PHYSICAL REVIEW A VOLUME 49, NUMBER 4 APRIL 1994

Ion production by positron-molecule resonances

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(Received 2 December 1993)

Ion production by low-energy positrons in low-density gases was reported by Passner, Surko, Mills, and Leventhal [Phys. Rev. A **39**, 3706 (1989)]. That work studied the ionization of hydrocarbons in a positron trap in the presence of a buffer gas of molecular nitrogen. We present further analysis of the data from this experiment, taking into consideration the ionization of the hydrocarbons by nitrogen ions created as a result of the positron trapping process. We conclude that ionization by positrons was the dominant ion production mechanism at times longer than the characteristic ion confinement time of approximately 1 s, while ionization by nitrogen charge exchange was dominant at earlier times. The details of the ionization spectra are also discussed.

PACS number(s): 36.10.−k, 78.70.Bj, 71.60.+z

The ionization of neutral molecules by low-energy positrons is an interesting fundamental physics question. It is also of potential practical significance in that it offers a qualitatively different method of producing ions for use in chemical analysis by mass spectrometry [1,2]. In the earliest work on this subject, Passner *et al.* [1] studied the ionization of neutral hydrocarbons introduced into a modified Penning trap. Due to the nature of the trapping process, molecular nitrogen ions were also present. In Ref. [1], the effect of ionization by these nitrogen ions was neglected. The present paper is a reanalysis of their data including this effect.

The main conclusion of our study is that molecular nitrogen ions dominate the ionization of test gases introduced into the trap at early times, until the $N_2{}^+$ diffuse radially out of the trap, which occurs in about 1 s. After this time, ions continue to be produced via ionization by low-energy positrons. The net result is that the ionization spectra reported in Ref. [1], at elapsed times of about 2 s and longer, arise from positron ionization, while those at elapsed times of less than about 1 s are dominated by ionization by $N_2{}^+$ ions.

In the experiment described in Ref. [1], positrons from a radioactive source were slowed to a few electron volts by a tungsten moderator. They were then guided by an axial magnetic field into an electrostatic potential well of depth approximately 40 eV, created by voltages on a set of cylindrical electrodes. The axial magnetic field in this region was 860 G. Nitrogen gas was introduced into the trap, and the resulting inelastic collisions of the positrons with the N_2 molecules provided a mechanism to trap the positrons in the electrostatic potential well. The trapping was accomplished in three stages, each with a successively lower pressure of nitrogen buffer gas. In the final stage, the N_2 gas pressure was approximately 1.5×10^{-6} torr. In the presence of the buffer gas, the positrons cool to room temperature with a characteristic $1/e$ time constant of approximately 0.6 s. Further details of the operation of the trap and the trapping mechanism are presented in Ref. [3]. The number of positrons in the trap was kept less than about 1×10^4. Also present in the final stage of the trap was approximately the same order of magnitude of nitrogen ions.

The positron lifetime is of the order of 60 s, which is limited by annihilation of the positrons on the N_2 molecules and on small amounts of other impurity molecules present in the vacuum system. Test gases of butane and heptane were introduced into this region at pressures less than 3×10^{-7} torr. The confinement time of the positrons was long compared to the annihilation time, since the positrons are highly magnetized, having Larmor radii of less than 0.01 mm. In contrast, the nitrogen ions and ions of the test gas molecules, which have much larger masses, are not highly magnetized (i.e., Larmor radii of the order of a few millimeters). Consequently, they have a characteristic confinement time of about 1 s, limited by radial diffusion across the magnetic field. Ion spectra were measured by dumping the contents of the trap and analyzing them with a time-of-flight mass spectrometer. A typical cycle was to fill the positron trap for 0.5 s, and then measure the ion spectra for a range of different storage times. Data from the Passner *et al.* paper for butane are reproduced in Fig. 1. In Ref. [1], data were also presented for heptane for storage times of 0.2, 2, and 4 s.

