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Photoionization and Fragmentation Study of Cyclopropene

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INTRODUCTION

The C_3H_4 isomeric system consists of only three members. This small number and the fact that they contain only a few atoms make this system an excellent candidate for ion isomerization and fragmentation studies. We have reported previously on the ion fragmentation of allene¹ and propyne² and on ion fragmentation kinetics of allene.³ In this paper we report on cyclopropene, the last member of the isomeric system, and compare the result with those of allene and propyne.

Previous work on cyclopropene includes a study of its photoelectron spectra (PES) by Bischof and Heilbronner.⁴ They reported an adiabatic ionization potential (IP) of 9.70 eV. Robin *et al.*⁵ also using photoelectron spectroscopy reported an adiabatic IP of 9.67 eV along with thresholds corresponding to six other excited states of the ion. The adiabatic first ionization potentials agree well with the one determined by Lossing using monoenergetic electron bombardment.⁶

Lossing also carefully measured the appearance potential (AP) of the $C_3H_3^+$ fragment from cyclopropene parent ions.⁶ He reported a value of 10.59 eV for the AP and from this derived a heat of formation (ΔH_f°) of 1075 kJ mol⁻¹ (257 kcal mol⁻¹) for the $C_3H_3^+$ ion. Lossing pointed out that this heat of formation of the $C_3H_3^+$ ion from cyclopropene was approximately the same as the $C_3H_3^+$ ion from both allene and propyne, and from additional measurements he concluded that the $C_3H_3^+$ ion in these instances was of the cyclopropenyl form.

Our work on allene and propyne established that the heats of formation of all the fragment ions from both parents were the same and furthermore the breakdown curves were nearly identical.

[‡] National Bureau of Standards, Intergovernmental Personnel Act Appointee (1978-1980).

In the study reported here we have used photoionization mass spectrometry and the threshold photoelectron-photoion-coincidence mass spectrometry to study the fragmentation of the cyclopropene ion from ionization threshold to 20 eV.

EXPERIMENTAL

The photoionization experiments, threshold photoelectron and photoelectron-photoion-coincidence experiments were performed on the same equipment and in the same manner as for allene and propyne.^{1,2}

Both instruments utilize the hydrogen many-lined spectrum and the Hopfield continuum of helium. The light is dispersed in both instruments with 1 m Seya-Namioka monochromators. Appropriate differential pumping allows for windowless operation.

The photoionization mass spectrometer is a 7.6 cm radius of curvature 60° section magnetic instrument featuring an ion lens of the slit lens type. The ions are detected with a channel electron multiplier and recorded with electronic scalars. The light intensity is monitored with a sodium salicylate coated photomultiplier which is assumed to have a constant quantum yield.

The details of the threshold photoelectron-photoion mass spectrometer have been published elsewhere, but due to its central importance to this work it will be reviewed briefly here.^{7,8}

An overall view of the apparatus showing the location of the major mechanical features is given in Fig. 1. An enlargement of the ion-electron source and the electronics associated with the data acquisition is shown in Fig. 2.

The light leaving the exit slit of the monochromator passes between two circular plates which form the ionization region. The light is monitored with a

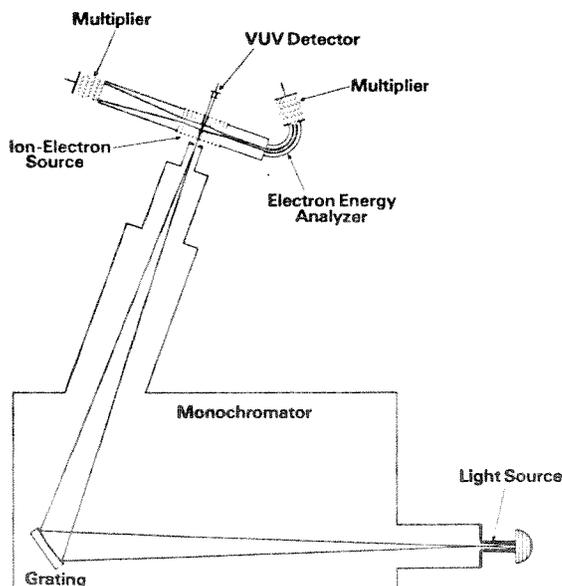


Fig. 1. Schematic of threshold photoelectron-photoion-coincidence mass spectrometer. The vacuum chamber and pumps are omitted for clarity.

