Internal Energy Effects on the Reaction of H_3^+ with Ethylene

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Abstract: The reaction rate constant and the product distribution for the reaction of H_3^+ with ethylene are reported as an explicit function of the average number of H_3^+-H_2 collisions occurring prior to reaction. The present results were obtained using a tandem mass spectrometer which mass analyzes the reactant ions and decelerates them to less than 0.1 eV translational energy. Presence of an endothermic reaction channel in the case of reaction of H_3^+ ions which have undergone no collisions with H_2 molecules shows that at least 14% of these ions are initially formed with a minimum of 1.1 eV of excitation energy. Complete deactivation of the excited H_3^+ ions appears to occur after 5 to 10 collisions with H_2. Isotopic studies show that H_3^+ reacts with ethylene by proton transfer initially giving a $C_2H_5^+$ ion which, if energetically feasible, undergoes random elimination of a hydrogen molecule. The $C_2H_5^+$ intermediate is shown to have a lifetime greater than 10^{-8} s and less than 10^{-6} s. Isotope effects in the unimolecular decomposition reaction are observed as a function of the internal excitation energy and are discussed in terms of similar effects observed for analogous hydrocarbon ions. Analysis of the observed product distribution shows that 31% of the hydrogen molecules produced in the first step of the reaction have translational energies in excess of 0.5 eV. This conversion of a portion of the reaction exothermicity into relative kinetic energy of the products is predicted by the "polarization stripping" model of ion-molecule reactions, and the present study supports the applicability of this model to ion-molecule reactions which occur with large cross sections under thermal energy conditions.

Several ion-molecule reactions of H_3^+ were originally studied using moderately high pressure, single source mass spectrometers.[1] Although such studies provided information on reaction pathways and, in some cases, reaction rate constants, the experimental conditions were such that one learned very little about the actual dynamics of the reactions. Since these experiments were carried out in a single ionization chamber, there was considerable uncertainty over which reactants led to which products. This is a particularly severe limitation in the case where multiple ion-neutral collisions occur. The ion-molecule product spectrum obtained in these experiments did show, however, that H_3^+ ions which are typically formed with considerable vibrational excitation energy are probably deactivated through collisions with H_2. Interpretation of such results is further complicated by the fact that raising the H_2 pressure may also change the product spectrum by changing the probability of collisional stabilization of highly excited product ions, which, in the absence of collisions, would undergo dissociation. Details of the collisional relaxation of H_3^+ are totally obscured in such experiments because of an inherent broad distribution in the number of H_3^+-H_2 collisions an ion undergoes before reaction with an additive molecule.

More recently ion-molecule reactions of H_3^+ have been studied by ion cyclotron resonance (ICR) mass spectrometry.[2] These results are more informative because the techniques of double resonance can often be used to relate reactants and products; however, this is still a single reaction vessel experiment and the possibility of sequential reactions and, to a certain extent, collisional stabilization of highly excited ions remains. Furthermore, since the probability of H_3^+ reacting with the additive substance is approximately constant throughout the reaction time, there is still a very broad distribution in the number of H_3^+-H_2 collisions an ion undergoes before reacting. Thus neither the single source mass spectrometer nor the conventional ion cyclotron resonance mass spectrometer is capable of measuring unambiguously the product spectrum resulting from reaction of H_3^+ as an explicit function of the number of H_3^+-H_2 collisions.

This paper reports results on the reactions of H_3^+ with ethylene obtained using a tandem mass spectrometer. H_3^+ ions are produced in a moderately high pressure source, mass analyzed, and injected into an ICR cell where reaction with ethylene follows. Because the collisional relaxation reactions of H_3^+ with H_2 and the reactions of H_3^+ with C_2H_4 occur in physically separated parts of the instrument, the product distribution characteristic of the reactions of H_3^+ with ethylene may be measured directly as a function of the average number of H_3^+-H_2 collisions occurring prior to reaction with C_2H_4.

It will be shown that a variety of different kinds of information may be obtained by detailed analysis of the results for the reaction of H_3^+ with C_2H_4. One question to be answered focuses on how the excess energy of an exothermic reaction is divided among the vibrational and translational degrees of freedom of the ion and neutral products. This information permits evaluation of the rate of deactivation of excited H_3^+ ions as they undergo collisions with H_2, and, in a broader sense, provides a basis for formulation of models which are useful in specifying parameters necessary for ion-molecule equilibrium studies. Results obtained using deuterium isotopes are used to elucidate the reaction mechanism and provide information on isotope effects in the unimolecular decomposition reactions of superexcited ions.