Under the conditions of the Passner *et al.* experiment, the positrons do not diffuse radially out of the trap on the time scale of the ion spectral measurements [4]. In addition, when hydrocarbons are introduced into the trap, the positron annihilation rate is proportional to the gas pressure of the hydrocarbon [5]. This indicates that positrons annihilate on the hydrocarbon molecules via a two-body interaction. There are two reasons for being confident that this annihilation occurs as a result of binding of the positrons to the butane molecules, in contrast to resulting

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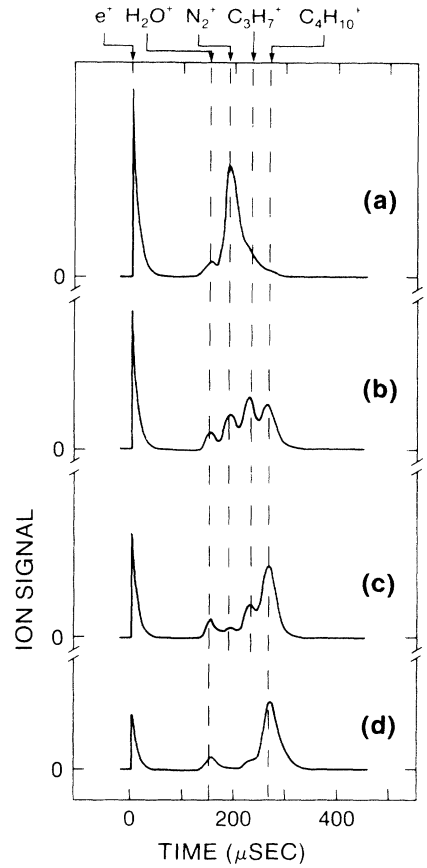

FIG. 1. Time-of-flight spectra of the ions when butane is present in the positron trap. The filling time was 0.5 s, the N_2 pressure was 0.5×10^{-7} torr, and the butane pressure was 2.5×10^{-7} torr. The traces correspond to storage times of (a) 0 s, (b) 0.5 s, (c) 1 s, and (d) 2 s. The identification of the peaks and their expected positions are indicated.

from positronium formation. First, the positrons cool to room temperature (~1/40 eV) in about 1 s [4]. This precludes positronium formation, which requires much higher positron energies, and leaves positron attachment as the only other plausible process for positron annihilation. Second, the annihilation gamma-ray spectra from positron-molecule interactions have recently been measured, including measurements of the interaction of positrons with hydrocarbons [6]. These spectra show no evidence of the characteristic feature expected for the annihilation spectrum of positronium, namely, a broad feature on the low-energy side of the 511-keV annihilation line, due to three-gamma decay [6]. Furthermore, the measured Doppler broadening of the 511-keV line is consistent with theoretical predictions for annihilation of positrons bound to hydrocarbon molecules and, in particular, to annihilation on the C—H bond [6]. Thus, there is good evidence that butane ions and/or ion fragments are produced by the annihilation of positrons following interaction of the positrons with the neutral molecules.

As shown in Fig. 1, there is also evidence of the presence of N_2^+ ions in the trap at early times. In order to quantify the role of these ions in ionizing the hydrocarbons, we have recently studied the ionization of butane and heptane by N_2^+ ions in a separate experiment using a quadrupole ion trap mass spectrometer [7]. Figure 2 shows the plot of the decrease in N_2^+ intensity versus time for butane and heptane. From the slopes of these curves, the charge-exchange rate constant can be determined. For N_2^+ reacting with butane, a rate constant of 1.2×10^{-9} $\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ is measured, while the rate constant for heptane reacting with N_2^+ is 2.3×10^{-9} $\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. These rate constants are, to within experimental error, the collision rates predicted by the average-dipole-orientation (ADO) theory [8,9].

Figure 3 shows representative mass spectra obtained at two different reaction times. The water peak arises from residual water in the system. Initially, the signal appears at $M/Z=18$, but the water molecular ion rapidly reacts with neutral water to form the hydronium ion observed at $M/Z=19$. From Fig. 3, it can be seen that the C_4 region of the spectrum is dominated by $C_4H_9^+$ (mass-to-charge ratio, $M/Z=57$) and its ^{13}C isotope. The C_3 region of the spectrum consists of two ionic species, $C_3H_5^+$ and $C_3H_7^+$. It can also be seen that two C_2 ions are formed. Due to the limited resolution of the Passner *et al.* experiment and the close proximity of the N_2 signal, they were not able to discern the presence of the C_2 ions, nor would they have been able to determine the presence of two species of comparable intensity in the C_3 region.

