The laser-ion beam photodissociation for \([C_4H_4]^+\) ions produced from a variety of precursors has been studied. Based on the data it is apparent that two structurally distinct forms of the \([C_4H_4]^+\) ion are produced by fragmentation of larger systems. The relative population of the various structural forms is very dependent on the internal energy of the fragmenting ion, with 1-buten-3-yn \([C_4H_4]^+\) ions being favored at low internal energies. As the internal energy of the reactant ion is increased, the relative population of butatriene \([C_4H_4]^+\) ions increases. The laser-ion beam photodissociation technique is able to selectively sample these two structural forms.

EXPERIMENTAL

The experimental apparatus used in this work has been described in detail elsewhere so it will only be briefly reviewed here. The apparatus consists of a Kratos (AEI) MS-902 double focusing mass spectrometer and a Coherent CR-18 argon ion laser. Ions are extracted from the ion source and accelerated into the first field-free region. The laser beam intersects the ion beam in two ways, coaxially and perpendicularly. The coaxial alignment gives better sensitivity but critical data were remeasured in a perpendicular laser-ion beam configuration. No significant differences in the experimental data were observed between the two configurations.

Discrimination against product ions with a large velocity component perpendicular to the ion beam direction is a problem with this experiment because of the finite slit widths in the \(Z\) direction. Of the data reported in this paper the branching ratio measurements will be most sensitive to \(Z\) axial discrimination. To minimize this error the branching ratios were calculated using peak areas. Also instead of reporting kinetic energy release distributions we calculated the
kinetic energy release values from the peak width at half-height.

The elemental composition of the \( m/z \) 52 ion from ionized pyridine and pyridazine was checked by high-resolution mass measurements. No detectable abundances of nitrogen-containing fragment ions at \( m/z \) 52 were observed, e.g. \([\text{C}_3\text{H}_2\text{N}]^+\) or \([\text{C}_2\text{N}]^+\). A referee has suggested that the presence of such ions could be the reason for the low photodissociation cross-sections for these two \([\text{C}_2\text{H}_4]^+\) ions.

The experiments were performed under low pressure (3–5 \( \times 10^{-7} \text{Torr} \)) electron impact conditions. All reagents were obtained from commercial sources: benzene, pyridine (MCB), pyridazine (Aldrich), 2,4-hexadiyne, 1,5-hexadiyne, 1-butene-3-yn (Pfalz and Bauer), benzene-\( d_6 \) (MSD Canada) and 2,4,6-cycloheptatrienone (Alpha). These samples were purified by a freeze–pump–thaw cycle to remove any non-condensable gases.

## RESULTS

As part of this work we investigated the visible (514.5–454 nm) wavelength photodissociation of a relatively large number of \([\text{C}_4\text{H}_4]^+\) ions, i.e. from secondary fragmentation of 2,4,6-cycloheptatrienone, from primary fragmentation of benzene, pyridine, pyridazine, 2,4-hexadiyne and 1,5-hexadiyne and from direct ionization of 1-butene-3-yne. All the systems studied, except pyridazine, give rise to \([\text{C}_4\text{H}_4]^+\) ions which photodissociate in the blue–green region.

The photodissociation reactions observed for \([\text{C}_4\text{H}_4]^+\) are loss of \( \text{H}^+ \), \( \text{H}_2 \) and \( \text{C}_2\text{H}_2 \):

\[
\begin{align*}
[\text{C}_4\text{H}_4]^+ + \text{hv} & \rightarrow [\text{C}_3\text{H}_3]^+ + \text{H}^+ \quad (1) \\
[\text{C}_4\text{H}_4]^+ + \text{hv} & \rightarrow [\text{C}_3\text{H}_3]^+ + \text{H}_2 \quad (2) \\
[\text{C}_4\text{H}_4]^+ + \text{hv} & \rightarrow [\text{C}_3\text{H}_3]^+ + \text{C}_2\text{H}_2 \quad (3)
\end{align*}
\]

Studies of the laser power dependence for the photofragment ion abundances are consistent with a single photon photodissociation process. Owing to the weak signal for \( \text{C}_2\text{H}_2 \) loss (<5% \( \text{H}^+ \) loss) this reaction channel was not studied in great detail.