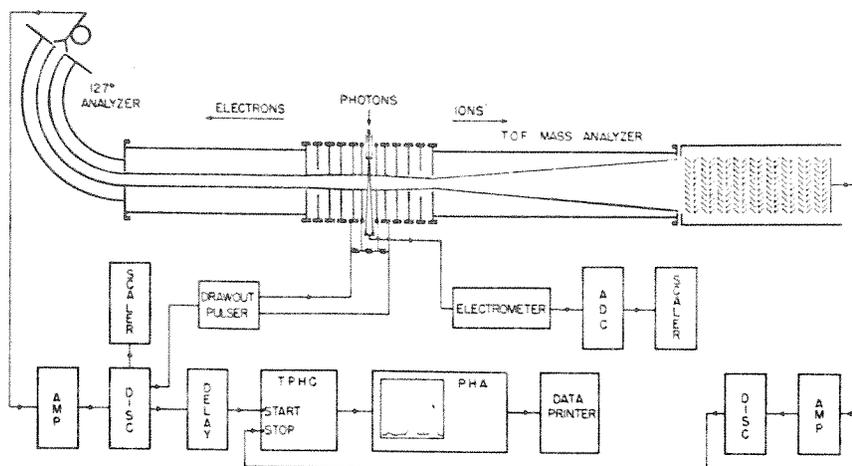


Fig. 2. Schematic of drawout region, electron energy analyser and ion TOF analyser and the associated electronics. The TOF analysis is performed with a time to pulse height converter (TPHC) and pulse height analyser (PHA). The pulses from the particle detectors are amplified (AMP) and passed through a level discriminator (DISC). The current from the tungsten photodiode is measured with an electrometer whose analog output is converted to a pulse stream with an analog to digital converter (ADC). These pulses are accumulated in a scaler.

tungsten photodiode. The holes in the circular plates allow for removal of electrons and ions and are covered with a wire mesh to enhance field homogeneity in the ionization region.

To obtain a threshold photoelectron spectra (TPES) the number of electrons for a given integrated photon flux are measured. Typically the electrons are accelerated to a few eV of energy and the 127° electric sector set for passing only this energy. The nominal energy resolution is about 25 meV.

To obtain the breakdown curves the other portion of the lens system and a time of flight (TOF) mass spectrometer are used. In these experiments the detection of a threshold electron initiates a chain of events culminating in the detection of the coincident ion from which it came. This is achieved by using the amplified threshold electron pulse to trigger a pulse amplifier which applies a high voltage (several hundred volts) to the lens system to draw out and accelerate the ion which has remained essentially stationary during the time of transit of the electron. The ion drift tube is about 22 cm and as operated the system gives a nominal mass resolution of about 80. An additional useful feature of the system is a delay capability between electron detection and high voltage pulse which allows for ion lifetime studies.

The cyclopropene sample was prepared by the procedure outlined by Closs and Krantz.⁹ Care was taken to remove the allyl chloride impurities during synthesis and as a result only a negligible amount showed up in the mass spectrum. The sample was stored in a liquid nitrogen refrigerator until used and introduced into the mass spectrometers through an all glass gas handling system. It was found that the exposure to metal surfaces at atmospheric pressures caused a significant change in the composition of the sample. These changes could be related to those reported in the literature.¹⁰ To help purify the sample during the

TPES and coincidence studies the liquid sample was maintained at 140 K with a pentane slurry. This had the effect of reducing any possible allyl chloride impurity since it was estimated that at this temperature the vapor pressure of cyclopropene would be at least 10 times larger than allyl chloride. From our analysis of the mass spectrum the only significant impurities could have been C_3H_4 isomers.

