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PHOTOIONIZATION OF ETHYLENE CLUSTERS

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Abstract

The energetics of the ethylene ion-molecule reactions has been investigated in more detail than previously possible in two body collision experiments by photoionization of the neutral van der Waals ethylene dimer. The stability of the ion-molecule collision complex as well as the highest potential barrier along the reaction coordinate for decomposition have been determined for this exothermic reaction.

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Introduction

The ethylene ion-molecule reaction has been the subject of many investigations. Previous experiments have generally concentrated on measuring the relative rate constants of the ethylene ion-molecule reactions and of the secondary reactions as a function of gas pressure in radiolysis,^{1,2} photolysis³ and high pressure mass spectrometric investigations⁴⁻⁹ and as a function of translational and internal energy in ion cyclotron resonance¹⁰⁻¹⁴ and gas cell photoionization experiments.¹⁵ The reactions most commonly studied are shown in

(1) - (8):

The common conclusion from these studies is that the primary reaction proceeds through some long-lived intermediate which can be collisionally stabilized to yield a butene structure.² If stabilization does not occur, the intermediate may decompose to form the initial reactants or the products shown in (1) and (2). Further experiments performed on reactions between ethylene ion and deuterated ethylene yield a statistical isotope distribution of the products consistent with the concept of the formation of a long-lived complex.⁷ This conclusion is also supported by a crossed beam experiment whose angular distribution indicates that an intermediate is formed which is long-lived compared to the rotational period of the complex.¹⁶

However, these experiments yield no information regarding the details of the energetics along the reaction coordinate. For instance, it is possible that a loosely bound collision complex $C_2H_4^+ \cdot C_2H_4$ is a precursor to the intermediate provided that there is a potential barrier to the formation of the $(C_4H_8^+)^{\ddagger}$ species. The stability of this collision complex cannot be determined in the two body exothermic reaction due to the large total energy of the system compared to the stability of the precursor. In addition, the large total energy prevents the determination of the potential barriers along the reaction coordinate. Knowledge of these barriers is essential to the understanding of the energy distribution of the long-lived complex as determined in the crossed beam experiment.

In this investigation, the stabilized collision complex has been formed as the initial reactant by photoionization of the ethylene dimer

and trimer species produced by adiabatic expansion in a beam. The stability of the ion cluster formed is determined from the threshold energy of formation, since the photoionization of the van der Waals polymer is viewed as ionization of only one of the species. Further excitation of the ion cluster allows the vibrational energy-induced ion-molecule reaction at zero kinetic energy to proceed. With the fine control of the ionizing energy attainable by photoionization techniques, the vibrational degrees of freedom of the complex are excited successively so that the highest potential energy barrier to decomposition along the reaction coordinate is determined.

Experimental

Since the experimental apparatus employed in this study has been described previously,^{17,18} only the details essential to this investigation will be related here.

The hydrogen many-line pseudocontinuum was used as a source of ionizing radiation. The light was dispersed by an MgF_2 coated grating of 1200 lines/mm with an 0.83 nm/mm reciprocal dispersion. With 300 μm entrance and exit slits a 0.25 nm photon bandwidth is achieved.

The ethylene polymers were produced by supersonic expansion of a mixture of ethylene and argon through a 0.003" diameter nozzle. A 13% mixture of C_2H_4 in Ar was determined to yield the largest ratio of dimer to monomer representing a 30% increase in dimer concentration

over a pure C_2H_4 beam. Below 13%, the dimer concentration decreased rapidly. The mixture was not optimized for trimer concentration. A typical product distribution of the beam after photoionization with the monochromator adjusted to zero order is shown in Fig. 1.

The ratio of polymers and fragments to Ar was also investigated as a function of stagnation pressure with a 13% C_2H_4 in Ar mixture at zero order. The results are shown in Fig. 2. The pressure dependence study serves to discover the condition of maximum intensity of the particular ion of interest and to clarify the nature of the parent clusters $(C_2H_4)_n$.