The photofragment spectra were derived in the following manner. The photofragment ion yields for each reaction channel were obtained from the peak areas. The signal intensities for loss of \( \text{H}^+ \) and \( \text{H}_2 \) were summed together and divided by the photon flux. The result is a relative photofragment ion yield which is plotted as a function of wavelength for each precursor in Fig. 1.

The photofragment spectra shown in Fig. 1 appear to be bimodal with maxima at 514.5 and 488 nm. Although all spectra are similar in this respect, there are notable differences for the various precursors. For example, the photofragment ion yields for benzene \([\text{C}_4\text{H}_4]^+\) are roughly equivalent at 514.5 and 488 nm. On the other hand, the photofragment ion yields at 514.5 and 488 nm differ somewhat for the other \([\text{C}_4\text{H}_4]^+\) ions. Finally, the photofragment spectrum for the 1-butene-3-yn \([\text{C}_4\text{H}_4]^+\) ion is significantly broader than the spectra for \([\text{C}_4\text{H}_4]^+\) ions formed by fragmentation of larger systems.

The photofragment ion branching ratios were obtained from the peak areas for each reaction channel. The data for 514.5 and 488 nm (the two maxima) are given in Table 1. The branching ratios for \([\text{C}_4\text{H}_4]^+\) from 2,4-hexadiyne, 1,5-hexadiyne, pyridine and 1-butene-3-yne are similar with loss of \( \text{H}^+ \) accounting for approximately 65% (514.5 nm) and 68% (488 nm) of the total photodissociation signal. Loss of \( \text{H}_2 \) accounts for approximately 35% (514.5 nm) and 32% (488 nm) of the photofragmentation. For \([\text{C}_4\text{H}_4]^+\) from benzene, tropone and benzene-\( d_6 \) loss of \( \text{H}^+ \) (\( \text{D}^+ \)) accounts for approximately 48% and 52% of the signal at 514.5 and 488 nm, respectively. Loss of \( \text{H}_2 \) (\( \text{D}_2 \)) accounts for approximately 52% of the 514.5 nm signal and approximately 48% of the 488 nm signal.

The relative photofragment ion yield was measured for \([\text{C}_4\text{H}_4]^+\) from benzene as a function of ionizing energy and the data are reported in Table 2. The data were obtained in the following manner. Peak areas for loss of \( \text{H}^+ \) and \( \text{H}_2 \) were measured at 70, 50, 30 and 20 eV of ionizing energy and corrected for the change in the reactant ion intensity by dividing the peak area by the reactant ion intensity. The photofragment intensities for the two reaction channels were summed at each electron energy and divided by the photon flux. The relative photofragment ion yield increased from 0.72 to 1.20 at 514.5 nm and decreased from 1.00 to 0.62 at 488 nm as the ionizing energy was decreased from 70 to 20 eV. Similar data were taken for \([\text{C}_4\text{H}_4]^+\) from 1-butene-3-yn by using ionizing energies of 70, 50, 30, 20 and 10 eV. The same general trend was observed in the data (see Table 2).

The relative photofragment ion yield was measured for each \([\text{C}_4\text{H}_4]^+\) ion precursor. These values were calculated from the photofragment peak areas for loss of \( \text{H}^+ \) and \( \text{H}_2 \) (70 eV) and summed together for each precursor ion. Because the abundance of the reactant