In general, due to the much smaller amounts of sample that were available, both the photoionization and the coincidence data were obtained using lower sample pressures than those used for the previous allene and propyne studies. For this reason the statistics for the present data are poorer than those for the previous data we have published on allene and propyne.

RESULTS AND DISCUSSION

The photoionization efficiency curve for the $C_3H_4^+$ parent ion 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. 3. The vertical scale of each of the curves has been adjusted to indicate the measured relative intensity. The abscissa is linear in wavelength measured in Ångstroms with a nonlinear energy scale shown for convenience and for comparison with the other data. Figure 4(a) gives the TPES of cyclopropene and Fig. 4(b and c) give the breakdown curves.

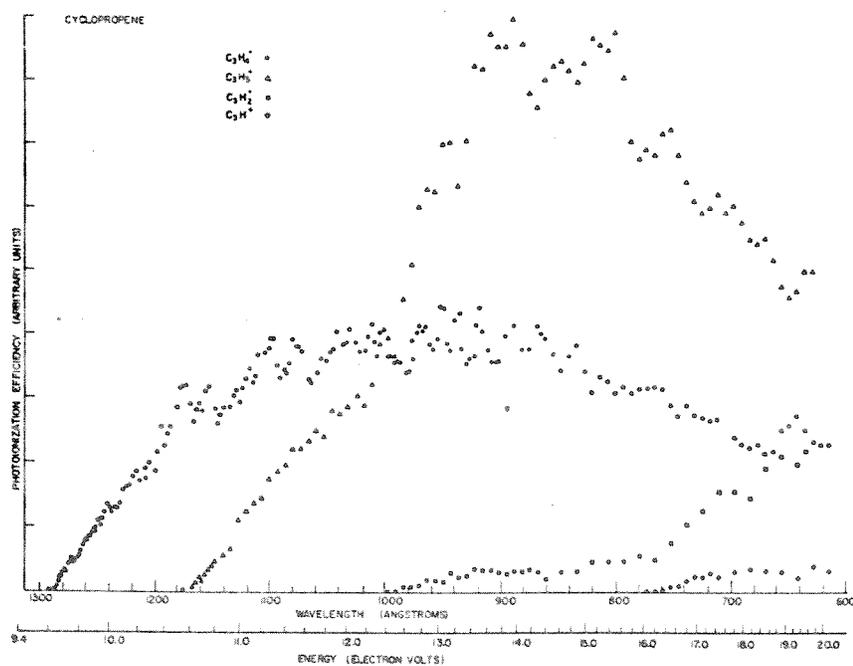


Fig. 3. Photoionization efficiency curve of cyclopropene and its fragment ions between threshold and 600 Å. The ordinate is the photoionization efficiency in arbitrary units. The abscissa is linear in wavelength given in Ångstroms with a nonlinear energy scale given in electron volts. The curves have been corrected to give the proper relative intensities of the parent and fragment ions.