Figure 4 shows a plot of the total ion current from each species as a function of the reaction time. As can be seen in Fig. 4(a), the rapid decrease in the component with $M/Z=28$ corresponds to an initial increase in C_3 and C_2 ions, but the rise in C_4 ions occurs slightly later. As the reaction time is increased, the C_3 and C_2 ions reach a maximum and then begin to decrease in relative intensity, while the C_4 ion continually increases in intensity. This indicates that two consecutive reactions are occurring. First, butane is ionized by dissociative charge exchange with N_2^+, forming the C_3 and C_2 fragment ions. Subsequently, the C_3 and C_2 ions react with butane by proton abstraction to form the C_4 ion. This is the

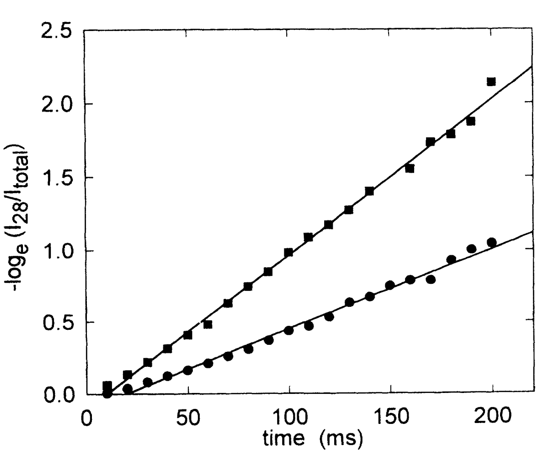

FIG. 2. The decay of the N_2^+ ion signal versus time in an ion-trap mass spectrometer in the presence of (■) butane at a pressure of 3.5×10^{-7} torr and (●) heptane at a pressure of 9.7×10^{-8} torr.

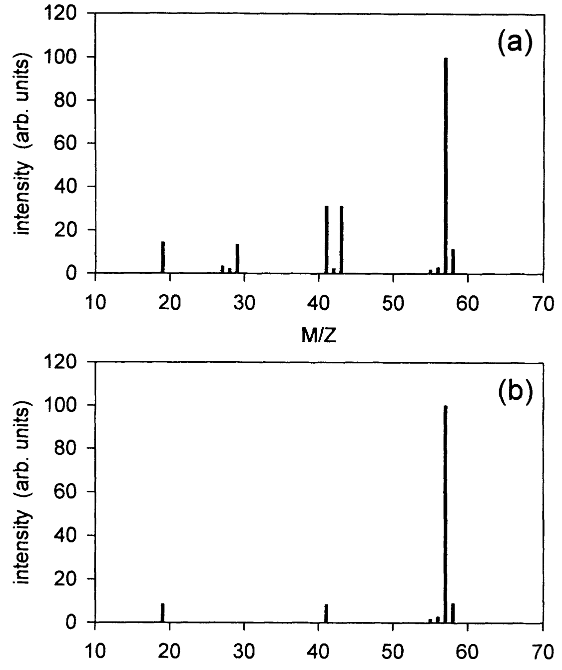

FIG. 3. Mass spectra for the reaction of N_2^+ with butane, studied in an ion-trap mass spectrometer: (a) 0.5-s reaction time and (b) 1.0-s reaction time.