Experimental Section

The tandem mass spectrometer used in this work (illustrated in Figure 1) has been described in detail elsewhere[3] and will be discussed only briefly here. The first stage of the instrument is a 180°, 5.7 cm radius mass spectrometer equipped with a source or primary ionization chamber capable of efficient operation at pressures up to approximately 100 μm. The magnetically collimated electron beam (electron energy of 50 eV) produces a sheath of ions within the source approximately midway between the split repellers and the ion exit slit. By choosing specific repeller fields and source pressures, the average number of ion-neutral collisions in the source may be changed from 0 to a maximum of approximately 30. Ions extracted from the source are mass analyzed, decelerated to less than 0.1 eV translational energy, and subsequently injected into the cavity of an ion cyclotron resonance mass spectrometer.

The ICR cell used in this apparatus contains two sections of equal length and assumes the dual role of a second reaction chamber with a mass analyzer. Typical drift fields and trapping plate voltages used in this work were 0.5 V/cm and +0.5 V, respectively. Relative ion power absorptions are determined using a conventional oscillator-detector which has been calibrated at different frequencies using ion beams whose absolute intensities are measured using the "total ion current" collector. The relative abundance of different ions is obtained by multiplying the relative ion power absorption by the ion mass.

Results

Because the present experiments are performed using two reaction chambers which, to a good approximation, are completely isolated, the reactions may be divided into two groups.

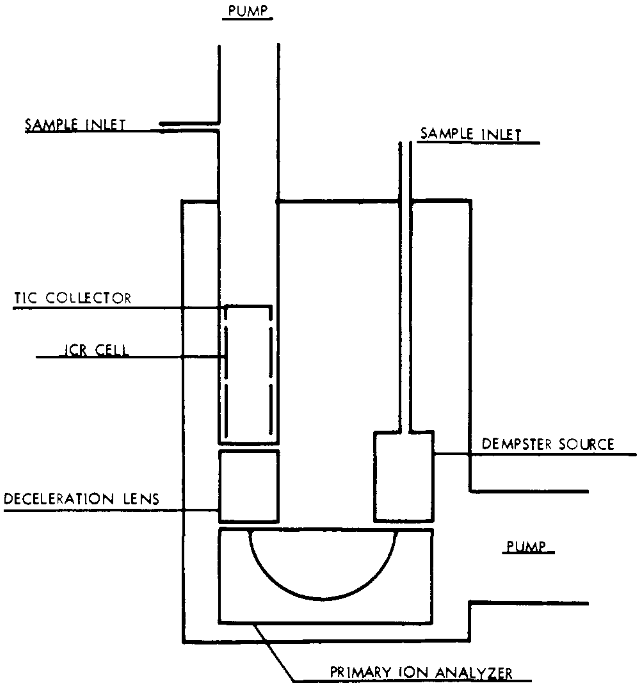

Figure 1. Block diagram of tandem mass spectrometer used in these studies.

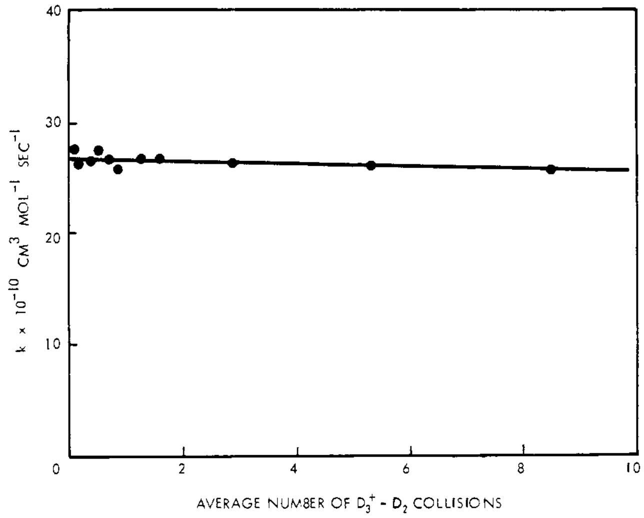

Figure 2. The total rate of reaction of D_3^+ with C_2H_4 as a function of the average number of D_3^+-D_2 collisions.

In the source of the first stage of the instrument, H_2^+ ions formed by electron impact may react as follows:

$$H_2^{+*} + H_2 \rightarrow H_3^{+**} + H \qquad \Delta H = -1.7\ \text{eV} \qquad (1)$$

$$H_3^{+**} + H_2 \rightarrow H_3^{+*} + H_2^* \qquad (2)$$

The H_2^+ ions are formed with a Franck-Condon distribution of vibrational states and will usually be converted into H_3^+ ions upon their first collision with a neutral hydrogen molecule.[4] Although the H_3^+ excitation energy is not known exactly, simple statistical calculations suggest that there should be a broad distribution with an average around 1.5 eV.[5] Since only a small fraction of the H_2^+ ions are produced in the ground vibrational state,[6] the exoergicity[7] given for (1) constitutes only an upper limit. If the source pressure is sufficiently high, energy relaxing collisions illustrated by (2) occur, giving H_3^+ ions that are at least partially deactivated.

