

Internal energy deposition into molecules upon positron-electron annihilation

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The dissociative ionization of organic molecules, induced by positrons having energies below the positronium threshold (0.5–3 eV), has been studied. Cross sections for the ionization-fragmentation processes increase as positron energies decrease. The data reveal that the energy required for dissociative ionization is supplied by the annihilation process, and that fragmentation occurs by breakage of C–C single bonds in preference to double and triple bonds.

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INTRODUCTION

Positron-induced dissociative ionization of molecules provides a tool that can be used in conjunction with other techniques, such as photoionization dissociation [1] and electron-induced dissociation [2], to understand energy transfer processes. The establishment of an understanding of the interactions of molecules with positrons having 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. Passner and co-workers [3] studied positron attachment for near-thermal positrons interacting with organic molecules. Schrader and co-workers [4] studied the formation of positronium compounds. Recently the authors [5] have reported some unexpected results showing that positrons having energies below the Ps thresholds induce extensive fragmentation of decane, tetraethylsilane, and butylbenzene. In this paper we present data for understanding dissociation processes that occur when the kinetic energy of positrons is less than Ps thresholds.

For a molecule, the energy threshold for ionization by Ps formation is $V_{IP} - 6.8$ eV, where V_{IP} is the ionization potential of the molecule and 6.8 eV is the energy liberated by Ps formation. The authors [6] have reported fragment ion yields for positron energies above Ps thresholds. Fragmentation was not expected to occur when the kinetic energy of the positron was less than the Ps thresholds, but this has been clearly seen [5]. The mechanism for this low-energy phenomenon must involve an energy transfer during an annihilation process.

EXPERIMENT

Descriptions of the experimental setup have been given in previous publications [6,7]. A time-of-flight (TOF) mass spectrometer, coupled with a Penning trap, is specially designed for the work. The Penning trap is 10 cm long and bounded at both ends by electrostatic grids. A 1-kG magnetic field is imposed along the axis of the Penning trap.

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The ORELA (Oak Ridge Electron Linear Accelerator) slow positron source delivers a 4-keV pulsed positron beam to a 100-nm tungsten foil located immediately in front of the input grid of the Penning trap. The positrons are thermalized in the foil and reemitted from the back side with energies in the range of 2–3 eV. The energy of the positrons being injected into the Penning trap is varied by biasing the moderator foil. As the remoderated positrons emerge from the tungsten foil, the potential of the input grid is pulsed to ground, allowing them to enter the Penning trap. The positrons are reflected from the output grid at the other end of the trap, but before they return to the entrance, the potential of the input grid is restored. The positrons are retained in the trap for times varying from 400 to 1800 μ sec. Depending on their energies, 0.5 to 3 eV, their collision paths with the organic molecules vary from 160 to 1800 m.

The Penning trap ionization source is attached to a 50-cm flight path, having a microchannel plate detector at the end. During the positron-molecule collision period, the potentials of the walls of the Penning trap are at ground potential. To measure the masses of the ions produced, a potential gradient is applied, from entrance to exit along the trap, to accelerate the ions toward the detector. As explained in Ref. [7], the acceleration potential is continuously varied, proportional to the square of the distance from the detector. This causes the times of flight of the ions to be independent on their starting positions in the 10-cm Penning trap. The ORELA pulse serves as the start signal, and the stop pulse is given by the arrival of the ions on the microchannel plate. Times-of-flight spectra for ions are recorded by a time-to-digital converter, interfaced through a computer-aided-measurement-and-control (CAMAC) unit to a personal computer.

The energies of the positrons injected into the Penning trap are also determined by a time-of-flight method. To accomplish this, the potentials on all grids and lenses of the spectrometer are set at ground. Positron energy is calibrated by measuring positronium formation thresholds of gases. With the moderator biased at zero potential, the energy distribution peaks at 2.25 eV, with a full-width-half maximum (FWHM) of 0.5 eV. It is possible to inject positrons with tunable energies as high as 20 eV into the Penning trap. Energies listed in the following

figures are the initial incident energies. It is the belief of the authors that some of the positrons undergo nonionizing inelastic collisions with the organic molecules, which lower their energies after long retention times in the trap.

RESULTS

Figures 1(a), 1(b), and 1(c) show mass spectra of 1-dodecene ionized by positrons having energies of 1.0, 3.5, and 9.5 eV, respectively. The mass spectrum in Fig. 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 Fig. 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 intensity. Note also that C₂ fragment ions are not produced under the conditions of Figs. 1(b) and 1(c), but they are produced by the 1-eV positrons [Fig. 1(a)].