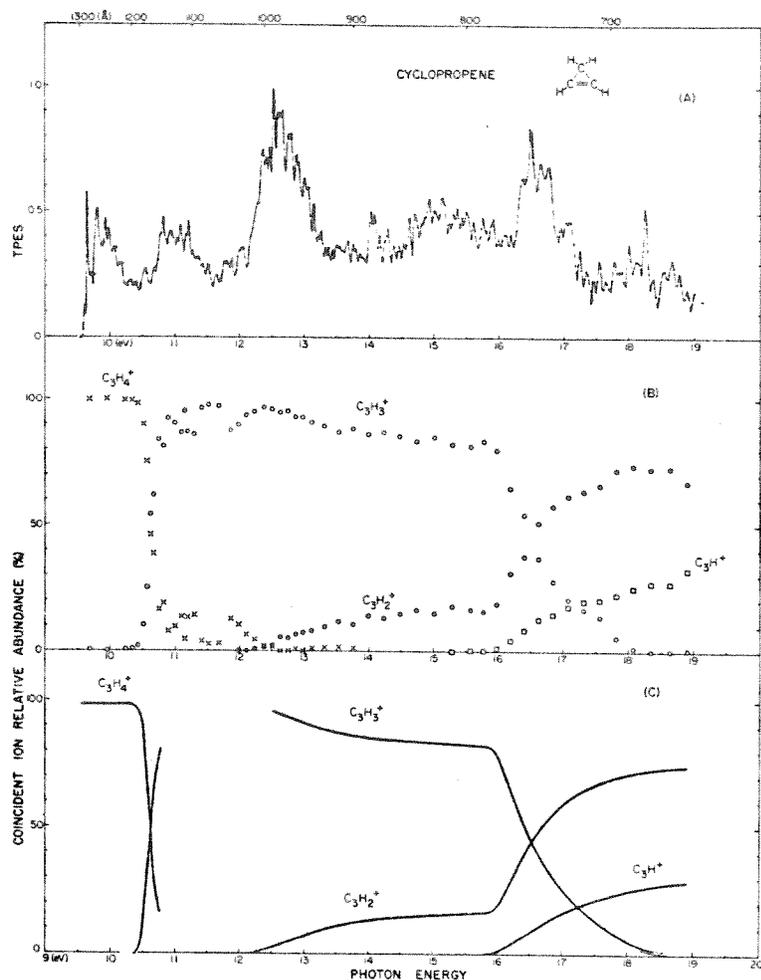


Fig. 4. (a) Threshold PES of cyclopropene from onset to 18.8 eV. The ordinate is electron rate per unit photon in arbitrary units and the abscissa is photon energy in electron volts with a nonlinear wavelength scale, in Angstroms. (b) Breakdown curve for cyclopropene and its fragments. The ordinate is relative coincident ion intensity and the abscissa is photon energy. (c) Breakdown curve for cyclopropene. Same as 2(b) with a smooth average line drawn through the data points except for the omission of the region between 10.8 and 12 eV.

The derived ionization onsets for the parent molecular ion and the fragments observed in this study are shown in Table I. Where other literature values are available our results compare well. It should be noted that the fragment onsets differ somewhat as determined in the photoionization mass spectrometer compared with those observed in the coincidence measurements. This is attributable in part to differing sampling times of the two instruments.

Using the value of the heat of formation of cyclopropene suggested by Rosenstock *et al.*¹¹ and ignoring thermal or kinetic shifts we obtain the heats of

TABLE 1
Onset energies for molecular and fragment ions of cyclopropene

Ion	This work		Other work		
	Photoionization	Coincidence	Value	Method ^a	Ref.
C ₃ H ₄ ⁺	9.67 ± 0.01 eV	9.668 ± 0.005 eV	9.67	PE	5
			9.70	PE	4
			9.69	EI	6
C ₃ H ₃ ⁺	10.59 ± 0.04 eV	10.25 ± 0.1 eV	10.59	EI	6
C ₃ H ₂ ⁺	12.51 ± 0.04 eV	12.15 ± 0.1 eV			
C ₃ H ⁺	16.3 ± 0.05 eV	15.7 ± 0.1 eV			

^a PE = photoelectron spectroscopy; EI = electron impact.

TABLE 2
Heats of formation in kJ mol⁻¹ (kcal mol⁻¹)

	Allene ^a	Propyne ^b	Cyclopropene ^c
C ₃ H ₄ ⁺	1126 (269)	1186 (283)	1209 (289)
C ₃ H ₃ ⁺	1084 (259)	1084 (259)	1079 (258)
C ₃ H ₂ ⁺	1494 (357)	1505 (360)	1481 (354)
C ₃ H ⁺	1594 (381)	1620 (387)	1632 (390)

^a Ref. 1.

^b Ref. 2.

