Photoionization of Propylene, Cyclopropane, and Ethylene. The Effect of Internal Energy on the Bimolecular Reactions of C₂H⁺₄ and C₃H^{+*}₆

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The ion-molecule chemistry occurring in photoionized ethylene, propylene and cyclopropane has been investigated in the NBS high pressure mass spectrometer. Emphasis has been placed on determining the overall effect of internal excitation on the absolute rate coefficients for the various reactions. This was accomplished by comparing the behavior found when ionization was induced by photon absorption at the ionization threshold with that found at higher photon energies. The values for the absolute rate coefficients for the formation of excited compound ions at various photon energies were as follows (units of 10^{-10} cm³/molecule \cdot s); C₂H₄⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV photons); C₃H₆⁺, 9.6 (10.6 eV photons); 8.5 (11.7 eV p 8.4 (10.0 eV photons); 6.8 (11.7 eV photons); $C_3D_6^+$, 7.8 (10.0 eV photons), 6.1 (11.7 eV photons); $c-C_3H_6^+$ and $c-C_3D_6^+$, 2.2 (10.0 eV photons); 2.2 (11.7 eV photons). The distributions of product ions obtained from the unimolecular decomposition of the compound ion in each system have also been determined at various photon energies, and considerable variation has been observed. In general, the variations are similar to those found elsewhere when the kinetic energy of the reactant ion is increased. The bimolecular reactions of the $C_6D_{12}^+$ compound ion obtained from $C_3D_6^+$ have been investigated at higher pressures, and separate experiments involving isotopically labeled ethylenes have provided new information concerning the nature of the compound ion in that system. Results obtained from other laboratories are discussed in some detail, and in most cases the differences found for the same system are explicable in terms of the energy content (internal and/or kinetic) of the reactant ion.

Key words: Collisional stabilization; hydrocarbons; ion-molecule reactions; photoionization; rate constants; structures of ions.

1. Introduction

Although a great deal of information has been accumulated concerning the effect of ion kinetic energy on the rates and mechanisms of ion-molecule reactions [1],¹ the effects of internal energy remain unexplored. However, several recent relatively investigations [2] of proton transfer reactions occurring in inorganic systems using high resolution photoionization mass spectrometry have demonstrated that the cross sections for certain processes may be extremely sensitive to changes in the vibrational energy content of the reactant ion. This behavior was quantitatively investigated in a recent study from this laboratory [3], which involved a determination of the absolute rate coefficient for the reaction $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ as a function of internal energy, including $\nu' = 0$ of NH₃⁺ as a standard. Investigations of this type have also been extended to a few complex organic systems using variable energy electron impact ionization coupled with Ion Cyclotron Resonance (ICR) mass spectrom-

etry [4], but only relative rate coefficients have been determined. This article describes a mass spectrometric investigation of the ion-molecule reactions occurring in ethylene, propylene, and cyclopropane under conditions of thermal kinetic energy using the photoionization technique to produce primary ions. Although these systems have been subjected to considerable study in other laboratories by electron impact mass spectrometry [4–29], the internal energy content of the reacting ions has always been indeterminate due to the electron energy spread (when low energy electrons were used) and the fact that, in may cases, ionization was induced by 100–200 eV electron bombardment. In the present study ionization was induced by photoabsorption at energies only slightly in excess of the ionization threshold; propylene, I.P.= 9.72 eV (10.0 eV photons); cyclopropane, I.P. = 10.09 eV (hot band ionization with 10.0 eV photons); and ethylene, I.P. = 10.48 (10.6 eV photons) [30]. Analogous experiments were also carried out at using 11.7 eV photons in order to specify the effect of internal excitation. Such absolute rate coefficient determinations are particularly important since they provide the only reasonable basis for standardizing the results

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¹ Figures in brackets indicate the literature references at the end of the paper.

obtained in other laboratories for the same systems. Some additional experiments were performed at elevated pressures both in the mass spectrometer and in closed systems in order to elucidate certain aspects of the effect of density on the reaction mechanism and to provide information concerning the structures of certain product ions.

2. Experimental Procedure

All experiments were carried out using the NBS high pressure photoionization mass spectrometer described in detail elsewhere [31]. The results presented here involve the interactions of thermal ions with a kinetic energy distribution corresponding to kT at 295 K. The techniques involved in deriving rate coefficients and other kinetic parameters have also been discussed elsewhere [31]. Ionization was induced via photolysis with 123.6 nm (10.0 eV), 116.5 nm (10.6 eV) and 106.7–104.8 nm (average energy of 11.7 eV) photons, henceforth referred to as 10.0, 10.6, and 11.7 eV.

3. Results

3.1. Propylene

Fragmentation of $C_3H_6^+$ was not observed at either 10.0 or 11.7 eV. The relative probabilities (given as percentages) for production of $C_3H_7^+$, $C_4H_7^+$, $C_4H_8^+$, and $C_5H_9^+$ via the overall process:

$$C_3H_6^+ + C_3H_6 \rightarrow C_6H_{12}^{+*} \rightarrow \text{ products other than}^2 C_3H_6^+$$
(1)

at the two energies are given in table 1. The relative probabilities for production of the various ions were found to be essentially independent of pressure up to approximately 1.5 millitorr, at which point ca. 50 percent of the $C_3H_6^+$ had reacted. The branching ratios could not be precisely determined at higher pressures due to consecutive reactions.