Figure 2 shows how the cross sections for dissociative

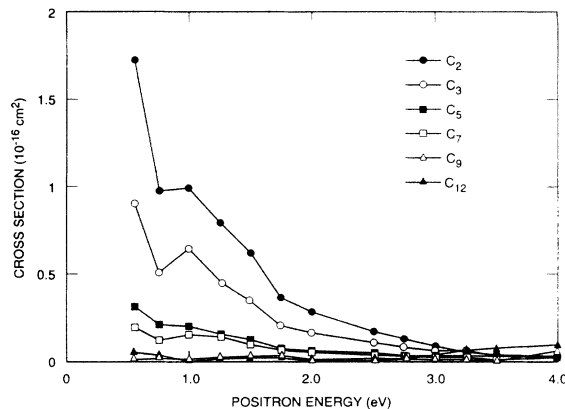


FIG. 2. Cross sections for fragmentation of 1-dodecene as functions of positron energy below the positronium formation threshold.

ionization of 1-dodecene vary as functions of positron energy below the Ps threshold. The cross sections are determined by measuring the ratio of ionization yields for both 1-dodecene and krypton and using the cross section of Ps formation for krypton measured by Kauppila and Stein [8]. It is clearly seen that the cross sections

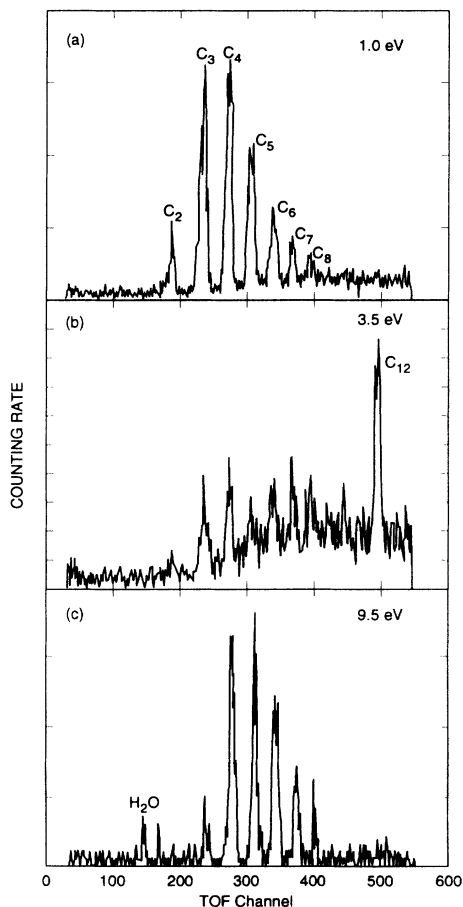


FIG. 1. Time-of-flight mass spectra of 1-dodecene produced by (a) 1.0 eV, (b) 3.5 eV, and (c) 9.5 eV positrons.

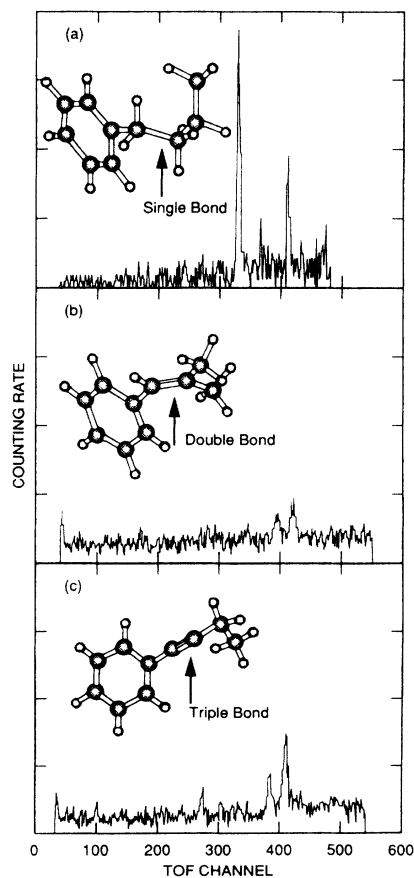


FIG. 3. Time-of-flight mass spectra of (a) butylbenzene, (b) 2-methyl-1-phenyl-1-propene, and (c) 1-phenyl-1-butyne, produced by 1-eV positrons.

increase as the positron energy decreases. This is opposite the energy dependence observed under Ps formation conditions where the degree of fragmentation increases as the positron energy increases. The energy dependence observed for decane, butylbenzene, tetraethylsilane, tetravinylsilane, and other organic molecules is similar to that of 1-dodecene.

As shown in Fig. 3(a), the $C_6H_3CH_3^+/C_6H_5CH_2^+$ fragment peak dominates the spectrum under the 1-eV positron impact on butylbenzene. The broken bond responsible for the fragment is a σ bond that links the propyl group. To investigate the role of molecular bonds in positron dissociative ionization, we selected 2-methyl-1-phenyl-1-propene molecules for which the σ bond is accompanied by a π bond (the double bond). As shown in Fig. 3(b), the $C_6H_5CH_3^+$ fragment peak, which dominates in butylbenzene, disappears for 2-methyl-1-phenyl-1-propene. Instead, the formations of the molecular ions and the fragments resulting from loss of a methyl group are relatively enhanced. Moreover, we select 1-phenyl-1-butyne molecules in which the σ bond is replaced by a triple bond. The result, shown in Fig. 3(c), is similar to the double bond case. These results show that fragmentation occurs by breakage of C–C single bonds in preference to double and triple bonds.