### Table 1. Precursor-dependent photodissociation branching ratios for \([\text{C}_4\text{H}_4]^+\) ions

<table>
<thead>
<tr>
<th>Precursor</th>
<th>514.5 nm</th>
<th>488.0 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H^+ ) loss</td>
<td>( H_2 ) loss</td>
<td>( H^+ ) loss</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.44</td>
<td>0.56</td>
</tr>
<tr>
<td>2,4-Hexadiyne</td>
<td>0.69</td>
<td>0.31</td>
</tr>
<tr>
<td>1,5-Hexadiyne</td>
<td>0.64</td>
<td>0.36</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.65</td>
<td>0.35</td>
</tr>
<tr>
<td>2,4,6-Cycloheptatrienone</td>
<td>0.48</td>
<td>0.52</td>
</tr>
<tr>
<td>Benzene-( d_6 )</td>
<td>0.52</td>
<td>0.46</td>
</tr>
<tr>
<td>1-Butene-3-yne</td>
<td>0.63</td>
<td>0.37</td>
</tr>
</tbody>
</table>

### Table 2. Relative photodissociation cross-section measurements for benzene and 1-butene-3-yn

<table>
<thead>
<tr>
<th>Ionizing energy (eV)</th>
<th>Benzene 514.5 nm</th>
<th>1-Butene-3-yn</th>
<th>Benzene 488 nm</th>
<th>1-Butene-3-yn</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.72</td>
<td>0.68</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>50</td>
<td>0.80</td>
<td>0.80</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>30</td>
<td>1.01</td>
<td>1.00</td>
<td>0.72</td>
<td>0.80</td>
</tr>
<tr>
<td>20</td>
<td>1.20</td>
<td>1.10</td>
<td>0.62</td>
<td>0.72</td>
</tr>
<tr>
<td>10</td>
<td>—</td>
<td>1.23</td>
<td>—</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Figure 1. Relative photofragment ion yields as a function of excitation wavelength for \([C_6H_5]^+\) ions produced from (a) 2,4,6-cycloheptatrienone, (b) 2,4-hexadiyne, (c) 1,5-hexadiyne, (d) pyridine, (e) benzene, (f) benzene-\(d_6\), and (g) 1-buten-3-yn. The line joining the points is a guide to give an indication of the shape of the absorption profile. The experimental conditions were: ionizing electron energy, 70 eV and ion source temperature, 450 K.
LASER-ION BEAM PHOTODISSOCIATION STUDIES OF $C_6H_6$ RADICAL CATIONS

Figure 1—(continued)
[C,H₄⁺]⁺ ion changes as a function of the precursor, the data were corrected for this change by dividing the summed peak areas by the [C,H₄⁺] reactant ion intensities. The data were taken at 514.5 and 488 nm and normalized with respect to the photofragment ion yield for benzene. The result is a measurement of the precursor-dependent photofragment ion yield at each wavelength. The data are tabulated in Table 3.

The photofragment relative kinetic energies were measured for [C,H₄⁺] and [C,H₄⁺]⁺ products at 514.5 and 488 nm. Data for other wavelengths are not reported due to low sensitivity at these wavelengths. The photofragment ion relative kinetic energies were obtained from the full width at half maximum (FWHM) of the photofragment peaks (corrected for the main beam contribution to the peak width) and converted to kinetic energy release (KER) values using Eqn (4).

\[
KER = \frac{m_e eV}{16m_n m_i} \left( \frac{\Delta V_{m*} - \Delta V_{mb}}{V} \right)^2
\]