H_3^+ ions extracted from the source are mass analyzed, decelerated, and injected into the second chamber (ICR cell) where the following reactions occur:

$$H_3^+ + C_2H_4 \rightarrow C_2H_4^+ + H_2 + H \qquad \Delta H = +1.1\ \text{eV} \qquad (3)$$

$$H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + H_2 \qquad \Delta H = -2.7\ \text{eV} \qquad (4)$$

$$H_3^+ + C_2H_4 \rightarrow C_2H_3^+ + 2H_2 \qquad \Delta H = -0.5\ \text{eV} \qquad (5)$$

The energetics given here assume that all reactants and products are in their ground state. In the case of (3), the heat of reaction is only a lower limit since, as will be discussed later, the products may always be formed with considerable translational energy.

The rate constant for reaction of D_3^+ with C_2H_4 is given in Figure 2 as a function of the average number of D_3^+-D_2 collisions which is varied from 0 to 10. This rate constant was measured by monitoring the decrease in the D_3^+ resonance signal as the C_2H_4 pressure is raised in the ICR cell. From application of pseudo-first-order kinetics we can write

$$\ln [D_3^+]^0/[D_3^+] = k\tau[C_2H_4] \qquad (I)$$

where $[D_3^+]^0$ and $[D_3^+]$ are the relative concentrations of D_3^+ in the ICR cell when the C_2H_4 pressure is zero and P, respectively, τ is the time ions spend in the ICR cell (the reaction time), and $[C_2H_4]$ is the C_2H_4 concentration in the cell for pressure P. The relative D_3^+ concentrations are obtained from the corresponding ICR signal, τ is measured by a pulsing technique,[8] and $[C_2H_4]$ is calculated from the C_2H_4 pressure which is measured using a calibrated ionization gauge. This same method has been used to measure the rate of reaction of CH_4^+ with CH_4 and gives results which compare well with previous measurements.[3]

Product distributions resulting from reaction of H_3^+ with C_2D_4 as well as from reaction of H_3^+ with C_2H_4 are given as a function of the average number of H_3^+-H_2 collisions occurring prior to reaction in Figures 3 and 4, respectively. The reaction chamber pressure and reaction time were chosen such that less than 20% of the H_3^+ ions actually underwent reaction with ethylene. Since the rate of this reaction is approximately collision limited, it follows that subsequent reaction of ion products may be neglected; that is, the reaction of H_3^+ with ethylene occurs under single-collision conditions. The product distributions given in Figures 3 and 4 may be interpreted as relative rate constants characteristic of the corresponding reaction channels.

The average number of H_3^+-H_2 collisions may be derived from the average number of ion-neutral collisions in the source, $\bar{n}$, which is given by $k\tau[H_2]$ where k is the ion-neutral collision rate constant, τ is the source residence time, and $[H_2]$ is the neutral density in the source. In the present work, the ion-neutral collision rate constant is replaced by the $H_2^+(H_2,H)H_3^+$ reaction rate constant. This simplification introduces only a small error since this reaction is known to occur on nearly every collision.[4] Due to the reduced mass effect, the H_2^+-H_2 collision rate constant is slightly larger than the H_3^+-H_2 collision rate constant and may be corrected for by multiplying $k_1\tau[H_2]$ by 0.9. The quantity $k_1\tau[H_2]$ is determined directly by measuring the H_2^+ and the H_3^+ ion current coming from the source and applying eq II.

$$\bar{n} = 0.9k_1\tau[H_2] = 0.9 \ln ([H_2^+] + [H_3^+])/[H_2^+] \qquad (II)$$

The H_2^+ and H_3^+ ion currents are measured by increasing the magnetic field until the beams strike a special collector located at a radius of curvature slightly less than that required for the ions to pass into the deceleration lens. This procedure eliminates possible mass and energy discrimination in the deceleration lens. Under high pressure conditions the average number of ion-neutral collisions is assumed proportional to the pressure in the main vacuum chamber; this pressure is measured using an ionization gauge.

