

PHOTOIONIZATION AND THRESHOLD PHOTOELECTRON— PHOTOION COINCIDENCE STUDY OF PROPYNE FROM ONSET TO 20 eV

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ABSTRACT

Photoionization efficiency curves are obtained for propyne and its fragments $C_3H_3^+$, $C_3H_2^+$, and C_3H^+ from threshold to 20 eV. Threshold photoelectron spectra and breakdown curves are given over the same energy range. The adiabatic ionization potential of the parent molecule, the appearance potentials of the fragments and the derived heats of formation of the ionic species are determined. The breakdown curve is almost identical to that obtained previously for allene [11] when the different heats of formation of the neutral molecules are taken into account. This suggests that the propyne ion isomerizes to the allene ion before fragmentation.

INTRODUCTION

Price and Walsh [1] first reported an absorption spectrum of propyne in the vacuum ultraviolet region 1000–2000 Å. They identified several Rydberg series with an apparent ionization limit of 11.24 eV. Photoionization techniques [2–4] have failed to confirm this limit and gave results of about 10.37 eV for the ionization limit of propyne. In addition, Nakayama and Watanabe [3] have measured the absorption coefficient of propyne in the wavelength region 1100–1700 Å. They identified several Rydberg series converging to an ionization limit of 10.36 eV.

The photoionization efficiency curves of the parent ion given in the literature are in general agreement as to onset and behaviour. Omura et al. [5] have measured the photoionization efficiency in the threshold region, 1200–1000 Å, and their data show some structure which they interpret in terms of excited vibrational levels and a second ionization potential agreeing with Price and Walsh's value of 11.24 eV. This interpretation is subject to some doubt, however, as their data indicate a peak instead of the step expected at

this point. Parr and Elder [4] observed autoionization in this region of the photoionization curve and suggested that this could in part explain the lines observed by Price and Walsh. Consequently the state reported by Price and Walsh would correspond to an excited state of the ion. The photoionization study by Person and Nicole [6] shows little structure and does not show the peak structure reported by Parr and Elder.

Baker and Turner [7] and Frost et al. [8] have reported the photoelectron spectra of propyne. Baker and Turner report an adiabatic ionization potential of 10.37 eV. Frost et al. report an adiabatic ionization potential of 10.37 eV and several excited states with adiabatic ionization limits of 13.93 eV, 15.15 eV and 16.97 eV. There is no indication of the state at 11.24 eV determined by Price and Walsh and suggested in some of the photoionization studies. A likely interpretation is that the structure observed in the photoionization results and by Price and Walsh is due to autoionization, and refers to bands which have as their limit some of the excited states observed by Frost et al.

It has been observed by Parr and Elder [4] and also by Matthews and Warneck [9] that the heat of formation of the $C_3H_3^+$ ion from propyne is the same as that from allene. Lossing [10] has concluded that this $C_3H_3^+$ ion is the cyclopropenyl ion. This suggests that the $C_3H_4^+$ parent ion from allene and propyne may isomerize to a common structure. To investigate this possibility we have measured the photoionization efficiency curves for propyne and its fragment ions from threshold to 20 eV. The breakdown curves were measured over the same energy region using the threshold photoelectron-photoion coincidence technique. The threshold photoelectron spectra (TPES) are given for comparison with photoelectron spectra. The results of this propyne study are compared with the previously published study of allene [11]. If both propyne and allene fragment from a common precursor ion, their breakdown curves should be similar.

EXPERIMENTAL

The photoionization experiments were performed on a photoionization mass spectrometer consisting of a 1-m focal length Seya-Namioka monochromator and a 3 in (7.62 cm) radius of curvature magnetic sector mass analyzer. Differential pumping of the monochromator and the use of hydrogen and helium discharge light sources gave radiation from 600 Å to beyond 2000 Å.