In Eqn (4) \( V \) is the main beam accelerating voltage, \( \Delta V_{m*} \) is the FWHM of the product ion peak, \( \Delta V_{mb} \) is the FWHM of the main beam peak and \( m_i \), \( m_n \) and \( m_e \) are the masses of the reactant ion, product ion and product neutral, respectively. For a Gaussian peak shape the KER values obtained from Eqn (4) correspond to the most probable kinetic energy. The data for the various [C₄H₄⁺]⁺ ions are contained in Table 4. The unimolecular KER values are all between 15 and 20 meV for H⁺ loss and which photodissociates in the wavelength range of the argon ion laser, e.g. the [C₄H₄⁺]⁺ ion produced by fragmentation of pyridazine did not photodissociate! It is difficult to make absolute photodissociation cross-section measurements but, comparing the photodissociation signal intensity for the [C,H₄⁺]⁺ ions with other systems we have studied, it is probable that a substantial fraction of the [C,H₄⁺]⁺ ions produced by fragmentation of benzene do not photodissociate in the blue–green spectral range. Thus, a non-photodissociating [C₄H₄⁺]⁺ ion structure is highly probable in all the systems studied. It is difficult to make a structural assignment for this third ion and it is quite possible, based on thermochemical data, that there are two additional structures formed (see Fig. 2). It is generally agreed⁶–⁹ that methylene cyclopropane [C₃H₄⁺]⁺ is the lowest energy structure; however, it is difficult to say whether the non-photodissociating structure(s) lie above, below or bracket the photodissociating structures in terms of energy.

Based on available thermochemical data for [C₄H₄⁺]⁺ ions it may be argued that as many as four [C₄H₄⁺]⁺ ions are produced by fragmentation of larger systems. In Fig. 2 we have placed the four neutral structures (1-buten-3-yne, butatriene, methylene cyclopropane and cyclobutadiene) on a common energy scale and added to the neutral heats of

### Table 3. Precursor-dependent photodissociation cross-sections for [C₄H₄⁺]⁺

<table>
<thead>
<tr>
<th>Precursor</th>
<th>514.5 nm</th>
<th>488.0 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2,4-Hexadiyne</td>
<td>0.40</td>
<td>0.60</td>
</tr>
<tr>
<td>1,5-Hexadiyne</td>
<td>0.36</td>
<td>0.52</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.21</td>
<td>0.28</td>
</tr>
<tr>
<td>2,4,6-Cycloheptatrienone</td>
<td>0.78</td>
<td>1.01</td>
</tr>
<tr>
<td>1-Buten-3-ylene</td>
<td>0.52</td>
<td>0.91</td>
</tr>
</tbody>
</table>

### Table 4. Kinetic energy release values for [C₄H₄⁺]⁺ ions

<table>
<thead>
<tr>
<th>Compound</th>
<th>H⁻ loss</th>
<th>H₂ loss</th>
<th>H⁺ loss</th>
<th>H₂ loss</th>
<th>H⁺ loss</th>
<th>H⁻ loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>225</td>
<td>40</td>
<td>270</td>
<td>30</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>1,5-Hexadiyne</td>
<td>260</td>
<td>40</td>
<td>280</td>
<td>40</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>2,4-Hexadiyne</td>
<td>230</td>
<td>35</td>
<td>275</td>
<td>55</td>
<td>310</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>215</td>
<td>50</td>
<td>245</td>
<td>35</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>2,4,6-Cycloheptatrienone</td>
<td>340</td>
<td>40</td>
<td>355</td>
<td>40</td>
<td>355</td>
<td></td>
</tr>
<tr>
<td>1-Buten-3-ylene</td>
<td>200</td>
<td>50</td>
<td>245</td>
<td>45</td>
<td>270</td>
<td></td>
</tr>
</tbody>
</table>

DISCUSSION

The bimodal photofragment spectra for [C₄H₄⁺]⁺ can be rationalized in two ways: (i) there are two structurally distinct [C₄H₄⁺]⁺ ions, one which photodissociates at a wavelength maximum of 514.5 nm and the other which photodissociates at a wavelength maximum of 488 nm or (ii) the bimodality is due to absorption fine structure of a single photodissociating [C₄H₄⁺]⁺ ion structure. This point will be discussed further as it relates to the ionizing energy dependence for the photodissociation cross-section. If there are indeed two structures, the second question is: what are the structures of the photodissociating [C₄H₄⁺]⁺ ions?