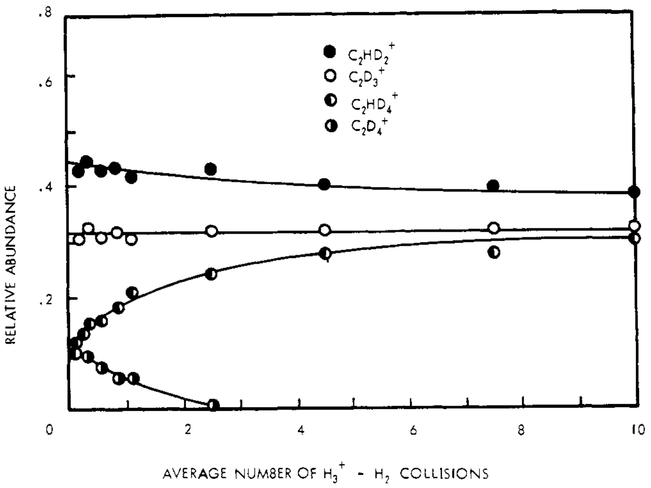

Figure 3. Distribution of products for the reaction of H_3^+ with C_2D_4 as a function of the average number of H_3^+-H_2 collisions in the source.

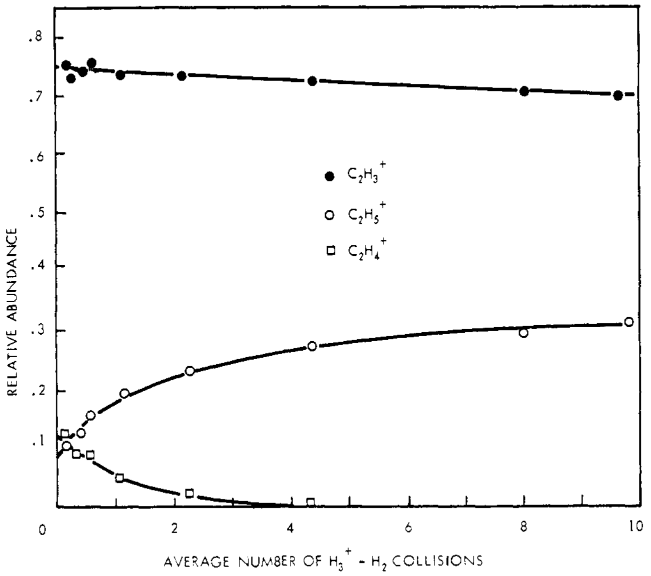

Figure 4. Distribution of products for the reaction of H_3^+ with C_2H_4 as a function of the average number of H_3^+-H_2 collisions in the source.

Except for the limiting case of no collisions, there will always be a substantial fraction of the ions which have experienced either more or fewer collisions than the average given by (II). We have considered this problem in detail in another publication[9] and have shown that the probability, P, of an ion undergoing exactly n collisions when the *average number* of ion-neutral collisions is $\bar{n}$ is given by

$$P(n,\bar{n}) = \frac{\bar{n}^n}{n!}e^{-\bar{n}} \tag{III}$$

which is the Poisson Distribution Law. Thus any interpretation of changes in the product distributions given in Figures 3 and 4 with variation of the number of ion-neutral collisions occurring in the source must take into account this distribution. While (III) shows that there is a relatively broad distribution in the number of ion-neutral collisions occurring prior to reaction in the present apparatus, experiments performed with single chamber instruments[1,2] have a much broader distribution than that given by (III) because these experiments also involve a distribution of reaction time.

The present results are given as a function of the average number of H_3^+-H_2 collisions which can be obtained from the average number of ion-neutral collisions. Assuming that reaction of H_2^+ with H_2 occurs on the first collision, and using (III), it can be shown[9] that the average number of H_3^+-H_2 collisions, $\bar{n}'$, is given by (IV)

$$\bar{n}' = 1 - P(0) \sum_{n=1}^{\infty} (n-1)P(n) \tag{IV}$$

where $P(n)$ is given by (II) and $P(0)$ is the probability of having no collisions. Thus each data point given in Figures 3 and 4 represents measurements of both the product distribution as well as the H_2^+-H_3^+ ion currents coming from the ion source. These latter quantities are used with (II) to give the average number of ion-neutral collisions, $\bar{n}$. The average number of H_3^+-H_2 collisions is then calculated using eq III and IV.

Results are given in Figure 5 for the $C_2H_3^+/C_2H_2D^+$ and $C_2D_3^+/C_2D_2H^+$ ratios for the reactions of D_3^+ with C_2H_4 and for H_3^+ with C_2D_4 as a function of the average number of D_3^+-D_2 or H_3^+-H_2 collisions occurring in the source. A small correction for contribution of the $C_2H_4^+$ ion to the *m/e* 28 ion in the case of reaction of D_3^+ with C_2H_4 has been made by using the relative abundance of the $C_2D_4^+$ observed for reaction of H_3^+ with C_2D_4.