The number of mass selected ions produced and the number of photons intersecting the beam was monitored at 0.1 nm intervals. The amount of background scattered light was measured at 85.0 nm where there is no emission from the H_2 discharge.¹⁹ This value was assumed to be constant over the wavelength region employed and subtracted from the light intensity before the photoionization efficiencies were calculated. For a few of the scans, the background scattered light was as much as 25% of the incident radiation reaching the scintillator depending on the wavelength and the condition of the grating. For a freshly coated grating the amount of scattered light could easily be below 0.1% of the incident radiation. Also, the photoionization efficiency at about 116.0 nm was arbitrarily chosen (there is a peak in intensity at approximately this wavelength) as a reference point with which to monitor the fluctuation in the beam and in the light intensity. The reference point was recorded approximately every 90 minutes. Thus, the photoionization efficiency curves are time normalized.

Results

The photoionization efficiency curves for the $(C_2H_4)_2^+$, $C_4H_7^+$ and $C_3H_5^+$ ions are shown in Fig. 3. The standard deviations are on the order of 10% at the thresholds of the curves and about 2% at 2.0 nm beyond the threshold values. The photoionization efficiencies for the corresponding trimer system are shown in Fig. 4. The standard deviations of the trimer fragments are about 15% at the thresholds. All curves are an average of 2-3 scans. Points were measured at much lower energies than the threshold values so that an average background ion intensity was obtained. The threshold values are labeled as such when the photoionization efficiency values increase monotonically. The threshold uncertainties were taken to encompass the thresholds obtained in two or three separate scans.

Discussion

The photoionization of the ethylene dimer at the threshold can be considered as removal of an electron from the $1b_{3u}$ orbital which is associated with the π bond between two carbon atoms of one of the ethylene molecules. This is evidenced by the vibrational structure present near the dimer ion threshold. The observed vibrational structure is similar to the fine structure of the Rydberg series converging to the ground state of the ion seen in vacuum ultraviolet absorption experiments.^{20,21} The totally symmetric C-C valence stretching vibration ν_2 and a twisting ν_4 of C_2H_4 have been observed

previously in photoelectron ($\nu_2 = 1230 \text{ cm}^{-1}$, $2\nu_4 = 430 \text{ cm}^{-1}$)²² and photoionization experiments ($\nu_2 = 1400 \text{ cm}^{-1}$, $2\nu_4 = 440 \text{ cm}^{-1}$)²³ ($\nu_2 = 1250 \pm 40 \text{ cm}^{-1}$, $2\nu_4 = 400 \text{ cm}^{-1}$).²⁴ The most obvious structure in the dimer ion curve in Fig. 5 is the excitation of one quantum of the ν_2 mode. It is more clearly seen in a log-log plot of the threshold region (Fig. 6) where a change in the initial slope occurs at $125.6 \pm 0.3 \text{ nm}$ when the available amount of phase space suddenly increases. The uncertainty is due primarily to the scatter in the data near the threshold. This breakpoint yields a vibrational frequency of $0.15 \pm 0.02 \text{ eV}$ or $1186 \pm 200 \text{ cm}^{-1}$ for ν_2 . Further excitation of this mode and excitation of the ν_4 mode are less discernible.

Similar log-log plots of the threshold region for C_4H_7^+ and C_3H_5^+ fragments are shown in Figs. 7 and 8. The break in the log-log plot of C_4H_7^+ suggests a value of $0.21 \pm 0.03 \text{ eV}$ or $1725 \pm 242 \text{ cm}^{-1}$ for the corresponding ν_2 mode as observed in photoelectron data of C_2H_4 . There is no evidence of this mode in the C_3H_5^+ threshold region as expected. It is apparent from the difference between the dimer ion and C_3H_5^+ threshold that four or five quanta of the ν_2 C-C stretching vibration are required to eliminate a CH_3 group from the dimer ion.