A critical aspect of photodissociation measurements is the correlation between the photodissociation spectrum and the electronic structure of a molecule as determined by photoelectron spectroscopy (PES). The early work of Beauchamp et al.⁴ and Dunbar et al.⁵ shows clearly that the photodissociation maximum often corresponds to the observed photoelectron bands. Thus, the PES data can be utilized to predict photodissociation maxima provided such data are available. The PES data for two [C₄H₄⁺]⁺ isomers have been reported, viz. butatriene and 1-buten-3-yne.⁶ Based on this data photodissociation maxima for these isomers should occur at 513 nm (1-buten-3-yne) and 487 nm (butatriene). These predicted values agree quite well with the strong photodissociation bands at 514.5 and 488 nm.

In the following sections it will be argued that two structural forms of [C₄H₄⁺]⁺ ion are sampled by the photodissociation process. However, there must also be at least one additional [C₄H₄⁺]⁺ ion which does not photodissociate in the wavelength range of the argon ion laser, e.g. the [C₄H₄⁺]⁺ ion produced by fragmentation of pyridazine did not photodissociate! When a single photodissociating structure is determined by photoelectron spectroscopy (PES) it may be argued that as many as four [C₄H₄⁺]⁺ ions are produced by fragmentation of larger systems. In Fig. 2 we have placed the four neutral structures (1-buten-3-yne, butatriene, methylene cyclopropane and cyclobutadiene) on a common energy scale and added to the neutral heats of...
LASER-ION BEAM PHOTODISSOCIATION STUDIES OF C,H, RADICAL CATIONS

Figure 2. Total energy diagram for four possible structures of [C,H,]+ ion; 1-buten-3-yne, butatriene, methylene cyclopropene and cyclobutadiene. The neutral heats of formation, ionization potentials and available PES data are taken from the literature.8,14-23

formation the best available ionization energy. From the available literature, it is clear that the heats of formation for these four [C,H,]+' isomers may differ by as little as 0.3 eV. The data for 1-buten-3-yne and butatriene are collected from both theoretical15 and experimental5,14,16,17 results. The heat of formation for neutral methylene cyclopropene neutral comes from an ab initio study15 and the experimental work of Rosenstock et al.16 The ionization energy for methylene cyclopropene comes from both an ab initio study18 and the experimental work of Ausloos.8 The heat of formation for neutral cyclobutadiene comes from the calculations of Kollmar,15 Schweig and Theil19 and Dewar and Komornicki.20 The ionization energy for cyclobutadiene was obtained from electron impact measurements21 and from the 'corrected' PES of some cyclobutadiene–iron compounds.22,23 Much of the work on methylene cyclopropene and cyclobuta-diene involves some form of estimation; nevertheless, the values appear reasonable and indicate that the difference in energy between methylene cyclopropene and the other [C,H,]+' ion structures may not be as much as generally believed.

Measurement of the relative photofragment ion yields as a function of ionizing energy can be used to address the question of two structures v. absorption fine structure. In general, photofragment ion yields may depend on the initial ionizing energy if the absorption cross-section changes significantly with internal energy.24 As the ionizing energy is lowered, the ions will be formed with lower average internal energies, and a greater amount of photon energy would be required to reach the excited state. If the photodissociation cross-section is dependent upon internal energy, i.e. photon absorption cross-section changes or the photodissociation is thermochemically limited, one would expect to see the photofragment ion yields decrease at lower photon energies and increase at higher photon energies. Our observations for the [C,H,]+' ion produced by fragmentation of benzene indicates the exactly opposite trend! Recall that the photodissociation cross-section for [C,H,]+' from benzene increases at 514.5 nm while it decreases at 488 nm as the ionizing energy is lowered from 70 to 20 eV, and that a similar change is observed for the [C,H,]+' ion from 1-buten-3-yne over the energy range 70–10 eV. The changes in the photofragment ion yield can be understood by examining the thermochemical data for [C,H,]+'. That is, ΔHf (butatriene [C,H,]+') > ΔHf (1-buten-3-yne [C,H,]+') and as the ionizing energy is lowered a larger fraction of the precursor ions dissociate to give the lowest energy [C,H,]+' ion. Since the lowest energy [C,H,]+' ion (1-buten-3-yne) photodissociates at 514.5 nm we would predict the trend observed in Table 2. Since an internal energy effect would cause the exact opposite trend, we believe this evidence supports the argument that two distinct forms of photodissociating [C,H,]+' ions are produced and sampled selectively by the laser photodissociation process. Note also that the observed trend is consistent with the results of the ion–molecule reaction chemistry reported by Ausloos.8