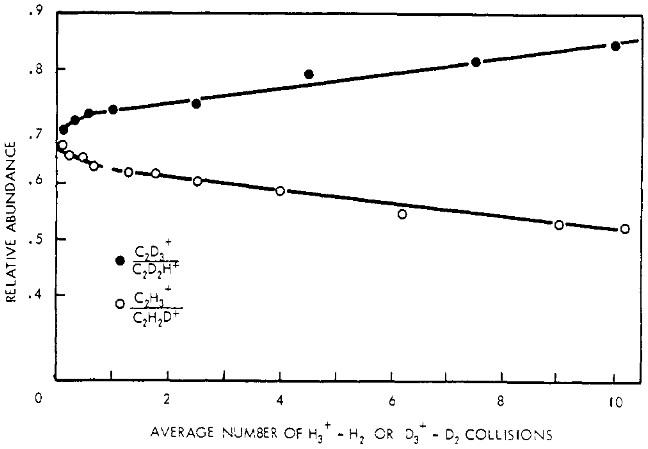

Figure 5. The $C_2H_3^+/C_2H_2D^+$ and $C_2D_3^+/C_2D_2H^+$ ratios resulting from the reaction of D_3^+ with C_2H_4 and H_3^+ with C_2D_4 as a function of the corresponding average number of D_3^+-D_2 or H_3^+-H_2 collisions in the source.

Table I. Summary of Rate Constants for the Rate of Reaction of D_3^+ (H_3^+) with Ethylene

Method	$k \times 10^9$ cm^3 mol^{-1} s^{-1}
Flowing afterglow[10] (H_3^+)	2.02
High pressure MS[11] (H_3)	0.99
Trapped ion ICR[12] (H_3^+)	3.6
Present (D_3^+)	2.8 ± 0.6
Langevin[13] (D_3^+)	2.4
(H_3^+)	2.9

Discussion

Rate of Reaction. Rate constants for the total rate of reaction of $H_3^+(D_3^+)$ with ethylene obtained previously[10,11,12] and in the present study are given in Table I. While the agreement is not particularly good, there is a general consensus that the reaction proceeds at a rate approaching the ion-neutral collision rate. If the reduced mass correction factor is taken into account, the present value is in very good agreement with the trapped ion ICR result. Because of inherent uncertainties in estimation of pressure and reaction time, the rather low value obtained using a high pressure mass spectrometry should be discounted in comparison with the other, more precise measurements.

There appears to be a serious discrepancy between the trapped ion ICR and the flowing afterglow measurements. Both instruments have previously been used with considerable success to measure absolute rates of ion-molecule reactions. While both methods are generally capable of precise measurement, the flowing afterglow apparatus has the advantage of having completely equilibrated reactants. Thus one might suspect that the discrepancy between these two measurements results from the presence of internally excited H_3^+ ions which react faster in the case of the trapped ion ICR measurements. However, the present results given in Figure 2 show that this rate remains constant as the average number of D_3^+-D_2 collisions occurring prior to reaction with ethylene is varied from 0 to 10. It will be shown that these collisions lower the average H_3^+ excitation energy by nearly 3 eV. From this we conclude that the discrepancy in the rate constants obtained using the trapped ion ICR method and the flowing afterglow technique is not due to presence of internally excited H_3^+ ions. The present results support the conclusion that the rate constant is very nearly that calculated from the Langevin collision limit.[13]

Reaction Mechanism. Product distributions for reaction of D_3^+ with C_2H_4 and H_3^+ with C_2D_4 were measured to gain information on the reaction mechanism. Results are given in Figure 3 as a function of the average number of H_3^+-H_2 (D_3^+-D_2) collisions occurring prior to reaction with C_2D_4. Since product ions containing more than one H, such as $C_2D_2H_3^+$, were not observed (that is, they accounted for less than 1% of all products) we conclude that reaction does not proceed through formation of a $C_2D_4H_3^+$ intermediate which then randomly eliminates a hydrogen molecule.

Information on the likelihood of random elimination of an X_2 molecule (where X may be either H or D) by a $C_2X_7^+$ ion may be obtained from work by Abramson and Futrell[14] who carried out a detailed study of (6)

$$CX_3^+ + CX_4 \rightarrow [C_2X_7^+] \rightarrow C_2X_5^+ + X_2 \qquad (6)$$
$$\Delta H = -1.0 \text{ eV}$$

using several isotopically labeled reactants. In addition, Huntress and Bowers[2] as well as Aquilanti, Galli, and Volpi[15] have studied the reaction

$$X_3^+ + C_2X_6 \rightarrow [C_2H_7^+] \rightarrow C_2X_5^+ + X_2 \qquad (7)$$
$$\Delta H = -1.1 \text{ eV}$$

While these studies do not provide a consistent view of the hydrogen molecule elimination process, they do clearly show that all combinations of X_2 occur when $C_2H_7^+$ is involved as an intermediate. The contrast between these previous studies and the present results permits us to conclude that H_3^+ does not react with C_2H_4 through formation of a $C_2H_7^+$ intermediate.