The decay curves found for $C_3D_6^+$ at the two energies are given in figure 1. Absolute rate coefficients for the production of products other than $C_3H_6^+$, have been derived under conditions where nonreactive scattering of ions is negligible (initial slopes) and are given in table 1. Analogous data has been obtained for the $C_3D_6^+-C_3D_6$ reaction pair. The observed branching ratios and rate coefficients are given in tables 1 and 2, respectively.

Experiments at 10.0 eV were also carried out at pressures up to approximately 0.1 torr in both C_3H_6

TABLE 1. Percentage yields in the overall reaction

 $C_{3}H_{6}^{+}$ (from propylene) + $C_{3}H_{6} \rightarrow$ products other than $C_{3}H_{6}^{+}$

Product ion	10.0 eV ^a	11.7 eV ^a	Zero field ^b	ICR ^c	Ref. [16]	Ref. [15]	Ref. [12]
$C_{3}H_{7}^{+}$ $C_{4}H_{7}^{+}$ $C_{4}H_{8}^{+}$ $C_{5}H_{9}^{+}$ Σ other	12 7 46 35 < 3	$20 \\ 10 \\ 35 \\ 30 \\ < 4$	21 11 42 26	19 12 42 27	23 12 40 25	27 18 34 21	29 26 22 15

 $C_3D_6^+ + C_3D_6 \rightarrow \text{products other than } C_3D_6^+$

Product ion	10.0 eV	11.7 eV	Ref. [9]
$C_{3}D_{7}^{+}$	6.5 ± 0.5	11.5	17.5
$C_4D_7^+$	< 1.0	8.6	14.8
$C_4D_8^+$	52	44	43
$C_{5}D_{9}^{+}$	35	31	24.7
$C_6 D_{12}^+$	5.0 ± 0.5	3.2 ± 0.3	0

^a Present work.

^b Reference [17].

^c Average values taken from references [17] and [7].

TABLE 2. Rate coefficients a for disappearance of primary ions

Reaction pair	10.0 eV $^{\rm b}$	11.7 eV ^b	Flash ^c	Electron impact
Ethylene Propylene Propylene-d ₆ Cyclopropane	$9.6 \pm 0.2 \\ 8.4 \pm 0.4 \\ 7.8 \pm 0.4 \\ 2.2 \pm 0.2$	$\begin{array}{c} 8.5 \pm 0.2 \\ 6.8 \pm 0.3 \\ 6.1 \pm 0.3 \\ 2.2 \pm 0.2 \end{array}$	7.3 7.9 11.4	^d 8.3 ^e 7.6 ^e 6.3 ^e 1.5, ^f 2.0, ^f 2.1

^a cm³/molecule \cdot s $\times 10^{10}$.

 $^{\rm b}$ This work, estimated accuracy better than 7 percent, ethylene values at 10.6 and 11.7 eV.

^c Flash photoionization, reference [8].

^d Reference [19].

^e Reference [9].

^fReference [36].

and C_3D_6 . The variation in the product ion mass spectrum for some major ions from C_3D_6 is given in figure 2.

3.2. Cyclpropane

Ion-molecule interactions occurring in cyclopropane were investigated using 10.6 and 11.7 eV photons in both c-C₃H₆ and c-C₃D₆. Photoionization of c-C₃H₆ at 11.7 eV yields 16 percent C₃H₅⁺, while the extent of fragmentation in c-C₃D₆ is ~ 2 percent. The decay curves found for c-C₃D₆⁺ at the two energies are given in figure 2, and the associated product ions are given in table 3. Rate coefficients for the overall conversion of C₃H₆⁺ (C₃D₆⁺) to products other than C₃H₆⁺ (C₃D₆⁺) are given in table 2.

3.3. Ethylene

Photolysis of C_2H_4 , CHD=CHD, CH₂CD₂, and C_2H_4 -- C_2D_4 mixtures were carried out at both 10.6

² The terminology "products other than – – – –" will be used extensively in this article and is intended to denote those chemical products which are distinguishable from the parent ion in the mass spectrometer; i.e., have a different m/e (mass to charge ratio). A chemical process in which hydrogens are exchanged, for example, cannot be detected without the use of isotopically labeled molecules since the products will still be C3H[°]₆ and C₃H₆ in photoionized C₃H₆. In addition, charge exchange reactions are not detected in like systems, although they may constitute a major reaction channel. Consequently, the rate coefficients derived for reactions of C₃H[°]₆, C₃H[°]₄, ct. in the pure system reflect only the rate of disappearance of the respective parent ions, and do not include contributions to the total reactivity which may be associated with hydrogen exchange or charge transfer.



FIGURE 1. Decay curves for $C_3D_6^+$ from propylene-d₆ (\Box -11.7 eV; \blacksquare -10.0 eV) and c- C_3D_6 (\bigcirc -11.7 eV; \blacklozenge -10.0 eV) following photoionization at 10.0 and 11.7 eV.

TABLE 3. Percentage yields in the overall reaction	on
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 $C_3H_6^+$ (from cyclopropane) + cyclopropane \rightarrow products other than $C_3H_6^+$

Product	eV a		ICP d	Elech e	Zero	Trapped	
1011	10.0 ^b	10.0 ^c	11.7 ^c	icn.	riasn	neid	ION
$C_3H_7^+$	4	4	8	7	4	8	12
$C_4H_7^+$	9	12	15	17	24	13	13
$C_4H_8^+$	75	73	69	68	47	75	66
$C_5H_9^+$	12	11	8	9	9	4	5
$C_3H_5^+$	0	0	0	0	9	0	4
$C_{3}H_{4}^{+} +$	0	0	0.	0	7	0	0
$C_3H_3^+$							

^a Present work.