The ions were detected with a continuous channel electron multiplier and the individual ion pulses scaled with an electronic counting system. The light intensity was monitored with a sodium salicylate coated photomultiplier. The light intensity was continuously monitored during the course of the experiments and the ion count divided by the light intensity gave the photoionization efficiency curve. It is assumed that the quantum efficiency of sodium salicylate [12] is constant in the wavelength region reported here.

The resolution of the monochromator was about 2 Å for the photoionization data reported. As a check on the photoionization data, the photoionization efficiency curve was remeasured on a 12 in (30.48 cm) radius of curvature photoionization mass spectrometer with a monochromator resolution of the order of 1 Å [13]. The results of the two different measurements are in general agreement. The parent curve is a composite of the results from the two photoionization mass spectrometers. The region from onset to 950 Å was measured on the 12 in radius of curvature instrument and the region to 600 Å on the 3 in radius of curvature instrument.

The threshold photoelectron spectra (TPES) and breakdown curves were measured with a threshold photoelectron-photoion coincidence mass spectrometer. The details of the instrument and its operation have been reported in the literature [11,14,15]. The instrument features a mass resolution of about 80 and a nominal electron energy resolution of 25 meV. Ions coincident with a given zero energy electron are detected with the instrument. The ratio of the number of ions of a particular mass to the total number of coincident ions as a function of photon energy gives the breakdown curve directly. A parent ion which is coincident with a zero energy electron takes up all the photon energy in excess of the ionization potential.

The light sources used were the many-lined hydrogen spectrum and the Hopfield continuum of helium. The light intensity was measured as a photocurrent with a vibrating capacitor electrometer. The response of the detectors was calibrated as described in ref. 11. The light intensity calibration cannot affect the coincident ion data used for determination of the breakdown curves since such curves are simply the ratio of the number of coincident ions at each mass to the total number of coincident ions detected. The TPES data are, however, dependent upon the light detector calibration for a correct determination of relative intensity.

The propyne sample was obtained from commercial sources and had a stated purity of 96%. Stated impurities were dimethyl ether (1.2%), allene (0.5%) and acetylene (0.1%).

RESULTS AND DISCUSSION

The photoionization efficiency curve for the parent ion $C_3H_4^+$ and the fragment ions $C_3H_3^+$, $C_3H_2^+$ and C_3H^+ from threshold to 600 Å (20.6 eV) are shown in Fig. 1. The curves have been adjusted to indicate the correct relative intensity. The abscissa has been plotted linearly with wavelength since the resolution of the monochromator is constant with wavelength. A non-linear energy scale is also given for each, for comparison with the photoelectron-photoion coincident data. Figure 2(A) gives the TPES of propyne. The breakdown curves are shown in Figs. 2(B) and 2(C).