The results in Figure 3 show that $C_2D_3^+$ and $C_2D_2H^+$ are the only $C_2X_3^+$ products observed for the reaction of H_3^+ with C_2D_4. Similarly, $C_2H_3^+$ and $C_2H_2D^+$ are the only dissociation products observed for reaction of D_3^+ with C_2H_4. The $C_2D_3^+/C_2D_2H^+$ and $C_2H_3^+/C_2H_2D^+$ ratios for these two reactions are given in Figure 5 and provide further information on the reaction mechanism. It should be emphasized that changing the number of collisions prior to reaction changes only the X_3^+ excitation energy and that all conditions in the reaction chamber analyzer remain constant.

These results show that the two ratios have a value of approximately 0.69 in the case of reaction of highly excited X_3^+ ions. If a $C_2D_4H^+$($C_2H_4D^+$) intermediate were to undergo completely random elimination of HD and D_2 (HD and H_2), a $C_2D_3^+/C_2D_2H^+$ or ($C_2H_3^+/C_2H_2D^+$) ratio of 0.66 would be observed. Since this is relatively close to the observed value, we tentatively conclude that X_3^+ reacts with C_2X_4 to give $C_2X_5^+$ which then randomly eliminates an X_2 molecule.

This interpretation is valid only if isotopic randomization within the $C_2X_5^+$ ion is fast compared to the elimination reaction. Voracheck, Meisels, Geanangel, and Emmel[16] have shown that the maximum activation energy for hydrogen atom migration in the $C_2H_5^+$ ion is 0.08 eV. Their results support the ab initio calculations of Hariharan, Lathan, and Pople[17] which predict the bridged form of the ethyl ion to be only 0.04 eV more stable than the classical form. Since the activation energy for hydrogen atom migration is over an order of magnitude smaller than the activation energy for hydrogen elimination, randomization prior to elimination is highly probable.

If reaction were to occur rapidly without randomization of energy among the $C_2X_5^+$ vibrational degrees of freedom, the $C_2D_3^+$ or $C_2H_3^+$ products are expected to dominate over the $C_2D_2H^+$ and $C_2H_2D^+$ products, respectively. An extreme case of this picture is X^- transfer to give the $C_2D_3^+$ and $C_2H_3^+$ products exclusively. In such a case, the $C_2D_3^+/C_2D_2H^+$ and $C_2H_3^+/C_2H_2D^+$ ratios would both be larger than the 0.66 statistical value. In addition, both ratios would be expected to decrease with decreasing X_3^+ energy. Since one ratio increases while the other decreases as the X_3^+ energy is decreased we conclude that any model which consistently predicts a preferential loss of the X that was originally part of the X_3^+ can be dismissed.

The behavior of the $C_2D_3^+/C_2D_2H^+$ and $C_2H_3^+/C_2H_2D^+$ ratios in Figure 5 may, however, be rationalized in part by expected isotope effects. Table II is a representative summary of observed isotope effects on the elimination of X_2 by CX_4^+, $C_2X_4^+$, and $C_2X_5^+$. These results have been chosen to illustrate the present state of our understanding of isotope effects for such reactions of "similar" ions. Very good data exist for these systems and illustrate the range of isotope effects observed as the method of ion preparation (structure, energetics) and observation time are varied.

The isotope effects given in Table II represent the experimentally measured ratio of probabilities for elimination of H_2 and HD or D_2 divided by the ratio for completely statistical elimination by the parent ion. Thus isotope effects greater than 1.0 indicate a preference for eliminating H_2 over HD or for HD over D_2. A ratio less than 1.0 corresponds to the opposite preference and an isotope effect of 1.0 indicates statistical elimination. The results for elimination by $CH_2D_2^+$ were obtained using a double focusing spectrometer to positively identify the ions and clearly show a strong preference for elimination of the lighter particle.[18] Similar results were obtained for other substituted methanes and also for the hydrogen atom elimination reaction. A recent study[19] of the $CHDCHD^+$ ion shows the same trend. In addition, this study shows that lowering the electron energy in the immediate vicinity of the threshold enhances the isotope effect. A similar observation was recently made in the collision induced dissociation spectra of substituted methanes.[20]

In the case of metastable ions[21-23] rather dramatic isotope effects may be observed, as shown in Table II. In this study the tandem ICR mass spectrometer has been used in a novel way to study the metastable ion decompositions. Using a deuterium/ethylene mixture in the source, $C_2H_4D^+$ ions produced by (4) are extracted, mass analyzed, and injected into the ICR cell where subsequent unimolecular decomposition products may be observed. The time interval between ion formation and injection into the ICR cell is estimated to be about 3×10^{-6} s, the time that the ion remains in the ICR cell is approximately 3×10^{-3} s. Details of this study will be published elsewhere.[23]