^b c-C₃H₆.

^c *c*-C₃D₆.

^dReference [17].

^e Reference [8].

^f Reference [36].



FIGURE 2. The fractional intensities of some major product ions resulting from the photoionization of C_3D_6 at 10.0 eV versus pressure.

Line A represents $\Sigma C_3 D_7^+ + C_3 D_7^+ (C_3 D_6) + C_3 D_7^+ (C_3 D_6)_2$.

and 11.7 eV. The decay curves found in photoionized C_2H_4 are displayed in figure 3, and the associated rate coefficients for the reaction:

 $C_2H_4^+ + C_2H_4 \rightarrow \text{products other than } C_2H_4^+$ (2)

are given in table 2. The secondary ion distribution is given in table 4.

a. Ethylene-d₂

The isotopic composition of the $C_3(H,D)_5^+$ ions from *cis*-1,2 dideuteroethylene (isotopic impurity 5.82% C_2H_3D) and 1,1 dideuteroethylene (isotopic impurity 2.46% C_2H_3D) were also determined. We found that the observed distribution of the $C_3(H,D)_5^+$ ions from both analogs exhibited subtle changes as a function of chamber pressure, although the respective distributions were essentially invariant at very low pressures where the probability for collision of initially produced C_3^+ ions with $C_2H_2D_2$ was negligibly small. The isotopic distributions of the $C_3(H,D)_5^+$ ions obtained from the two analogs under conditions where only 2–5 percent of the parent ions had reacted are given in table 4. Also included for comparison is the distribution obtained with CHD=CHD under conditions where the fractional intensity of $C_2H_2D_2^+$ constituted 10 percent of the composite mass spectrum (90% reacted).

TABLE 4.Ethylene

Isotopic composition of $C_3X_5^+$ products from labeled ethylenes ^a								
Molecule	Photon energy	- CH ₃	$-\mathrm{CH}_{2}\mathrm{D}$	$-CD_2H$	– CD 3	<i>m</i> / <i>e</i> 41		
cis-CHDCHD cis-CHDCHD CH ₂ CD ₂ CH ₂ CD ₂ CH ₂ CD ₂ ^b cis-CHDCHD ^c	10.6 11.7 10.6 11.7 (e ⁻) 11.7	8.34 8.30 8.34 8.67 8.23 8.42	37.78 39.39 38.65 39.43 40.7 39.06	$\begin{array}{r} 40.57\\ 39.80\\ 41.18\\ 40.87\\ 41.1\\ 38.49\end{array}$	11.97 11.25 10.87 10.12 9.88 12.02	1.35 1.27 0.98 0.91 n.d. 2.01		

Product yields ^d	obtained	from the	overall	sequence
$C_2H_4^+ + C_2H_2$	₄ → Produ	ucts Othe	r Than	$C_2H_4^+$

Photon energy	$C_3H_4^+$	$C_3H_5^+$	$C_3H_6^+$	$\mathrm{C_4H_7^+}$	$C_2H_5^+$
10.6	$5.6 \\ 4.4$	80.0	0.8	13.7	0.00
11.7		85.0	0.9	9.8	≤ 0.4

^a Collected for C_{13} contributions, but includes $C_3X_4^+$ where x=H or D. Values given as percentage yields.

^b Taken from reference [22].

^c Yields of 90 percent conversion, this work.

 $^{\rm d} \, {\rm As} \,$ percent of secondary ion mass spectrum, conversions ≤ 2 percent.

b. C₂H₄-C₂D₄ Mixtures

Equimolar mixtures of C₂H₄ and C₂D₄ (5.58%) C_2D_3H) were investigated at 11.7 eV in order to determine the contribution from exchange reactions such as $C_2D_4^+ + C_2H_4 \rightarrow C_2D_3H^+$, etc. It was found that the total probability for formation of C₂D₃H⁺, $C_2H_2D_2^+$, and $C_2H_3D^+$ was 1.1 percent of the total probability for production of C_3^+ and C_4^+ ions. Since only ~ 50 percent of the collisions are between perdeuterated and perprotonated reactants, the total probability for exchange is 0.022 assuming no isotope effects and making no corrections for collision frequency due to differences in the thermal velocities of $C_2H_4^+(C_2H_4)$ and $C_2D_4^+(C_2D_4)$ at 300 K. The isotopic distribution obtained for the exchanged products, after correcting for the C_2D_3H impurity, was as follows; $C_2D_3H^+$, 0.3; $C_2D_2H_2^+$, 0.5; and $C_2H_3D_2^+$, 0.2. It was not possible to investigate such processes quantitatively at 10.6 eV due to the fact that the total ion signal at this energy was approximately a factor of 20 lower than that associated with the photoionization of ethylene at 11.7 eV.



FIGURE 3. Decay curves for $C_2H_4^+$ following photoionization of C_2H_4 at 10.6 and 11.7 eV.

The relative rate coefficients for reaction of $C_2D_4^+$ and $C_2H_4^+$ in a $C_2H_4-C_2D_4$ mixture containing 1 percent C_2D_4 were also determined at 11.7 eV. It was found that the reaction:

$$C_2D_4^+ + C_2H_4 \rightarrow \text{products other than } C_2D_4^+ \quad (3)$$

is approximately 7 percent faster than the rate of removal of $C_2H_4^+$ in such mixtures. Analogous experiments with dilute mixtures of C_2H_4 and C_2D_4 gave a similar result; i.e., the conversion of $C_2H_4^+$ to products other than $C_2H_4^+$ is approximately 8 percent faster in C_2D_4 than in C_2H_4 . The difference in residence times between $C_2H_4^+$ and $C_2D_4^+$ was taken into account in determining these values.