^c Present work.

formation of the ions as shown in Table 2. For convenience the values of heats of formation as obtained for the equivalent ions from allene and propyne are shown. In all cases the photoionization mass spectrometric thresholds were used. The energies for C₃H₂⁺ and C₃H⁺ production were calculated assuming H₂ loss and H₂ + H loss respectively.

The general features of the TPES shown in Fig. 4(a) are also in agreement with the PES.^{4,5} Evidence for the excited states observed in the PES are observed in the TPES as well. The relative intensities are different but this is understandable in terms of contributions by autoionization and by cross-section variations.

The TPES differs from the PES in that the TPES shows considerably more structure. Most of this structure is probably due to autoionization processes which produce low energy electrons. As in allene¹ and propyne² these low electron energy autoionization processes allow us to study the fragmentation of the parent ion in energy regions not accessible by direct ionization and therefore not accessible with PES. The breakdown curve corrected for background is shown in Fig. 4(b). The data have been redrawn and given as smooth curves in Fig. 4(c) with the exception of the region between 10.9 and 12 eV. In this region directly above the parent-first fragment cross-over the data contained structure which was outside statistical error. Since time did not permit a thorough investigation of the pressure dependence of this structure, this region was omitted in the curves in Fig. 2(c).

As in allene and propyne, the only fragmentation observed involves C—H bond ruptures. The first fragmentation observed is H atom loss occurring near 10.5 eV. The competitive fragmentation, H_2 loss, occurs near 12 eV. Above 16 eV, the secondary processes, loss of H and H_2 from the primary fragments, occurs to form $C_3H_2^+$ and C_3H^+ .

Figure 5 shows the breakdown curves from allene, propyne and cyclopropene. The energy axis has been shifted to account for the differences in the heats of

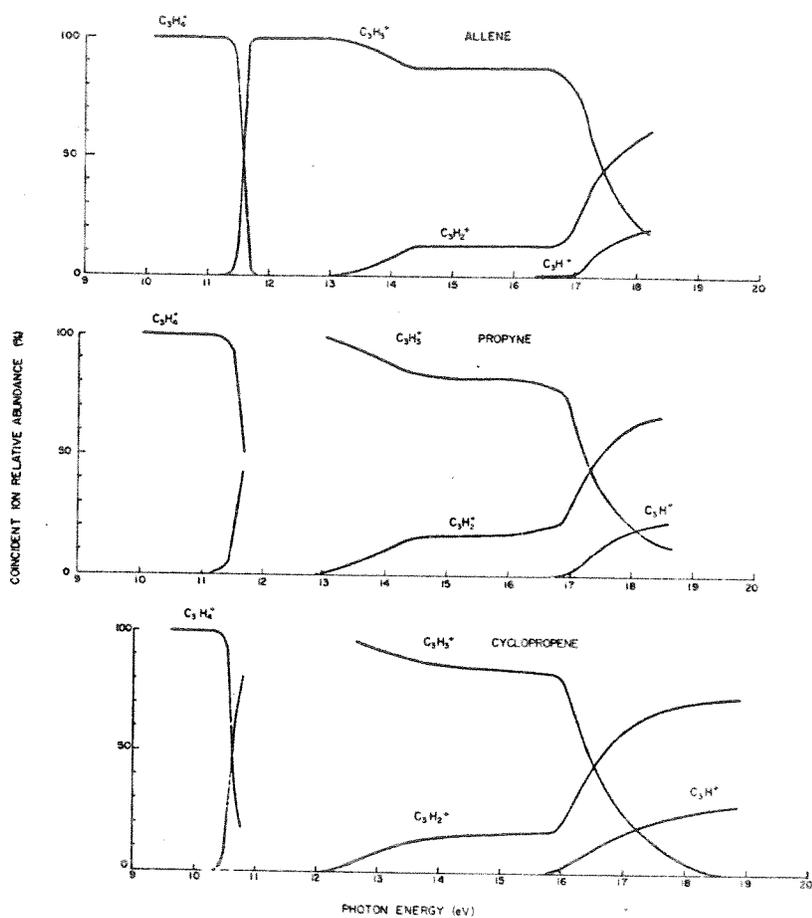


Fig. 5. The breakdown curves from allene, propyne and cyclopropene. The horizontal axes have been shifted to account for the differences in the heats of formation of the parent molecule.