Because energy distributions of reacting species are not precisely defined in the present experiments, isotope effects cannot be calculated reliably from current theories of isotope effects. Qualitatively the data can be rationalized in terms of different frequencies in the reaction coordinate for H and D bond cleavage.[18,19] Thus the increased probability of elimination of H over D is caused by a larger zero-point energy in the case of H and because of a higher vibrational frequency of the lighter particles. The larger zero-point energy effectively lowers the activation energy barrier. Since the rate of reaction is strongly dependent on the excitation energy when it is in the vicinity of the threshold, it follows that isotope effects will become much larger in the case of parent ions with very small excitation energies. Thus large isotope effects are observed in the case of reactions occurring at their thresholds as illustrated by studies of metastable ions.

Table II shows that for the case of reaction of highly excited X_3^+, the resulting $C_2X_5^+$ eliminates X_2 with essentially no isotope effect. As will be discussed later, X_3^+ is initially formed with an average excitation energy of nearly 2 eV. Since (5) is exothermic by 0.5 eV for ground state X_3^+ ions, it follows that the $C_2X_5^+$ ions probably have around 2 eV of energy in excess of the dissociation energy. Under these conditions, a minimal isotope effect is expected. Increasing the number of X_3^+-X_2 collisions decreases the excitation energy in the X_3^+ ion as well as in the $C_2X_5^+$ ion. Under high collision conditions the X_3^+ ion is completely deactivated and the $C_2X_5^+$ ion can have no more than 0.5 eV excitation energy. Under these conditions an isotope effect of 1.3 is observed. Thus the present results are qualitatively consistent with our simplistic understanding of isotope effects in unimolecular reactions.

The present results show only modest isotope effects while the results of Lohle and Ottinger[22] as well as the metastable studies using the tandem ICR[23] show that hydrogen elimination by the $C_2X_5^+$ ion is characterized by large isotope effects when the reaction occurs in the threshold energy range. The rather small isotope effect observed in the present study suggests that dissociation of the $C_2X_5^+$ ions primarily occurs at energies substantially above the threshold energy of the reaction. This is discussed further later.

H_3^+ Excitation Energy. Information on the amount of excitation energy with which H_3^+ is initially formed as well as the rate at which this ion is relaxed through collisions with H_2 may be deduced from product distributions observed for reaction of H_3^+ as the number of H_3^+/H_2 collisions in the ion source of the tandem ICR is varied. Limits on the initial H_3^+ excitation energy may be obtained from the observation of endothermic reaction channels such as (3), as shown in Figure 4. Since $C_2H_4^+$ accounts for 14% of the product distribution in the zero collision limit, we may conclude that at least 14% of the H_3^+ are formed with a minimum of 1.1 eV of excitation energy.

The value of 1.1 eV for the endothermicity of (3) is obtained by assuming that all products are formed with negligible internal and translational energy. This model would be appropriate if the "charge-transfer" reaction occurred through protonation followed by adiabatic, random elimination of an H or D atom. However, since $C_2H_4^+$ and $C_2D_4^+$ are by far the major isotopic products observed for reaction of D_3^+ or H_3^+ with C_2H_4 and C_2D_4, respectively, we conclude that charge transfer does not proceed through this mechanism. Rather, the isotopic results suggest that charge transfer occurs as the ion and neutral are being drawn together by the attractive ion-neutral interaction potential but before an intimate collision actually occurs. This same mechanism has been proposed and discussed in more detail elsewhere for the reaction of H_3^+ with ammonia[24] and methanol.[9]

If, as discussed above, the neutral product of charge transfer is H_3 rather than H_2 and HX, the endothermicity of the charge-transfer channel is likely substantially greater than 1.1 eV. Porter, Stephens, and Karplus[25] and Conroy[26] have shown that the potential energy surface for H_3 is repulsive and that this species should immediately dissociate into H_2 and H. Depending upon the geometry (triangular or linear) and internuclear separation of the H_3, the H_2 and H products are expected to have between 0.5 and 1.0 eV of translation energy. Adding this to the intrinsic endothermicity of the reaction implies that production of $C_2H_2^+$ may be as much as 2 eV endothermic.

The total amount of excitation energy which could appear in principle as excitation energy in H_3^+ is given by

$$E_{(\text{excess})} = \epsilon^{P}_{\text{int}} + \epsilon^{P}_{\text{trans}} = -\Delta H + \epsilon^{R}_{\text{int}} + \epsilon^{R}_{\text{trans}} \quad \text{(V)}$$

where $\epsilon^{P}_{\text{int}}$ and $\epsilon^{P}_{\text{trans}}$ are the internal excitation energy and center-of-mass translational energy of the products; ΔH is the heat of reaction calculated from the standard heats of formation of ground state reactants and products; and $\epsilon^{R}_{\text{int}}$ and $\epsilon^{R}_{\text{trans}}$ are the internal excitation energy and center-of-mass translational energy of the reactants.