A second piece of information gained from the photofragment spectra comes from the broadness of
the 1-buten-3-yne spectrum as compared to the photodissociation spectra of the other [C₄H₄]+ ions. [C₄H₃]+ ions formed by direct ionization of 1-buten-3-yne may have a broader distribution of internal energies than those formed by fragmentation of larger systems. This interpretation of the data indicates that the photodissociation process samples a broad range of internal energies as opposed to selectively sampling specific rovibrionic transitions. Honovich and Dunbar have reported that photodissociation cross-sections can increase significantly as the vibrational energy is increased, leading to selective sampling of particular vibrational transitions. This effect, however, has been reported only for halogenated systems and has not been seen in aromatic hydrocarbons (i.e. styrene, 1-methylnaphthalene and 2-methylnaphthalene).²⁴

The photodissociation product ion branching ratios show differences which reflect a consequence of internal energy on the photodissociation process. For example, photodissociation of the [C₄H₄]+ ions is accomplished by the ions in the range of 2.41 eV (514.5 nm) to 2.71 eV (458 nm). The appearance energies for [C₄H₃]+ and [C₄H₃]^+ from [C₂H₄]^+ are c. 2.7–2.9 eV. Therefore, the photodissociation process occurs at or near the thermochemical threshold. The best available energetic data on [C₄H₃]^+ and [C₄H₃]^+ are the photoionization breakdown curves reported by Rosenstock.¹⁶ These data show that these two ions have approximately the same appearance energy (AE = 13.05 eV); however, at energies of 0.5–0.7 eV above threshold, loss of H' is favored over loss of H₂. That is, the rate of formation (k(E)) for [C₄H₃]^+ rises much more steeply than the k(E) for [C₄H₃]^+. This effect could explain the predominant loss of H' from 2,4-hexadiyne, 1,5-hexadiyne, pyridine and 1-buten-3-yne [C₄H₄]^+ ions as compared to benzene and tropone [C₄H₄]^+ ions. That is, the photodissociation results suggest that the [C₄H₃]^+ ions from 2,4-hexadiyne, 1,5-hexadiyne, pyridine and 1-buten-3-yne have higher average internal energies than do the [C₄H₃]^+ ions from benzene and tropone. This effect would also explain the observed increase in loss of H' at 488 nm as compared to 514.5 nm. That is, the energy of the photoejected ion formed by absorption at 488 nm is greater than that for 514.5 nm because it has been excited by a more energetic photon and again loss of H' is favored.

The photofragment ion yield data show dramatic precursor-dependent differences. Fragmentation of benzene gives rise to a [C₄H₄]+ ion population containing the largest fraction of photodissociating [C₄H₃]^+ ions. Pyridine, producing the smallest fragment, gives rise to only 20–30% as much photodissociating [C₄H₃]^+ ions as does benzene. These precursor-dependent differences may be explained in two ways: (i) internal energy effects or (ii) structural differences in the precursor and/or product ions. It is possible that the fragmentation of the various precursor ions results in a [C₄H₄]^+ ion population with very different internal energies even if the precursors sample a common potential energy surface. As the internal energy of the precursor ion changes, the reaction channel leading to [C₄H₄]^+ may involve a different transition state, i.e. a tight versus orbiting transition state.²⁵ On the other hand, the precursor-dependent differences in the [C₄H₃]^+ ion photodissociation cross-section may arise from differences in the structure of the reactant ions. If this is the case, it would not be surprising for the various precursors to give rise to very different structural populations of the [C₄H₃]^+ ion. In a recent study from our laboratory we present strong evidence that 2,4-hexadiyne [C₄H₃]^+ ions do not isomerize to a cyclic structure prior to fragmentation to [C₄H₄]^+. The similarity in the [C₄H₃]^+ data for 2,4-hexadiyne and 1,5-hexadiyne may indicate partial isomerization between these two linear structures or a common transition state leading to [C₄H₄]^+.