4. Discussion

4.1. Propylene

The overall reaction of $C_3H_6^+$ with C_3H_6 has probably been subjected to more scrutiny by mass spectrometry in various laboratories [4–18] than any other reaction involving complex olefinic ions. When the collision frequency is sufficiently low to preclude stabilization of C₆H₁₂ compound ion produced via process (1), there is general agreement that the unimolecular decomposition of the complex leads to the formation of $C_3H_7^+$, $C_4H_7^+$, $C_4H_8^+$, and $C_5H_9^+$ as the major ions. Other studies [15] have provided detailed information concerning the nature of the intermediate ion and the associated unimolecular fragmentation processes. As pointed out in the introduction, the purpose of the present study was to determine the overall mechanistic effect, if any, of changes in the internal energy content of the reactant ions and to search for additional reaction paths for the molecular ion at elevated pressures which may have escaped the attention of previous investigators.

a. Effect of Energy

The branching ratios obtained in the present study at the two energies are compared with representative data obtained by electron impact ionization in table 1. The citations for the Zero Field and ICR techniques (ICR citations are average values taken from several laboratories), reflect the interactions of $C_3H_6^+$ ions which are essentially thermal. The other electron impact entries reflect the ratios obtained under conditions where the reactant ion has been accelerated to kinetic energies slightly in excess of kT, while the final entry gives results obtained by photoionization at 10.2 eV at a field strength of 10 V/cm. Within experimental error there is good agreement between the ratios obtained at 11.7 eV (2 eV above the ionization potential of C_3H_6) and those obtained by electron impact using both the Zero Field and ICR techniques, indicating that the photoionization of C_3H_6 at 106.7-104.8 nm gives an internal energy distribution roughly equivalent to that obtained with "low energy" electrons. It is difficult to draw any exact correlations since the electron energies used in other laboratories are usually not specified.

When the photon energy is increased from 10.0 to 11.7 eV the fractional yields of $C_3H_7^+$ and $C_4H_7^+$ increase while $C_4H_8^+$ and $C_5H_9^+$ decrease in relative importance. Consideration of the literature values given in table 1, and the results of systematic studies involving propylene in which kinetic energy has been varied over a wide range [13, 16] confirms that the same trends are observed as the kinetic energy of the reactant ion is increased; i.e., $C_3H_7^+$ and $C_4H_7^+$ increase and $C_4H_8^+$ and $C_5H_9^+$ decrease. This is a clear demonstration that an increase in the internal energy content of a reactant ion gives the same overall effect as an increase in kinetic energy for a relatively complex set of competing unimolecular decomposition processes involving a compound ion. Although the conversion of kinetic into internal energy has been well documented in various laboratories, the mechanism has always proceeded through an otherwise endothermic reaction channel (such as the formation of a dissociative charge exchange product).

A similar variation in the distribution of product ions with photon energy was obtained for the $C_3D_6^+$ - C_3D_6 reaction pair, but in this case the fractional yields of $C_3D_7^+$ and $C_4D_7^+$ are reduced compared to the perprotonated system. This effect is probably related to the fact that the $C_6D_{12}^+$ intermediate ion contains slightly less energy at the time of fragmentation. We have also observed (table 1) stable $C_6D_{12}^+$ ions in C₃D₆ at pressures where collisional stabilization of the intermediate ion is negligible (pressures ≤ 0.5 millitorr). Under the same experimental conditions the yields of $C_6H_{12}^+$ from $C_3H_6^+$ were negligibly small (< 1%). Peers [16] has also observed the bimolecular formation of stable $C_6H_{12}^+$ in propylene, but again with a fractional yield < 1 percent. The bimolecular formation of large yields of stable $C_6D_{12}^+$ in C₃D₆ may be attributed to the increased dissociative lifetime of the perdeuterated system. A change in the internal energy also affects the relative probability for formation of stable $C_6D_{12}^+$ as evidenced by the fact that the fractional yield decreases substantially ($\sim 40\%$) when the energy is increased from 10.0 to 11.7 eV.

Up to this point we have dealt only with the effect of internal energy on the relative rates of unimolecular decomposition of the compound ion along various competing channels. An equally important effect is the role of internal energy in affecting the overall rate coefficient for conversion of $C_3H_6^+$ into products other than $C_3H_6^+$. Reference to figure 1 and the rate data given in table 2 indicates that an increase in energy from 10.0 to 11.7 eV results in an approximately 20 percent decrease in the rate coefficient. The present values are compared with those available from other laboratories, and the general agreement is quite satisfactory considering the differences in experimental techniques. The reduction in the total rate coefficient with increasing internal energy has been reported for other systems [4], and has been attributed either to a decrease in the lifetime of the compound ion or an increase in the probability for charge exchange. In this context we would like to point out that a clear distinction must be made between the effect on the apparent overall rate coefficient and the effect on the relative probabilities for fragmentation of the compound molecule-ion (once formed) along various competing channels. For example, it is incorrect to discuss the formation of $C_5H_9^+$ from $C_3H_6^+$ in terms of a rate constant or reaction cross section for the reaction $(C_3H_6^+ +$ $C_3H_6 \rightarrow C_5H_9^+ + CH_3$). In our view, once the $C_6H_{12}^{+*}$ compound state is formed the reaction of $C_3H_6^+$ with C₃H₆ is over. The unimolecular fragmentation patterns, as well as the relative probability (lifetime) for dissociation into $C_5H_9^+ + CH_3$ will certainly depend on the internal energy content of the excited hexene ion, but this is a problem in unimolecular, not bimolecular, reaction kinetics.