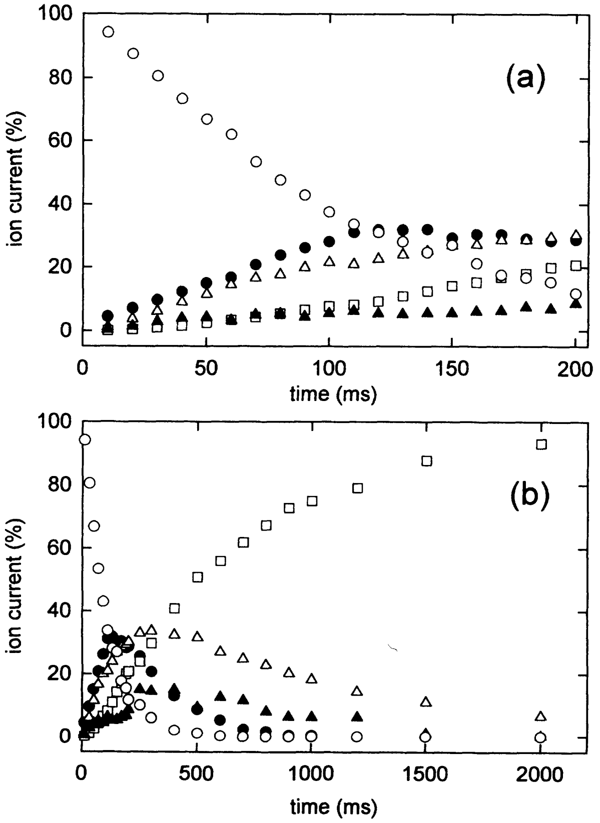

FIG. 4. Ion currents as a function of time, measured in an ion-trap mass spectrometer, for the reaction of N_2^+ ions with butane: (a) 0–0.2 s, and (b) 0–2 s; for (○) N_2, (●) C_2, (△) C_3, (□) C_4, and (▲) H_2O.

most stable species that can be formed, and thus it is the terminal ion in the reaction sequence. The reaction sequence is summarized below.

$$N_2^+ + C_4H_{10} \rightarrow C_3H_7^+ + CH_3 + N_2 \quad (1)$$

$$\rightarrow C_3H_5^+ + CH_3 + H_2 + N_2 \quad (2)$$

$$\rightarrow C_2H_5^+ + C_2H_5 + N_2 \quad (3)$$

$$\rightarrow C_2H_3^+ + C_2H_5 + H_2 + N_2 \;, \quad (4)$$

$$C_nH_m^+ + C_4H_{10} \rightarrow C_4H_9^+ + C_nH_{(m+1)} \;. \quad (5)$$

It is likely that the ionic products in reactions (2) and (4) actually result from the unimolecular dissociation of the ion products of reactions (1) and (3), respectively. However, this would not be discernible on the time scale of the experiment. The reactions (5) have been previously studied [9,10], and typical rate constants are in the range of $4-8\times10^{-10}$ $cm^3\,mol^{-1}\,s^{-1}$. From the present data, we determine a rate constant for the reactions (5) for butane in a quadrupole ion trap to be 2×10^{-10} $cm^3\,mol^{-1}\,s^{-1}$.

The ion-molecule reaction study described above was performed in a quadrupole ion trap in which the ion-confinement time is much longer than the time scale of the experiment. In contrast, the experiment of Passner *et al.* was performed in a Penning trap, with a magnetic field of 860 G, and consequently, the ions were confined for only about 1 s. In order to demonstrate the short ion confinement time of the butane and nitrogen ions in the Passner *et al.* experiment, we measured the decay of the number of ions in the Penning trap under the conditions relevant to that experiment for each species, and these data are shown in Fig. 5. The conditions of the experiment for the data shown in Fig. 5 were such that the respective species under study was the dominant species

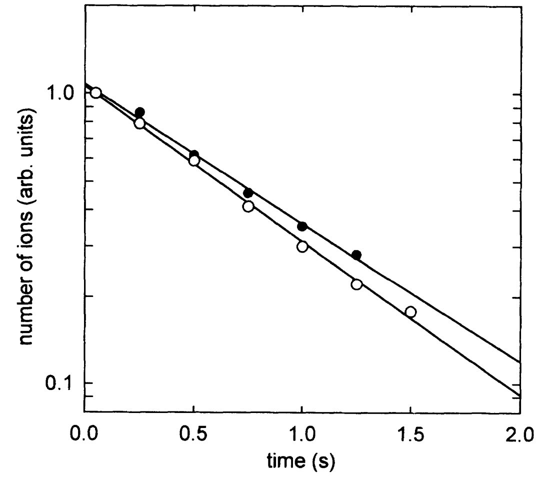

FIG. 5. Number of ions remaining in the Penning trap as a function of storage time for a magnetic field of 1075 G: (○) nitrogen and (●) butane. These data were taken under conditions where each ion species was dominant. Fits to exponentials give confinement times of $\tau=0.82$ and 0.91 s for nitrogen and butane, respectively.

at the beginning of the experiment. Chemical reactions can therefore be ignored [11], and the loss of the ions is then due to diffusion across the magnetic field. We note that the short ion-confinement times evident in Fig. 1 are similar to those obtained by Passner *et al.* from the model presented in their paper, and they are also consistent with theoretical estimates of ion confinement under the conditions of the experiment [1].