The photoionization efficiency curves for both the dimer and trimer system are relatively featureless above the threshold region. No autoionization of the Rydberg states that are converging to the first excited state of the ethylene ion at 12.38 eV is apparent.²¹ The first excited state of the C_3H_5^+ ion occurs at $11.6 \pm 0.08 \text{ eV}$ (106.5 nm) as is seen from these data.

Since the photoionization of these clusters involves ionization of one of the C_2H_4 molecules, the stable ion-cluster, a precursor to the intermediate in ion-molecule reactions, is produced. The stability of the ion cluster is determined from its threshold energy of formation. The appearance potentials for $(C_2H_4)_2^+$ and $(C_2H_4)_3^+$ along with the ionization potential²⁵ of C_2H_4 and the neutral interaction energy of 0.42 ± 0.03 kcal^{26,27} (assuming the clusters to be formed from ground state molecules) yield the $(C_2H_4)_2^+C_2H_4$ well depth as 18.2 ± 0.5 kcal and the $(C_2H_4)_2^+C_2H_4$ well depth as 4.2 ± 0.7 kcal:

With increased internal excitation both the dimer and the trimer exhibit hydrogen atom and methyl radical elimination. The threshold

energy of formation then corresponds to the highest barrier along the reaction coordinate for decomposition. The experimental appearance potential of $C_4H_7^+$ yields 206 ± 1.5 kcal as the heat of formation for that fragment, in good agreement with the tabulated heats of formation for several structures indicated in Tables I and II. Thus, there exists no activation energy barrier for H atom elimination. The experimental appearance potential for $C_3H_5^+$ together with the heats of formation in Tables I and II indicates that there is a barrier of 8.4 ± 1.5 kcal for methyl radical elimination. These values are in rough agreement with previously measured exit channel barriers for hydrogen atom and methyl radical elimination from propylene and the butenes.²⁸⁻³¹

The photoionization fragments from the trimer appear to be $C_3H_5^+$ and $C_4H_7^+$ fragments solvated by another ethylene. That is, if the $C_6H_{11}^+$ or $C_5H_9^+$ fragments formed from the trimer are considered to be of a straight chain or a cyclic structure, then the activation energy barrier for their corresponding reverse reactions $C_6H_{11}^+ + H \rightarrow C_6H_{12}^+$ and $C_5H_9^+ + CH_3 \rightarrow C_6H_{12}^+$ as calculated from the thresholds and tabulated heats for formation are unrealistically large. Thus, it appears that the trimer upon ionization does not rearrange but remains as a solvated complex.

Assuming that there is no barrier to hydrogen atom elimination as in the dimer case, the binding energy of the $(C_4H_7^+)C_2H_4$ complex is calculated to be 8.7 ± 1.5 kcal:

Since the barrier to methyl radical addition is mainly due to steric hindrance and since the trimer ion is considered as a dimer ion solvated by another ethylene molecule, the exit channel barrier heights of the dimer and trimer systems are expected to be nearly equal. Thus, the $(C_3H_5^+)C_2H_4$ binding energy is calculated to be 16.22 ± 1.1 kcal:

Shown in Fig. 9 and 10 are proposed reaction coordinates for the dimer and trimer systems. The dots on the reaction coordinate indicate energies that were measured in this investigation. Recently, the nature of the intermediates of the ethylene ion-molecule reaction^{2,14,15,32} or of the decomposition of the cyclobutane ion³³ has undergone considerable speculation. The energies and structures of the two $C_4H_8^+$

intermediates depicted in Fig. 9 and 10 have been proposed by Le Breton et al.¹⁵ The ion cluster initially formed first rearranges into a "loose" tetramethylene radical ion³⁴ and then isomerizes into a more stable butane structure.¹⁴ Since the experimental thresholds correspond to the lowest energy at which the ion cluster can decompose only the highest energy barrier in the reaction coordinate can be measured. Thus, since the thresholds for methyl radical and hydrogen atom elimination are not equal, the experimental barrier is placed in the exit channel assuming that both products originate from the same initial dimer structure.