An additional point may be made concerning the results contained in tables 1 and 2. Even after taking into account the 20 percent decrease in the overall rate coefficient for removal of $C_3H_6^+$ and $C_3D_6^+$ as the photon energy is increased, one still finds a substantial increase in the absolute rate of production of C₃H⁺₇ and $C_3D_7^+$. As mentioned earlier, tandem experiments [15] have shown that the production of these ions proceeds through a long range process which is chemically distinct from that (those) responsible for subsequent production of C_4^+ , C_5^+ , and \hat{C}_6^+ ions, in which $\hat{C} - C$ bonds are formed and extensive randomization of hydrogen is observed. The evidence is clear that this long range transfer process is favored both when the reactant ion is produced in high vibrational states and under conditions of high kinetic energy.

b. Reactions Occurring at Higher Pressures

In a previous article from this laboratory [32] it was shown that propane was obtained in large yields via an ionic mechanism when propylene was photoionized at 10.0 eV at pressures greater than 2 torr. The mechanism proposed to account for propane formation was as follows:

$$C_3 H_6^+ + C_3 H_6 \rightarrow C_6 H_{12}^+$$
 (4)

$$C_6H_{12}^+ + C_3H_6 \rightarrow C_6H_{10}^+ + C_3H_8$$
 (5)

Although several laboratories have carried out mass spectrometric experiments at high pressures of propylene (0.1 [8], 0.25 [15], and 0.9 torr [11]) this particular reaction sequence has not been detected. However, large yields of $C_6H_{12}^+$, as well as $C_9H_{18}^+$ were observed directly in a recent flash photoionization study [8]. In order to resolve these apparently contradictory results we have investigated the photoionization of propylene at pressures up to approximately 0.1 torr. We chose the deuterated analog for detailed study due to the fact that $C_3D_6^+$ forms $C_6D_{12}^+$ at 10.0 eV in large yields compared to the perprotonated analog. Typical results are given in figure 2, which reproduces the fractional composition of the product ion mass spectrum for some major ions from C_3D_6 at pressures up to approximately 100 millitorr. The successive addition of C_3D_6 to $C_3D_7^+$ is clearly indicated, as well as the conversion of $C_4D_8^+$ into $C_5D_{10}^+$, etc. These sequences have been reported previously for the perprotonated system [16]. We have also observed the addition of C_3D_6 to $C_4D_8^+$, $C_4D_9^+$, and $C_5D_9^+$ ions, as well as other concurrent reactions, but these processes are not germaine to this discussion and the associated fractional yields of these species have been omitted from the figure. The important experimental observation is the rapid formation of substantial yields of $C_6D_{12}^+$ and its subsequent reaction with C_3D_6 to give $C_6D_{10}^+$ via D_2 transfer:

$$C_3D_6^+ + C_3D_6 \xrightarrow{M} C_6D_{12}^+ \xrightarrow{C_3D_6} C_6D_{10}^+ + C_3D_8.$$
(6)

The sum of the fractional contributions from $C_6D_{12}^+$ and $C_6D_{10}^+$ reaches a value of 0.19 ± 0.1 at

approximately 10 millitorr and remains constant up to the maximum pressure studied (100 millitorr). Reactions occurring at higher pressures could not be investigated quantitatively due to the complexity of the resulting spectrum. The direct observation of the D_2 transfer reaction involving the $C_6D_{12}^+$ ion verifies the mechanism proposed earlier in this laboratory [32] to account for propane formation in photoionized propylene, and the ion-pair yield of 0.19 derived in this study compares well with the value of 0.14 reported for C_3H_8 formation in photoionized C_3H_6 . Recent mass spectrometric experiments from this laboratory [33] have confirmed that the analogous reaction scheme also occurs in *i*-C₄H₈ and *i*-C₄D₈, although in this case the fractional yield for the $H_2(D_2)$ transfer product is approximately 0.5. We mentioned earlier that other investigators were unable to detect processes (4) and (5) in C_3H_6 . Although our own experiments with C_3H_6 over the pressure range covered in figure 2 did reveal the formation of $C_6H_{12}^+$ and $C_6H_{10}^+$, the sum of the fractional yields of these products was extremely low (≤ 0.02) at our highest pressure (100 millitorr). It is likely that the formation of such ions would have been overlooked in previous experiments involving high energy electron impact ionization which would yield a variety of fragments from $C_3H_6^+$ in addition to the molecule-ion. One intriguing feature of the sequences represented by processes (5) and (6) is that they are not quantitative for removal of $C_3H_6^+$ and $C_3D_6^+$ even at pressures up to one atmosphere based on chemical evidence (the ion-pair yields for propane formation reach a constant value ≤ 0.2). A possible explanation for this effect is that proposed previously; namely, that the $C_6H_{12}^+$ ions which do react via H₂ transfer have cyclic structures whereas the majority of the $C_6H_{12}^+$, $C_9H_{18}^+$, etc., ions are acyclic and disappear simply by consecutive olefinic condensation reactions. Other investigators have, on occasion, suggested unique structures for those $C_6H_{12}^{+*}$ compound ions which unimolecularly fragment at low pressures [15]. However, as pointed out by Harrison [13, 17], and as indicated in a recent study in this laboratory [34], the modes of decomposition of a compound ion depend critically on the internal energy of the system. Many different isomeric structures may exist under these conditions, and the dissociation is likely to occur from any or all of these configurations. Therefore, it is not surprising that ten or more C₆H₁₂ isomeric products were recovered when the photoionization of propylene was carried out in a closed system in the presence of $(CH_3)_3N$ (I.P. = 7.8 eV), which acts as a charge acceptor in the process:

$$C_6 H_{12}^+ + (CH_3)_3 N \rightarrow C_6 H_{12} + (CH_3)_3 N^+.$$
 (7)