Using the rate constants described above and the measured ion confinement times, we calculated the production of butane ions by nitrogen ionization as a function of time expected for the Passner *et al.* experiment, and the results are shown in Fig. 6. The butane data from that experiment are shown as circles, and the predicted ion intensity based on ion-molecule reactions and ion confinement times is shown by the solid line. Figure 6 shows that N_2^+ ions can account for much of the butane ion signal at early times, but that they have a relatively small contribution to the observed butane ion signal at times greater than about 1 s. We note that the model described in the paper of Passner *et al.* included the parameter, η, which represented the relative detection efficiencies of butane ions versus positrons. The best fit to the data was obtained with $\eta=4.5$. This value is somewhat higher than the expected value which is in the range between 2 and 3. If the charge-exchange ionization process reported in this paper is included, the effect would be to bring the fitted value of η closer to the expected value.

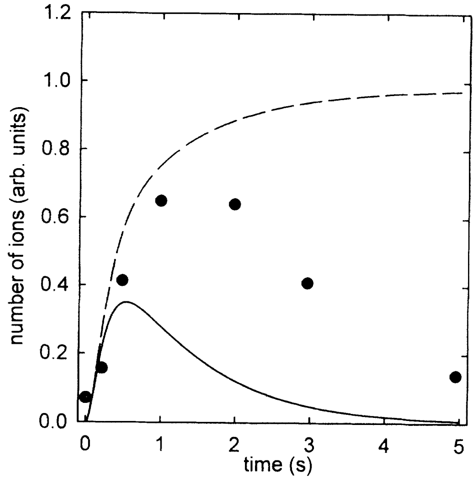

FIG. 6. Number of butane ions remaining in the positron trap as a function of storage time. The solid points are from Ref. [1]. All data are normalized to the number of nitrogen ions at time $t=0$. The expected signal from reactions (1)–(5) is shown by the solid line. The dashed line is that expected from reactions (1)–(5) if the ion confinement time were long compared to the time scale of the experiment.

We conclude that, in the experiment of Passner *et al.*, the butane ion signal was dominated in the first second after the end of the filling phase by charge-transfer reactions involving nitrogen ions. However, the conclusions of the paper of Passner *et al.* are valid at later times, (i.e., delay times greater than about 1 s). For these times, positron ionization of butane was the dominant ionization process. We note that the Passner *et al.* data at later times show that low-energy positron ionization of butane results in ions with four carbon atoms, in contrast to data from larger alkanes where many fragments are observed [1,10]. This may be intrinsic to the ionization of butane by positrons. An alternative explanation is that the positron ionization produces fragment ions, similar to ionization by N_2^+. Then, these fragment ions subsequently react with neutral butane to produce ions similar to the molecular ion, thus giving the appearance of the molecular ions being formed by slow positron annihilation. Resolution of this issue will require further study.

With regard to the heptane data in Ref. [1], we have not made a quantitative analysis such as that presented here for butane. However, if one considers the relatively short ion confinement time in the Passner *et al.* experiment and the data shown in Fig. 4 of their paper, the ion spectra at later times [i.e., Figs. 4(b) and 4(c)] indicate that the dominant contribution from positron ionization is the $C_3H_7^+$ ion fragment. This is consistent with subsequent measurements using a different technique [2].

In summary, we conclude that there was a large contribution to the ion signals in the Passner *et al.* experiment at early times from charge-transfer reactions of the alkane under study with N_2^+ ions. However, the fact that the ion confinement time was of the order of 1 s, while butane ion production occurred on longer time scales from 3 to 5 s, together with the fact that the positrons disappear by annihilation *in situ* in the trap, give evidence that positron ionization was the dominant ion production mechanism at later times.

This study highlights the complicating role of chemical reactions in interpreting positron ionization mass spectra in positron traps that use a buffer gas for trapping. In future experiments, it would be desirable to eliminate these complications. This can be accomplished using a modified gas-handling system, with the capability of shutting off the buffer-gas feed after the positrons have been loaded and cooled. The N_2^+ ions could then be allowed to diffuse out of the trap, leaving the cold positrons, which have a much longer confinement time. The test gas might then be introduced in a separate phase. An alternative is to shuttle the cold positrons to a separate UHV stage, free of the contaminating N_2^+ ions. Such experiments are currently in preparation [12].

The work at Oak Ridge National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The work at the University of California, San Diego, was supported by the Office of Naval Research.

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