The kinetic energy release (KER) data for the H' and H₂ loss reaction channels show dependence on wavelength and precursor. In each case the photodissociation KER values are greater than the unmolecul- lar (metastable) value. This is undoubtedly due to small differences in the total energies of the photoexcited ion. In addition, for loss of H₂ the KER values at 488 nm are generally greater than those at 514.5 nm. This trend may arise from two sources: (i) from structural changes as the [C₄H₃]^+ ion structures sampled by the laser at 514.5 nm and 488 nm are different or (ii) if the KER values for the two structures are similar, from small differences in excess internal energy of the photoexcited ion. A similar trend is not detectable in the H' loss reaction channel; however, for the H' loss reaction channel the difference may not be detectable at the energy resolution employed for these studies. The KER values are also precursor-dependent, which is probably due to changes in the internal energy of the [C₄H₃]^+ ions as a function of precursors.

In an earlier study Ausloos⁸ demonstrated, using ion–molecule reaction chemistry, that dissociative ionization of benzene, 1,5-hexadiyne, 2,4-hexadiyne and pyridine give rise to two ion structures for [C₄H₄]^+. In addition, he showed that the population of the two structural forms have a strong dependence on the internal energy of the fragmenting precursor. For example, dissociative charge exchange ionization of benzene at a total energy of 14.8–16.6 eV yields a [C₄H₃]^+ ion population ranging from <5% to >80% 1-buten-3-yne [C₄H₄]^+ ions. Ausloos also reported that 1,5-hexadiyne, 2,4-hexadiyne and pyridine radicals cations produce 60%, 65% and 50% 1-buten-3-yne [C₄H₄]^+ ions at 15 eV ionizing energy. Comparing the relative photofragment ion yields (assuming 80% 1-buten-3-yne ions from benzene) we obtain values of 29%, 32% and 17%, respectively. Although these values differ significantly from those reported by Ausloos,⁸ they do show the same order in terms of % 1-buten-3-yne [C₄H₄]^+ formed. The differences in the absolute numbers are not surprising considering the different ionizing energies and time-scales for the two studies. As we deduced from the photodissociation cross-section measurement at different ionizing energies (Table 2), the fractional population of 1-buten-3-yne [C₄H₄]^+ decreases as the internal energy of the precursors increases.
CONCLUSIONS

Based on the results from this study we conclude that at least three structurally distinct \([\text{C}_4\text{H}_4]^+\) ions are produced by fragmentation of larger systems as well as by direct ionization of 1-buten-3-yne. The distribution of the \([\text{C}_4\text{H}_4]^+\) ions among the accessible structural forms is highly dependent upon the internal energy of the fragmenting precursors. In agreement with the results of Baer and Ausloos, at threshold energies the fragmenting precursors. In addition, we cannot rule out the formation of cyclobutadiene and it may be that pyridazine radical cations do indeed produce a cyclobutadiene \([\text{C}_4\text{H}_4]^+\) ion in agreement with Weininger and Thornton.2

Changes in internal energy can have quite a dramatic effect on photodissociation measurements, including the appearance of the photofragment spectra. It is therefore important to account for, or rule out, this effect when making structural assignments by the photodissociation process. With this caution in mind, we suggest that the dramatic differences in the precursor-dependent relative photofragment ion yield may be due to the lack of complete structural isomerization of the reactant \([\text{C}_4\text{H}_4]^+\) ions.

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ORGANIC MASS SPECTROMETRY, VOL. 20, NO. 10, 1985 613