This process was very efficient as evidenced by the fact that the total ion-pair yield of the C₆ products resulting from the photoionization of a mixture containing 10 mole percent of $(CH_3)_3N$ in 4 torr of C_3H_6

was 0.70. When NO (I.P. = 9.2 eV) is substituted for $(CH_3)_3N$ to yield decreases by approximately a factor of four. This effect can be ascribed to the fact that the ionization potentials of many of the C_6H_{12} isomers are lower than that for NO, rendering the charge transfer process endothermic.

The observation of a large number of isomeric structures does not, however, indicate that the isomerization processes are dictated solely by statistical factors since five of the ten major products account for 80 percent of the yield. It has also been confirmed by Henis [5] that randomization of hydrogen atoms in the compound ion occurs only to a limited extent for the higher olefins. Additional information concerning the $C_6H_{12}^{+*}$ ion has been derived by Wagner [35], who investigated the solid phase radiolysis of propylene under conditions where deactivation of $C_6H_{12}^{+*}$ will essentially freeze the ion in its initial configuration. Although a large number of C_6H_{12} isomers were observed, the major products were 1-hexene and 3-methyl-1-pentene.

4.2. Cyclopropane

For the $c-C_3H_6^+-c-C_3H_6$ reaction pair the rate coefficients obtained at 10.6 and 11.7 eV are in excellent agreement with recent values from Harrison's laboratory [36] by the Zero Field Pulse and trapped ion techniques. However, the values of 2.2, 2.1, and 2.0×10^{-10} cm³/molecule s are considerably lower than that (11.4 ± 2.4) derived by Strausz, et al. [8] using the flash photoionization technique. This latter method involves flash photoionization via a continuum lamp (useful energies extending from the ionization threshold for the molecule to approximately 11.7 eV) followed by time-resolved analysis using mass spectrometry. We find no variation in the rate coefficient with increasing photon energy, and are unable to account for the observed difference in reactivity.

The following overall processes were also observed by the flash technique:

$$c - C_3 H_6^+ + c - C_3 H_6$$

 $\rightarrow C_3 H_4^+ + C_3 H_8 \qquad (\Delta H = -0.12 \text{ eV}) \quad (8)$

$$\rightarrow C_3 H_3^+ + C_3 H_8 + H$$
 ($\Delta H = 1.1 \text{ eV}$). (9)

(Heats of reaction assume ground state reactants and the thermodynamically favored structures for products). These products have not been observed in studies involving electron impact ionization of cyclopropane under thermal conditions [9, 13, 17] and were not observed in the present study at any photon energy. This result indicates that even though a fraction of the $C_3H_6^+$ ions resulting from photoionization of cyclopropane at 11.7 eV may be in the second electronic state (11.07 eV) [37] the additional energy is not effective in overcoming the energy barrier for these processes.

The product distribution resulting from the overall sequence:

$$c-C_3H_6^+ + c-C_3H_6 \rightarrow \text{ products other than } C_3H_6^+ \quad (10)$$

does vary with photon energy (table 3), and the distribution obtained at 11.7 eV agrees very well with the electron impact values. In this context it is important to note that those products which decrease in relative importance as the photon energy is increased ($C_4H_8^+$, $C_5H_9^+$) are also those which decrease in relative importance as the kinetic energy of the reactant ion is increased. Alternatively, the relative rate of formation of $C_3H_7^+$ in cyclopropane increases as both the photon and kinetic energy are increased.

The high relative abundance of the C₄H₈ produced in the cyclopropane system (table 3) as compared to the propylene system (table 1) is of interest. This is due to the fact that once a C-C bond is broken in the neutral partner of the $c-C_3H_6^+ - c-C_3H_6$ collision collision complex, elimination of ethylene from the neutral can occur rapidly without extensive rearrangement. The analogous reaction has been found to occur in a recent study of the C_4H_8 isomers. In this case the methylcyclopropane system exhibits an unusually high relative abundance of the $C_5H_{10}^+$ as an overall reaction product compared with the other C₄H₈ isomers. As pointed out for cyclopropane, elimination of the neutral molecule (propylene) in methylcyclopropane would also occur without rearrangement once a C-C bond is broken in the neutral reacting partner.

4.3. Ethylene

The overall reaction of $C_2H_4^+$ with C_2H_4 has been subjected to considerable investigation in both the closed system photolysis [34, 38–39] and radiolysis [34, 39] as well as very extensively by kinetic mass spectrometry [4–5, 8, 18–29]. The evidence favors formation of an excited butene-like reaction intermediate which, at low pressures, decomposes mainly into $C_3H_5^+$ and $C_4H_7^+$

$$C_{2}H_{4}^{+} + C_{2}H_{4} \rightarrow C_{4}H_{8}^{+*} \rightarrow C_{3}H_{5}^{+} + CH_{3}$$
 (11)

$$\rightarrow C_4 H_7^+ + H.$$
 (12)