This raises an interesting point. The fact that the $C_3H_5^+$ and $C_5H_9^+$ fragments peak at a lower stagnation pressure than their corresponding parent ions as shown in Fig. 2 may indicate the presence of two discrete van der Waals structures of the neutral dimer and trimer formed in the expansion. That is, a T-shaped dimer fragmenting exclusively to $C_3H_5^+$ would have a larger cross section for collision and thus attenuation in the nozzle-skimmer region of the source chamber would occur at lower stagnation pressures. The $C_4H_7^+$ and $C_4H_8^+$ ions may be formed from an ethylene dimer structure which would have a smaller collision cross section. The question of two distinct van der Waals structures could be resolved by attenuation experiments. That is, the $C_3H_5^+$ and $C_4H_8^+$ photoion intensities at a stagnation pressure where there is no substantial contribution from the trimer could be monitored as a function of the intensity of a secondary beam of ethylene. A similar decay of the intensities of the two ions due

to their like cross sections would rule out two structures of the van der Waals dimer.

However, contamination of $(C_2H_4)_2^+$ and $C_4H_7^+$ from fragmenting ethylene trimer should occur more readily than fragmentation of the trimer to $C_3H_5^+$ thus shifting these peak intensities to higher stagnation pressures. If one assumes that the $C_3H_5^+$ and $C_5H_9^+$ fragments originate only from the dimer and trimer ions respectively and then adds together the $C_3H_5^+$ and $C_5H_9^+$ pressure dependence curves each multiplied by an appropriate factor and the result then scaled to the $C_4H_8^+$ curve, the resulting curve fits the $C_4H_8^+$ curve very well between 700-1800 torr. At low stagnation pressures (300 torr) the resultant curve is a factor of four too large indicating that there are species which fragment exclusively to $C_3H_5^+$. At higher stagnation pressures the resultant curve is about 25% too large. Thus fragmentation from higher polymers at higher pressures cannot be ruled out. This may cause some of the smearing of vibrational structure seen near the $(C_2H_4)_2^+$ threshold. Attempts to uncover the power dependence of the intensity on pressure for the different species were frustrated due to the inability to control the very low stagnation pressures where attenuation of the beam does not occur.

The ethylene ion-molecule reaction has been studied in a crossed-beam mode where it was determined that the reaction to form $C_3H_5^+$ proceeded through a persistent complex intermediate at relative collision energies less than 3.25 eV.¹⁶ Several statistical calculations of the unimolecular decay of this complex have been carried out to test

the assumption of complete energy equilibration prior to decay. No energy barrier to decomposition other than the centrifugal one was employed in these calculations. The center of mass $C_3H_5^+$ translational energy distribution as a function of incident energy was fit well by decreasing the number of active modes in a "loose complex" model for the critical configuration.³⁵ It is well known that the broadening of the product translational distribution can be achieved by decreasing the number of active vibrations but that it can also be effected by including an exit potential barrier.^{35,36} The resulting product translational energy distributions of both treatments, however, are slightly more narrow than experiment and their deviation becomes greater with increasing collision energy. It is known that the potential energy barrier contributes mainly to the translational and rotational degrees of freedom of the product. Inclusion of the nonrandomized energy available from descending the barrier certainly broadens the calculated distribution since the barrier height is approximately equal to the average translational energy of the $C_3H_5^+$ fragment. Thus, no conclusion about the extent of energy randomization in the ethylene ion-molecule reaction at low energy can be drawn until the details of the reaction coordinate as measured here are included in the calculations.