formation of the neutral molecules. The cross-over region for $C_3H_4^+$ and $C_3H_3^+$ has been omitted from the drawings for propyne and cyclopropene for the reasons mentioned above. Inspection of the figure shows that the breakdown curves for all those molecules are virtually identical, the onsets are the same, the cross-over occurs at about the same point and the relative abundances are approximately the same.

These equivalences strongly suggest that the parent ions isomerize to a common structure before they fragment, even for nearly 10 eV of internal energy of the parent ion, i.e. $C_3H_4^+$ formation. From the breakdown curves alone we can not conclude anything about the details of the common parent ion structure. However, by inspection of Table 2 we note that $C_3H_4^+$ ions from both propyne and cyclopropene are metastable in energy with respect to the $C_3H_4^+$ ion from allene. This, combined with the observation of Stockbauer and Rosenstock³ that the allene ion retained its structure before the H loss fragmentation, suggests that the common parent ion has the allene structure at lower internal energy. As mentioned earlier the $C_3H_3^+$ ion is known to be of the cyclic structure so the H loss to form $C_3H_3^+$ is accompanied by the bending of the molecular ion to form a ring structure at the onset for $C_3H_3^+$ production. The implication for cyclopropene is that the initial ring structure is lost upon ionization and returns upon first fragmentation.

CONCLUSIONS

The equivalence of the energetics of all three C_3H_4 species can be summarized in Fig. 6. The appearance potentials and ionization potentials are shifted upward

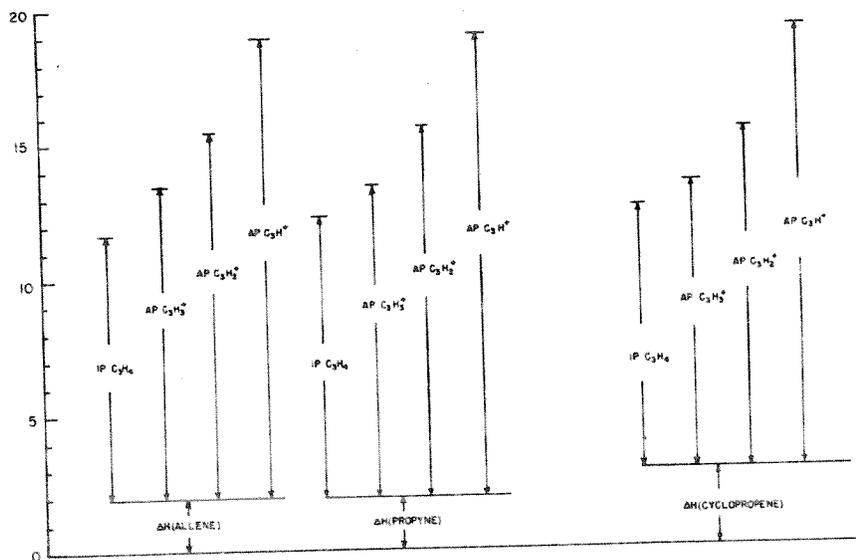


Fig. 6. The total energies of the various ions observed as measured and with the heat of formation of the neutral accounted for. The vertical scale is energy in electron volts.

by the heats of formation of the neutrals, hence a measure of the total energy of each species. The figure shows that the parent molecular ion $C_3H_4^+$ from propyne and cyclopropene is metastable with respect to that from allene. However, all the fragment ions have their onsets at the same total energy. The interpretation is that at threshold the fragment ions are coming from the same parent molecular ion and that the propyne and cyclopropene parent molecular ions rearrange to the allene or some common structure before fragmentation.

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