Parent ion $C_3H_4^+$

The parent ion onset from the photoionization data, taken as the mid-

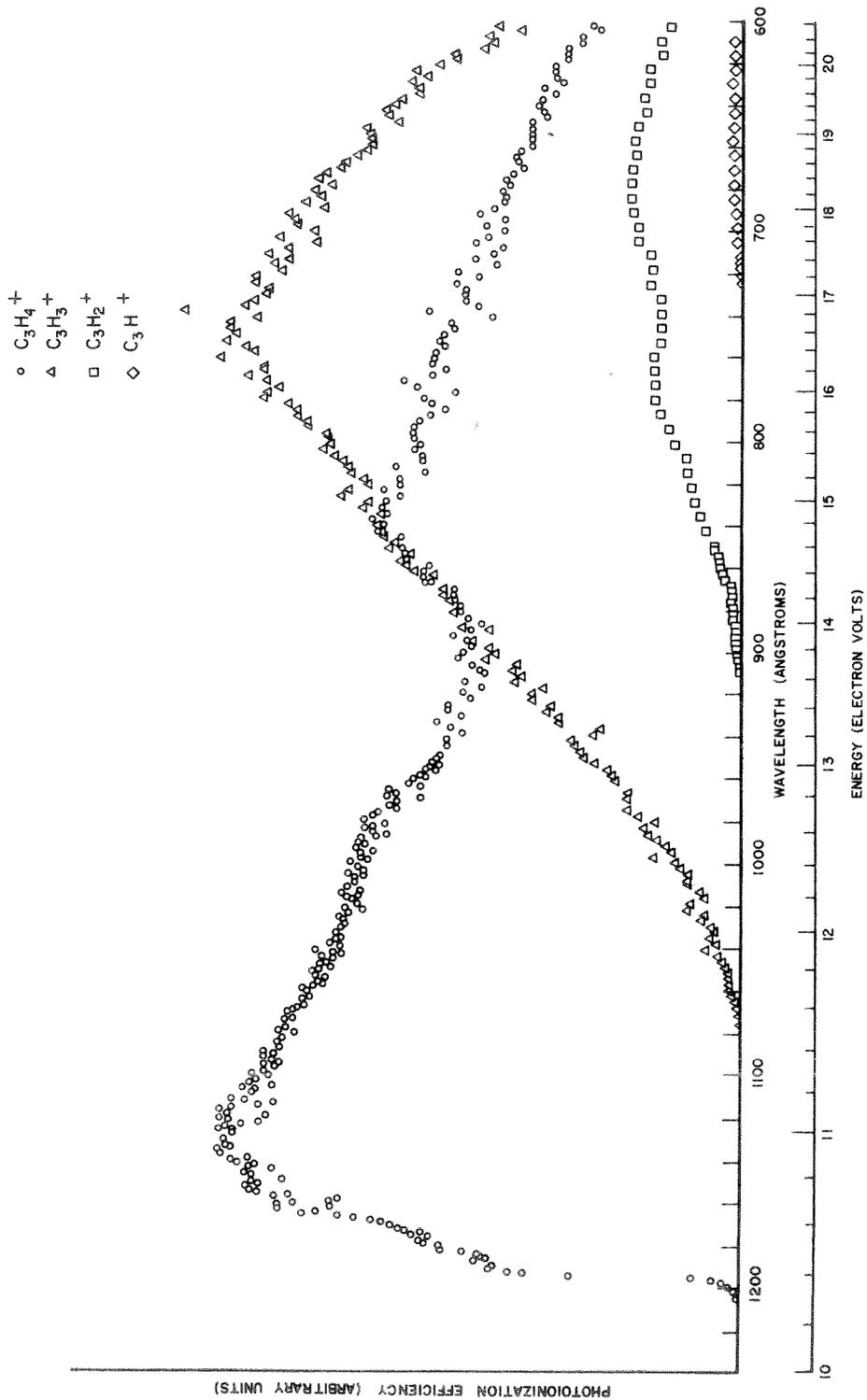


Fig. 1. Photoionization efficiency curve of propyne and its fragment ions between threshold and 600 Å. The ordinate is the photoionization efficiency in arbitrary units. The abscissa is linear in wavelength given in Angstroms with a non-linear energy scale given in electron volts. The curves have been corrected to give the proper relative intensities of the parent and fragment ions.