At higher densities, where collisional stabilization of $C_4H_8^{+*}$ is effective, the chemical studies in closed systems have provided a great deal of information concerning the various isomerization processes and structures associated with the intermediate ion [34, 38–39]. The present results concern the interactions of ethylene ions produced in the ground electronic state (the maximum photon energy of 11.7 eV is approximately 0.6 eV below the threshold for electronic excitation) [40] under conditions where stabilization of $C_4 H_8^{+*}$ is negligible.

a. Effect of Internal Energy

The fractional yields of the C_3^+ and C_4^+ products associated with the $C_2H_4^+ - C_2H_4$ reaction pair exhibit several rather subtle variations with photon energy. The major effect involves the change in the ratio $C_4H_7^+/C_3H_5^+$, which decreases from 0.17 to 0.11 as the energy is increased from 10.6 to 11.7 eV. Comparison of the breakdown patterns and appearance potential measurements for the various C₄H₈ isomers [41] indicates that the energy threshold for the formation of the $C_4H_7^+$ fragment from $C_4H_8^+$ in those systems is consistently lower than that for $C_3H_5^+$. Consequently an increase in the internal energy content of the $C_4H_8^+$ ion produced in the $C_2H_4^+ - C_2H_4$ system would be expected to favor production of $C_3H_5^+$, and this is the trend observed experimentally. In the present study we have not observed the production of $C_2H_5^+$ as a secondary ion (possibly a fractional yield of 0.004 at 11.7 eV) although previous results indicate the formation of this ion in significant yields. Apparently overall formation of $C_2H_5^+$ occurs only for highly excited $C_2H_4^+$ or under conditions of excess kinetic energy.

The decay curves of figure 3 indicate a decrease of approximately 11 percent in the overall rate coefficient for process (2) when the photon energy is increased from 10.6 to 11.7 eV. As was found for the $C_3H_6^+ - C_3H_6$ reaction pair the absolute value of the rate coefficient obtained at 11.7 eV is in excellent agreement with the "low energy" electron impact results and compares well with that obtained by flash photoionization. Gross and Norbeck [4] have recently investigated the effect of internal energy on the cross section for production of $C_3H_5^+$ (process 11) using variable energy electron impact ionization. Their results indicated a decrease of approximately 30 percent in the cross section when the electron energy was increased from threshold to 25 eV. Considering our respective absolute rate coefficients at the two energies (our measurement at 10.64 eV is only slightly in excess of the photoionization threshold of $10.51 \pm .04$ eV) and the respective overall product distributions given in table 4, we calculate a decrease of approximately 7 percent in the rate of production of $C_3H_5^+$ at 11.7 eV when compared to threshold. This change is consistent in magnitude with that observed by Gross and Norbeck, over this limited range, but the vibrational energy distribution in $C_2H_4^+$ is unknown in both cases.

It has been suggested [4] that under those conditions where the rate coefficient for process (2) is substantially reduced from the threshold value one should observe an increase in the yields of isotopically exchanged ethylenes in $C_2H_4 - C_2D_4$ mixtures; i.e., an increase in the probability for return to starting material should favor overall processes such as:

$$C_{2}H_{4}^{+}+C_{2}D_{4} \rightarrow C_{4}D_{4}H_{4}^{+}$$

$$\rightarrow C_{2}H_{3}D^{+}+C_{2}D_{3}H, \text{ etc.} \quad (13)$$

Some exchange has been observed in $C_2H_4 - C_2D_4$ mixtures in single stage mass spectrometer [19] and when $C_2H_4^+$ is impacted onto C_2D_4 in a tandem instrument [20]. We have investigated the exchange processes at 11.7 eV and have found (see Results) that exchanged products account for only 2.2 percent of the sum total of all processes (excluding charge exchange) which may occur at this energy. Furthermore, the tandem results of Tiernan and Futrell [20] indicate a total contribution from exchange processes < 5 percent even when ionization is induced with 100 eV electrons. These observations indicate that dissociation of the complex ion into reactants occurs with very little hydrogen exchange. The only alternative overall channel is that which is empirically equivalent to simple charge exchange:

$$C_2H_4^+ + C_2D_4 \rightarrow C_2D_4^+ + C_2H_4$$
, etc. (14)

Such processes have been observed by ICR [22] in $C_2H_4 - C_2D_4$ mixtures as well as in tandem experiments [20]. We have found (see Results) that the rate coefficient for the process $C_2D_4^+ + C_2H_4 \rightarrow$ products other than $C_2D_4^+$ is approximately 7 percent faster than that for $C_2H_4^+ + C_2H_4 \rightarrow \text{products}$ other than $C_2H_4^+$. Charge exchange between $C_2H_4^+$ and C_2H_4 would not be detected in our instrument, whereas charge exchange from $C_2D_4^+$ to C_2H_4 would be detected as an increase in the apparent rate coefficient for removal of $C_2D_4^+$. Essentially the same result was found for the reaction of $C_2H_4^+$ with C_2D_4 . Tiernan and Futrell [20] observed substantially more charge exchange in the $C_2H_4^+ - C_2D_4$ reaction pair (~ 30%), but whether this was due to the fact that the internal energy content of $C_2H_4^+$ was higher (100 eV electrons) or the ions were slightly epithermal (0 < E < 0.4 eV)cannot be determined from their data. Finally, Bowers, et al. [22] have concluded that an increase in kinetic energy results in a corresponding increase in the probability for charge exchange in ethylene, but that the total reaction probability (charge exchange plus contributions from process 13) remains constant. In any event, the accumulated data indicates that the separation of the interaction pair into $C_2H_4^+ + C_2H_4$ proceeds without significant hydrogen randomization among the reactants.

