similar structure, with the exception that a double bond joins the alpha and beta carbons of the 4-carbon group. In Figure 2(b) it is seen that fragmentation no longer occurs between the alpha and beta carbons; methyl groups are split off instead. Figure 2(c) was recorded for 1 eV positrons interacting with 1-phenyl-1-butyne, which is also similar in structure to butylbenzene, with the exception that the alpha and beta carbons are joined with a triple bond. For this molecule also the molecular ion shows a higher population, and fragmentation does not occur between the alpha and beta carbons of the 4-carbon group; in this compound also fragmentation occurs at sigma bonds, splitting off methyl groups. We conclude from the spectra of Figure 2 that fragmentation induced by sub-positronium ionization tends to occur at sigma bonds. Multiple bonds tend to stabilize the molecules toward fragmentation.

Figure 3 shows the dependence on

positron kinetic energy of the relative yields of molecular ion and fragment ion, $C_6H_5CH_2^+$, produced from butylbenzene. Both the sub-positronium and positronium regions are shown. There is a relatively large energy range, from about 2 eV to 3 eV, in which the parent ion is the predominant product. Above about 3.5 eV, in the positronium formation region, large amounts of fragment ion form. Below 2 eV, in the sub-positronium ionization region, the parent ion production is low, with the fragment ion predominating. Note that in the sub-positronium ionization region fragmentation yield increases as the positron energy decreases. This is opposite to the energy dependence observed for positronium formation conditions. The energy dependences observed for the sub-positronium ionization of decane, 1-dodecene, tetraethylsilane, and tetravinylsilane are similar to that of butylbenzene.

For dissociative ionization to occur, both the energies required to remove the electron and to fragment the molecule must be supplied. When dissociative ionization occurs as a result of the formation of positronium, the kinetic energy of the positron plus the energy released by Ps formation (6.8 eV) supply the necessary balance. If the positron energy is below the positronium formation threshold, the required energies must be transferred through the annihilation process. The following model has been proposed for describing the energy transfer process [4].

Figure 3. Ion Yields for the parent ion and the fragment ion of butylbenzene as a function of positron kinetic energy.

Annihilation by the positron removes an electron from one of the molecular orbitals. If the electron is annihilated from the highest occupied molecular orbital (HOMO), the molecular ion is left in the ground state. If the electron is removed from a lower energy orbital, and excitation energy is imparted to the molecule that is equal to the difference between the bonding energy of the orbital from which the electron was annihilated and that of the HOMO. If the energy is sufficient to dissociate the molecular ion, fragmentation will occur. One might think that there would be a higher probability for annihilating HOMO electrons, causing molecular ions to be the predominant product, but calculations [4] for hydrocarbons indicate that annihilation probabilities for electrons in the lower energy molecular orbitals are comparable to those of the HOMO. Most of the ions are therefore formed initially in excited states, and a large fraction of them have sufficient energy for dissociation.

In summary, mass spectra resulting from the dissociative ionization of organic molecules by positrons having tunable energies below the positronium formation thresholds have been recorded. Mass spectra resulting from the low-energy processes show more extensive molecular fragmentation than those produced by positrons of much higher energy. The spectra also demonstrate that fragmentation resulting from sub-positronium ionization tends to occur at σ -bonds rather than at multiply bonded sites. The sub-positronium ionization-fragmentation yields were observed to be enhanced by decreasing the incident positron energies in the range of 0.5-3 eV.

It is necessary to conclude that the energy required for ionization and fragmentation by the sub-positronium regime is transferred through the annihilation process. We wish to emphasize that we *do not* suggest that the energy is transferred by a Compton scatter process in which the gamma rays interact with the molecule as they are generated by the annihilation.

Acknowledgement: The authors wish to acknowledge the valuable help given to us on multiple occasions by D. E. Pierce and other members of the ORELA staff. This work was supported by the Chemical Sciences Division of the U.S. Department of Energy Office of Basic Energy Science, Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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