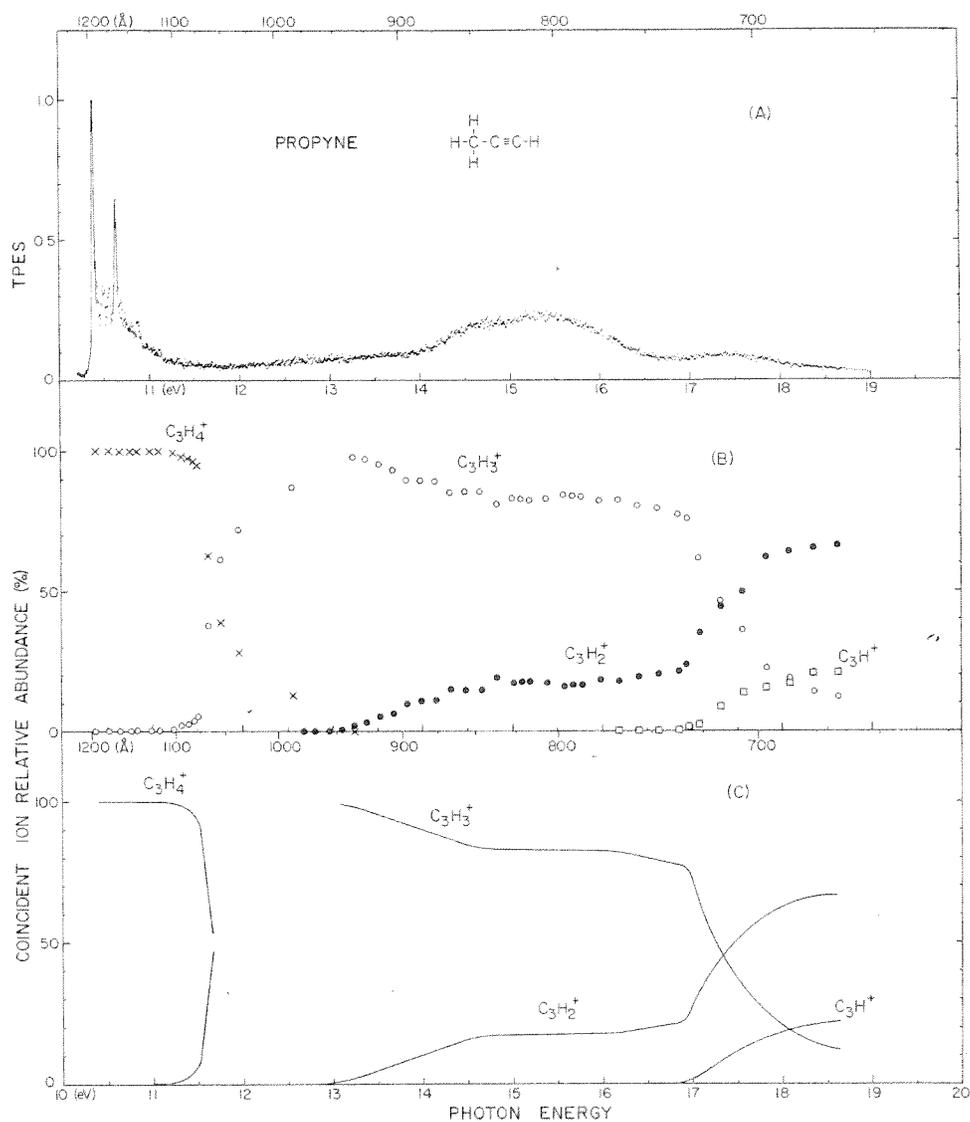


Fig. 2. (A) Threshold photoelectron spectra of propyne from onset to 18.6 eV. The ordinate is electron rate per unit photon in arbitrary units and the abscissa is photon energy in electron volts with a non-linear wavelength scale in Ångstroms. (B) Breakdown curve for propyne and its fragments. The ordinate is relative coincident ion intensity and the abscissa is photon energy in Å. (C) Breakdown curve for propyne. Same as 2(B) except for the omission of the pressure dependent portion. A smooth average line has been drawn through the data points.

point of the first linear portion of the curve, is at 10.37 ± 0.01 eV. This agrees well with the results of the TPES data in Fig. 2, as well as with other reported photoionization and photoelectron spectra. The onset is rapid and is interpreted as the adiabatic onset. Above the onset, the photoionization efficiency curve consists of three broad bands, one centered at 11 eV, another at 12.4 eV and the third at 14.8 eV. Some of the structure in the first band is most probably due to autoionization levels having as series limit the excited state of the ion observed by PES [7,8] and by TPES at about 14 eV. Some of the lines observed by Price and Walsh [1] in absorption are in the same region as the structure observed here. This suggests that the lines Price and Walsh observed above 10.38 eV were due to this autoionization structure. The direct transitions (which should appear as steps), while fairly intense in the threshold region, are most likely obscured by the autoionization structure above threshold.