In summary, van der Waals clusters are excellent parent molecules for determination of ion-molecule binding energies and the highest barrier along the reaction coordinate for the decomposition in an ion-molecule reaction. The appearance potential of the ethylene dimer ion and trimer ion yields the $(C_2H_4^+)C_2H_4$ binding energy to be $18.2 \pm$

0.5 kcal relative to C_2H_4^+ and C_2H_4 and the $(\text{C}_2\text{H}_4)_2^+ \text{C}_2\text{H}_4$ binding energy to be 4.2 ± 0.7 kcal relative to $(\text{C}_2\text{H}_4)_2^+$ and C_2H_4 . In addition the exit channel potential barrier heights for hydrogen atom and methyl radical elimination in the exothermic ethylene ion-molecule reactions have been determined.

Acknowledgement

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Table I. Experimental Thresholds

	nm	kcal mol ⁻¹
$C_2H_4^+$	118.2 ± 0.2	242.0
$(C_2H_4)_2^+$	127.5 ± 0.3	224.3
$C_4H_7^+$	124.5 ± 0.8	229.7
$C_3H_5^+$	119.2 ± 0.4	239.9
$(C_2H_4)_3^+$	129.7 ± 0.3	220.5
$C_6H_{11}^+$	129.2 ± 0.8	221.4
$C_5H_9^+$	127.6 ± 0.4	224.1

Table II. Literature Values of ΔH_f°

		ΔH_f° ^a kcal mol ⁻¹
$C_2H_4^+$		257
$C_4H_8^+$	1 - $C_4H_8^+$	221 ^b
	2 - $C_4H_8^+$	208
	c - $C_4H_8^+$	238
$C_4H_7^+$		206 ^b
$C_3H_5^+$		226 ^b
$C_6H_{12}^+$	1 - $C_6H_{12}^+$	208 ^b
	c - $C_6H_{12}^+$	198
C_2H_4		14.52
CH_3		34.8
H		51.63

^a Reference 25.

^b ΔH_f° (298 K).

FIGURE CAPTIONS

- Fig. 1. Product distribution of the beam after photoionization with the monochromator adjusted to zero order. The stagnation pressure is 800 torr.
- Fig. 2. Intensity ratio of dimers, trimers and fragments to Ar after photoionization with the monochromator adjusted to zero order versus pressure of 13% C_2H_4 in Ar behind the nozzle.
- Fig. 3. Photoionization efficiency (PIE) of $(C_2H_4)_2^+$, $C_3H_5^+$, and $C_4H_7^+$ normalized at 116.0 nm.
- Fig. 4. Photoionization efficiency (PIE) of $(C_2H_4)_3^+$, $C_5H_9^+$ and $C_6H_{11}^+$ normalized at 116.0 nm.
- Fig. 5. Threshold region of photoionization efficiency curve of $(C_2H_4)_2^+$.
- Fig. 6. Log - log plot of the photoionization efficiency curves in the threshold region. Least squares fit for $(C_2H_4)_2^+$ points yields two lines which intersect at $E - E_T = 0.15$ eV or 125.6 nm, where E_T is threshold energy and PIE_B is average background ion intensity.
- Fig. 7. Log - log plot of threshold region of $C_4H_7^+$. Change in slope occurs at 121.8 nm.
- Fig. 8. Log - log plot of threshold region of $C_3H_5^+$.
- Fig. 9. Reaction coordinate for ethylene ion-molecule reaction. Solid dots indicate experimental values. Ordinate is heat of formation.

Fig. 10. Reaction coordinate for ethylene dimer ion-molecule reaction.
Solid dots indicate experimental values. Ordinate is heat of formation.

Fig. 1

XBL 786-5237

Fig. 2

XBL 77 12-10925

XBL 779-4878

Fig. 3

Fig. 4

XBL 779-4879

Fig. 5

XBL 786-5238

XBL 786-5241

Fig. 6

XBL 786-5239

Fig. 7

Fig. 8

XBL 786-5240

XBL 7710-6833

Fig. 9

Fig. 10

XBL 7712-10947

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