b. Randomization of Hydrogen in C₄H₅*

There is general agreement among various workers that the $C_4H_8^{+*}$ compound ion involved in processes (11) and (12) has a relatively long lifetime ($\geq 10^{-8}$ s) with respect to dissociation. Consideration of the isotopic composition of the $C_3X_5^+$ (X=H or D) ions produced in $C_2H_4 - C_2D_4$ mixtures and the partially labeled analog $CH_2 = CD_2$ has also resulted in a consensus opinion that all hydrogens are equivalent in that $C_4H_4D_4^{+*}$ compound ion obtained in such systems. For example, in a recent ICR study by Bowers et al. [22], the distribution of the $C_3X_5^+$ products obtained from the $CH_2 = CD_2^+ - CH_2 = CD_2$ reaction pair was found to be essentially equivalent to that obtained from a $C_2H_4 - C_2D_4$ mixture and complete randomization was concluded. Unfortunately, such agreement is

not proof of complete randomization if a cyclic structure (cyclobutane ion) is assumed to represent the configuration of $C_4H_4D_4^{+*}$, since in this case the carbon atoms may retain the original H or D atoms and give the same distribution of $C_3X_5^+$ products after dissociation. Complete randomization of hydrogen in the $C_4H_4D_4^+$ ion would be verified, however, irrespective of the assumed structure, if the same distribution were obtained from the $CHD = CHD^+ - CHD = CHD$ and $CH_2 CD_2^+ - CH_2 CD_2$ reaction pairs, particularly if the relative probabilities for loss of CH₃ and CD₃ were the same for both analogs. The results of such experiments are given in table 4, and the distribution obtained by Bowers et al. [22], for $CH_2 = CD_2$ is included for comparison. Consideration of the data obtained for the two analogs indicates that the effect of increasing photon energy for any particular analog is minimal, and those subtle variations which do occur can probably be ascribed to a decrease in the probability for loss of CX_4 (methane) from $C_4H_4D_4^+$ at 11.7 eV (see product distribution from the $C_2H_4^+ - C_2H_4$ reaction pair, table 4). The important feature of the results is the agreement between the distributions obtained from CHD = CHD and $CH_2 = CD_2$, which is excellent considering the fact that the isotopic purities of the starting materials are slightly different (see Results). On this basis we conclude that randomization of hydrogen atoms is complete in the compound ion.

The extensive scrambling in $C_4H_4D_4^{+*}$ which does occur is not unreasonable in view of the relatively long dissociative lifetime $(5\times10^{-6}~{\rm s})$ for $C_4H_8^{+*}$ observed in the 11.7 eV photoionization of C_2H_4 [38]. Somewhat lower lifetimes have been estimated as a result of mass spectrometric studies [28], but under conditions where ionization of C₂H₄ was induced by high energy electron impact.

Some additional remarks are appropriate concerning the nature of $C_4H_8^{+*}$. It has been shown that i-C₄H₈⁺ is one of the isomeric structures formed in the photoionization [34, 38-39a] and electron impact ionization of C_2H_4 [34]. The fact [34] that the *i*- $C_4H_8^+$ structure increases relative to linear structures as the internal energy of $C_4H_8^{+\,*}$ increases indicates that methyl elimination may be occurring via this configuration. However, dissociation does not necessarily proceed through a specific intermediate since it has been shown [34] that highly unstable $1-C_4H_8$ and methylcyclopropane ions are formed as important intermediates following ionization of cyclobutane. In view of the chemical evidence to the contrary it is very doubtful that dissociation occurs quantitatively via a $2 \cdot C_4 H_8^+$ structure in ethylene as assumed recently [42] in a quasi-equilibrium treatment (QET) of this system by Butrill. In fact, the accumulated evidence indicates that $2 \cdot C_4 H_8^+$ structures play a very minor role compared with $1-C_4H_8^+$, $i-C_4H_8^+$, and $CH_3 - C_3H_5^+$. Consequently, the agreement between the experimental and calculated fragmentation pattern of C₄H₈^{+*} must be considered only as tentative since the QET treatment assumed an incorrect structure for the activated complex.

Finally, as indicated under Results, we observed some variation in the isotopic composition of the $C_3X_5^+$ products as the total pressure in the reaction chamber was increased. Under our conditions these changes cannot be ascribed to further reaction of ethyl ions produced by the initial reaction of ethylene ions with ethylene, as suggested by Tiernan and Futrell. The changes which are observed are apparently associated with exchange reactions involving $C_3X_5^+$ and CH_2CD_2 such as:

$$C_{3}H_{3}D_{2}^{+} + C_{2}H_{2}D_{2} \rightarrow C_{3}H_{4}D^{+} + C_{2}D_{3}H, \text{ etc.}$$
 (15)

Based on recent measurements, the $(C_3H_5 - C_2H_4)^+$ collision complex has a lifetime ≥ 100 microseconds, and this is certainly sufficient for hydrogen exchange to occur prior to dissociation.

5. Summary

The absolute rate coefficients for reaction of parent ions in ethylene and propylene have been found to decrease as the average internal energy content of the reactant ion is increased, and the distribution of products also shows considerable variation. In general, the variations observed in the product distribution are similar to those found elsewhere when the kinetic energy of the reactant ion is increased. We have also directly detected for the first time the formation of stable C₆H⁺₁₂ dimeric ions in photoionized propylene, and have determined that these species react further with propylene via H2 transfer. Finally, isotopic labeling experiments have confirmed that the C₄H⁺₈ compound ion produced in the reaction of ethylene ions with ethylene has a structure in which all hydrogen atoms are equivalent.

6. References

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