An ionic state at about 14 eV is indicated by the rise in the photoionization efficiency curve at this point. This corresponds well with the excited state at 14 eV observed by PES [7,8] and TPES. The state at about 17 eV observed in PES and TPES was not observed in this study. After 15 eV the $C_3H_4^+$ photoionization decreases slowly with some evidence of structure characteristic of autoionization. An analysis of the autoionization structure will not be presented here as it is not central to the topic of this work and because the many-lined hydrogen spectrum is used as a light source over part of the region. Although the hydrogen source can be considered quasi-continuous, its lined nature may adversely affect the intensities observed in resonant absorption phenomena such as autoionization. There is considerable evidence that autoionization is present, i.e. from the TPES data and other photoionization data reported in the literature [4,5].

$C_3H_3^+$ ion

The $C_3H_3^+$ ion has an appearance potential of 11.58 ± 0.04 eV measured by photoionization techniques, and 11.2 ± 0.1 eV measured by the coincidence technique, where the error limits represent uncertainty in determining the onset. The reason for the difference in the two measurements is the different sensitivities and sampling times of the instruments [11]. The photoionization curve for $C_3H_3^+$ begins a linear rise a few tenths of an electron volt above onset. The linear rise continues for about 5 electron volts. At 16.5 eV the curve peaks and then decreases approximately linearly. The parent curve also falls off in this region. The $C_3H_3^+$ intensity exceeds the parent ion intensity beyond about 15 eV.

Ignoring thermal and kinetic shifts (typically 10 kJ mol^{-1}) which tend to cancel, a heat of formation of $C_3H_3^+$ of 1084 kJ mol^{-1} ($259 \text{ kcal mol}^{-1}$) can be derived from the photoionization data. This agrees, within experimental error, with the value of 1075 kJ mol^{-1} ($257 \text{ kcal mol}^{-1}$) for the cyclic structure suggested by Rosenstock et al. [16] and otherwise reported in the literature [4,9,10].

between 14 and 16.5 eV. The fourth band appears above 16.5 eV.

There are, however, differences in the details of the TPES and PES. The first band in the TPES shows several features not resolved in the PES. As these are not pertinent to this fragmentation study, a full discussion will be published elsewhere. The most important difference relevant to this study appears in the region between 11 and 14 eV. The PES shows little, if any, ionization in this region, while the TPES shows an intensity 5–10 times the background intensity. As with the earlier allene study [11], this is most probably due to autoionization processes which produce electrons of energy low enough to be detected as threshold electrons.

Without these processes it would not be possible to study the fragmentation in this region. The PES shows that few, if any, ions are produced with the correct internal energy in the 11–14 eV region by direct ionization. However, this does not mean that no ions are produced in this region, since the photoionization data show an abundance of ions present. It can be inferred from the PES that few of these ions are produced with zero energy electrons by direct ionization.

The propyne ion breakdown curve from the coincidence data is shown in Fig. 2(B). The breakdown curves represent the fraction of each fragment ion detected in coincidence with a threshold electron. Approximately 600–1600 coincidence ions were accumulated at each data point. Ion residence time was approximately 0.7 μ s. Fig. 2(C) shows the same data redrawn using smooth curves with the exception that the data between approximately 11.6 and 13 eV have not been plotted. This portion of the curve has not been drawn due to the uncertainty introduced by what we assume to be collisional deactivation. The curve in this region is pressure dependent and this effect will be discussed below.