ANNIHILATION-INDUCED INTERNAL ENERGY DEPOSITION

For dissociative ionization to occur, both the energies required to remove the electron and to break 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 [9]:

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 a ground state. If the electron is removed from a lower-energy orbital, an 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, then, given sufficient time, the ion will fragment. An argument arises that more molecular ions would be produced due to a higher probability for annihilating the HOMO electrons than the deeply occupied electrons. However, calculations [9] for positron annihilation in hydrocarbons indicate that an electron may be annihilated from any one of several molecular orbitals with comparable probability. Most of the ions are therefore formed initially in excited electronic states, and a large fraction of them have sufficient excitation energy for dissociation.

Present-day mechanisms by which ions are believed to be produced by the low-energy positrons are (1) electron pickoff, proposed by Dirac [10] and developed by Massey [11] for molecules, and (2) positron attachment before annihilation. The “electron pickoff” depicts it as the annihilation of an electron by a positron as it passes by. The probability of this occurring depends on an overlap of the densities of the electron and the positron. Dirac concluded that the degree of overlap should be inversely proportional to the velocity of the positron. The positron attachment mechanism has been suggested by Passner and co-workers [3] to explain their observations of thermal positron interactions. The positron undergoes an inelastic collision, which absorbs some of its kinetic energy, causing it to become trapped by the molecule. It is not clear from these data which process is involved in the annihilation.

In describing the positron annihilation cross section, Fraser [12] defined the effective number of annihilatable electrons per molecule, Z_{eff} , as shown below:

$$\sigma = \pi r_0^2 \frac{c}{v} Z_{\text{eff}}(E),$$

where v is the positron velocity, r_0 is the classic electron radius, and c is the speed of light. In our measurements, Z_{eff} is determined to be 3.7×10^6 . This number is consistent with that measured by Surko *et al.* [13] on positron annihilation of alkane molecules. Based on calculations for rare-gas atoms in the frozen-core polarized-orbital approximation, McEachran and co-workers [14] predict that Z_{eff} is reduced by increased positron energy. Z_{eff} is expected to decrease with energy in large molecules, also, if annihilation is preceded by capture into Feshbach resonance. The behavior of Z_{eff} in this case may be a consequence of the energy dependence of the positron attachment cross section [9]. The energy dependence of dissociative ionization rates measured in our experiments is a test of these suggestions. The ionization rates that occurred in the Penning trap were proportional to the annihilation cross sections and to the velocities of the positrons. As shown by the energy relation above, the cross section for annihilation is inversely proportional to the positron velocity [11]. If Z_{eff} were independent of energy, the ionization rate would not vary with positron energy. But our data show a strong dependence of dissociative ionization rates on positron energies; therefore, we conclude that Z_{eff} increases as positron energy decreases. The data of Fig. 2 are a measure of the energy dependence of Z_{eff} and are in qualitative agreement with the above predictions.

In summary, mass spectra resulting from the dissociative ionization of 1-dodecene, butylbenzene, 2-methyl-1-phenyl-1-propene, and 1-phenyl-1-butyne by positrons having tunable energies below the positronium formation thresholds have been recorded. Mass spectra resulting from the low-energy processes show more extensive fragmentation than those produced by positrons of much higher energy. It is necessary to conclude that the energy required for ionization and fragmentation is transferred through the annihilation process. The re-

sults also demonstrate that σ -bond electron annihilation has higher probabilities for fragmentation than those of multiple-bond electrons. The fragmentation yields of the molecules were observed to be enhanced by decreasing the incident positron energy in the range of 0.5–3 eV. These data support models predicting that effective atomic numbers of atoms and molecules are increased by polarization effects of the slow-moving positrons. To interpret the low-energy positron-induced fragmentation, a model is proposed which suggests that electrons lying

in orbitals below the HOMO are removed, leaving the molecules in excited states.

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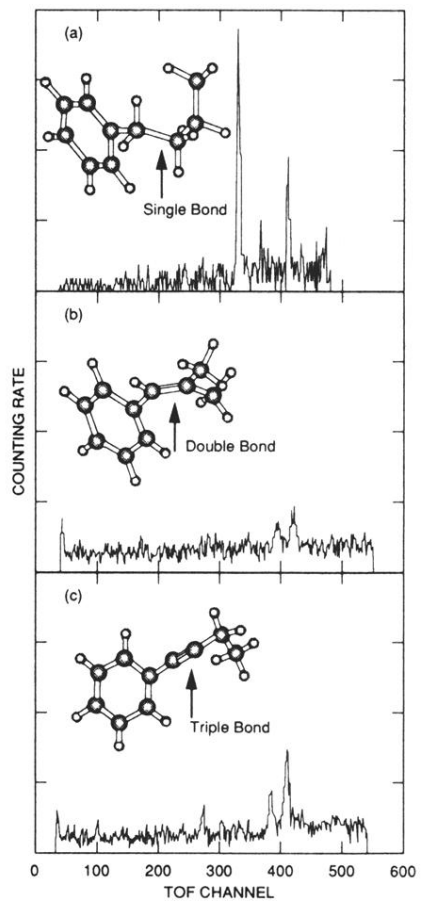


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