It should be noted that the photoionization and coincidence data are inherently different. The photoionization curves give a picture of the fragmentation of the parent ion as a function of photon energy (photoionization efficiency curves). This is the fragmentation of the parent ion at a particular photon energy regardless of the energy of the ejected electron. The coincidence data give the fragmentation of only those parent ions produced with a threshold electron. This is fragmentation as a function of parent ion internal energy (breakdown curves).

BREAKDOWN CURVE

The breakdown curve for the propyne ion is remarkably similar to that obtained for the allene ion [11]. In both, the first fragmentation is loss of a hydrogen atom H to form $C_3H_3^+$. Near 13 eV the loss of a hydrogen molecule H_2 occurs in competition with the H loss. At higher energy, near 17 eV, the secondary processes, loss of H and H_2 from $C_3H_3^+$, occur.

It is significant that no C–C bond ruptures occur in this energy range in propyne. These would appear as CH_n^+ or $C_2H_n^+$ fragments in the breakdown

curve above 14.3 eV. While a small amount of CH_3^+ and C_2H_2^+ was observed, it could be attributed almost entirely to the dimethyl ether and acetylene impurities. The total CH_n^+ and C_2H_n^+ fragments from propyne was within 1% of zero.

The similarities in the propyne and allene ion breakdown curves lead to a number of conclusions. First, the near identity of the two sets of curves for the secondary process above 17 eV weakens, if not negates, the argument that these fragments arise directly from the excited states of the parent ions near 17 eV.

The second conclusion is that the fragmentation of these two ions occurs from a common precursor. The absence of C—C bond ruptures suggests that the common precursor is the allene ion, which has the lower heat of formation. It is likely that the propyne ion isomerizes to the allene form before fragmentation. However, the lack of C—C bond ruptures may be due to the kinetics of fragmentation i.e. the onsets for these fragments may be sufficiently above that of C_3H_3^+ that they do not compete effectively. A definite conclusion cannot be reached until theoretical breakdown curves have been calculated.

Other evidence for a common precursor is seen in the metastable transition peak shapes for the C_3H_3^+ ion. The same metastable transition peak shapes are produced by both allene and propyne [19].

While the propyne and allene ion breakdown curves are largely similar, there are several differences between them. A few of these can be explained by the different heats of formation of the parent molecules, 44.3 kcal mol⁻¹ for propyne and 46 kcal mol⁻¹ for allene [20]. Thus the C_3H_3^+ fragment curve is shifted ~100 meV toward higher energy in propyne [21]. A similar shift is seen in the second break in the C_3H_2^+ curves near 17 eV, though the statistics and different intensity of the C_3H_2^+ plateaux make such a comparison difficult.

One difference, however, is not easy to explain and may indicate a difference in the detailed fragmentation or isomerization processes in propyne and allene. This is the difference in intensity of the C_3H_2^+ ion in its plateau region between 14.5 and 16.5 eV. It is ~18% in propyne compared to ~12% in allene, but should be identical if fragmentation occurs from a common precursor.

To verify that this difference was not an experimental artifact, the experiment was repeated in this region for propyne and allene under identical conditions. The pressure was also varied by a factor of 8. No change in the intensity of the C_3H_2^+ curves as reported above was observed.

The C_3H_2^+ intensity has been measured in allene by Dannacher and Vogt [22] using fixed wavelength photoelectron-photoion coincidence. Their branching ratio is approximately 6 to 1, in agreement with that observed previously with our instrument [11].

No fluorescence has been observed from either propyne or allene [23], so that radiative processes are an unlikely explanation for the difference. A pos-

sible explanation, however, could be incomplete isomerization of the propyne ion before fragmentation.

The equivalence of the heats of formation of all the fragment ions from allene and propyne is quite striking. It would appear that, at least at the threshold for these processes, the ions are structurally the same. This would suggest that one or both of the molecular ions are isomerizing during, or prior to, fragment ion formation. Stockbauer and Rosenstock [24] concluded that in the case of allene, the formation of cyclic $C_3H_3^+$ and H loss occur in one step. They further suggested that, in the case of allene, the $C_3H_4^+$ parent ion had the allene structure. This conclusion was based primarily upon the activation energy available and the corresponding expected lifetimes of the excited ions. Since the heat of formation of the $C_3H_4^+$ ion obtained from propyne lies approximately 0.6 eV above that of the $C_3H_4^+$ ion obtained from allene, it would be possible for this isomerization reaction to precede the fragment formation.

PRESSURE EFFECTS

One other major difference between the propyne and allene experiment was observed. The high energy tail of the parent ion curve above the first fragment onset is more pronounced in propyne than in allene (see Fig. 2(B)).

Evidence points to this tail being due to two factors. The first is an adverse electron energy distribution brought about by the fact that the ions are produced almost entirely by autoionization in this region. As has been discussed previously [24], this autoionization could produce a non-uniform electron energy distribution dominated by high energy electrons. Some of these electrons are detected due to the high energy tail of the transmission function of the electron energy analyzer. The parent ions corresponding to these higher energy electrons would not have the full amount of internal energy and therefore would not fragment as rapidly as the others. However, due to the design of the electron analyzer this tailing is negligible ~ 0.3 eV above the parent—first fragment crossover. The data show tailing a full volt above the crossover.

A second contribution to the tailing is likely to be collisional deactivation of the excited parent ions. Evidence for a collision process is provided by the increase of the parent ion curve with increasing pressure in this region. While the propyne and allene curves both showed a pressure dependence, the effect was 2–4 times more pronounced in propyne. The curves given previously for allene [11,24] were run at pressure low enough that the effect was minimal. This was not possible for propyne. The curve still showed a pressure dependence at the lowest pressure which allowed a reasonable signal-to-noise ratio. Similarly, the photoionization parent ion curve for propyne had to be run at reduced pressure to avoid collision effects.

Other evidence for a collision process was noted when the ion residence time was changed in an attempt to observe a kinetic shift. Below 11.65 eV

the kinetic shift was approximately equal to that observed previously for allene [24] i.e. fewer parent ions were observed at longer residence times. Above 11.65 eV, however, the shift occurred in the opposite direction, that is, more parent ions at longer times. This is consistent with the collisional deactivation hypothesis since the parent ions would have more time to collide and lose part of their internal energy before fragmentation.

The observation of more parent ions at longer residence times also rules out kinetic effects as the cause of the tailing. It might be tempting to explain the tail as being due to a fragmentation process slow enough that not all the parent ions had time to fragment. If this were true, a large kinetic shift in the opposite direction would be expected i.e. fewer parent ions at longer residence times.

SUMMARY

Table 1 gives the appearance potentials of the various ions measured in this work. The onsets measured by photoionization and TPES agree well for the parent ions. The fragment ion appearance potentials measured by TPES and photoionization show differences which are discussed in the text and are similar to the differences observed in the previously reported allene study [11]. The overall fragmentation of the propyne molecule can be interpreted as an isomerization to the allene structure with subsequent fragmentation. This view is supported by the equivalence of the heats of formation of the fragment ions from allene and propyne and the near identity of the breakdown curves.

TABLE 1

Appearance potentials in electron volts for the parent and fragment ions of propyne

Ion	This work		Other work		
	Photoionization	Coincidence	Value	Method *	Ref.
$C_3H_4^+$	10.38 ± 0.01	10.38 ± 0.01	10.37	PI	2,3,4
			10.36	S	3
			10.37	PE	7,8
$C_3H_3^+$	11.58 ± 0.04	11.2 ± 0.1	11.56	PI	9
			11.55	PI	4
$C_3H_2^+$	13.68 ± 0.04	13.0 ± 0.1	14.00	EI	17
C_3H^+	17.12 ± 0.06	16.9 ± 0.1	15.4	EI	17
			17.5	EI	25

* PI = Photoionization, S = Spectroscopic, EI = Electron Impact, PE = Photoelectron spectra.

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