The participation of $E_{(\text{excess})}$ among the internal and translational degrees of freedom has been estimated[5] by assuming that the energy is deposited randomly among all possible vibrational and translational states of the products. Since details of the calculation are published, only the results will be given here for comparison with the present experimental results. The probabilities of H_3^+ being formed in various vibrational levels and having the corresponding vibrational excitation energies are given in Table III. If this simplistic model is even approximately correct, H_3^+ ions are expected to have excitation energies from 0 eV up to over 3 eV. The calculated average H_3^+ excitation energy is approximately 1.5 eV and compares well with an experimental measurement of 2.0 eV made by Durup and Durup.[27]

Table II. Representative Summary of Isotope Effects on the Elimination of H_2, HD, and D_2 by CX_4^+, $C_2X_4^+$, and $C_2X_5^+$

Parent ion	Neutral products	Isotope effect	Method
$CH_2D_2^+$	H_2/HD	5.1	Electron impact (70 eV)[18]
$CH_2D_2^+$	HD/D_2	2.3	Electron impact (70 eV)
CHDCHD$^+$	H_2/HD	1.8	Electron impact (20 eV)[19]
CHDCHD$^+$	HD/D_2	1.4	Electron impact (20 eV)
CHDCHD$^+$	HD/D_2	1.8	Electron impact (13.5 eV)
CHDCHD$^+$	H_2/HD	33	Metastable ions, DFMS[21]
CHDCHD$^+$	HD/D_2	23	Metastable ions, DFMS
$C_2H_2D_3^+$	H_2/HD	5.4	Metastable ions, DFMS[22]
$C_2H_2D_3^+$	HD/D_2	31	Metastable ions, DFMS
$C_2H_4D^+$	H_2/HD	6.3	Metastable ions, tandem ICR[23]
$C_2H_4D^+$	H_2/HD	1.1	Present (0 D_3^+-D_2 collisions)
$C_2H_4D^+$	H_2/HD	1.3	Present (10 D_3^+-D_2 collisions)
$C_2D_4H^+$	HD/D_2	1.0	Present (0 H_3^+-H_2 collisions)
$C_2D_4H^+$	HD/D_2	1.3	Present (10 H_3^+-H_2 collisions)

Table III. Calculated Distribution of Vibrational Excitation Energy in H_3^+

H_3^+ vibrational quantum number	Probability	Vibrational excitation[a] energy, eV
0	0.031	0
1	0.085	0.4
2	0.147	0.7
3	0.204	1.1
4	0.203	1.5
5	0.147	1.9
6	0.082	2.2
7	0.039	2.6
8	0.013	3.0
9	0.001	3.4

[a] Each H_3^+ quantum of vibrational energy is worth 0.37 eV.

The results in Table III show that, if the excess energy in the reaction of H_2^+ with H_2 is distributed randomly among the vibrational and translational states of the products, 73% of the H_3^+ are expected to have 1.1 eV or more excitation energy. If, on the other hand, the charge-transfer reaction channel requires 2.0 eV excitation energy, Table III suggests that only 18% of the initially formed H_3^+ ions could undergo this reaction. Until the kinematics of this reaction are better understood, a more detailed analysis of the present data is not possible. However, the experimental results appear consistent with the notion that H_3^+ ions are formed with a broad distribution of excitation energy. This conclusion is supported by similar results obtained for reaction of D_3^+ with methane,[5] ammonia,[24] and methanol.[9]

As the number of X_3^+-X_2 collisions is increased from zero, the endothermic charge-transfer reaction channel closes and the relative abundancies of the other products, $C_2X_3^+$ and $C_2X_5^+$, remain constant, as shown in Figures 3 and 4. Further, the product distributions remain constant as the number of X_3^+-X_2 collisions is increased from 10 to over 20. As will be discussed later, the relative abundance of $C_2X_3^+$ is expected to depend only on the amount of excitation energy in the initially formed $C_2X_5^+$ ion. Consequently we shall assume that, when the $C_2X_5^+$ excitation energy remains constant, the X_3^+ excitation energy is also constant. Thus the present results, as well as results obtained for reaction of H_3^+ with methane,[5] ammonia,[24] and methanol,[9] indicate that H_3^+ ions are probably completely deactivated after 5 to 10 collisions. This conclusion, coupled with a recent measurement of the D_3^+-H_2 rate of reaction,[28] shows that 2 to 3 reactive collisions are necessary to deactivate X_3^+ completely.

$C_2H_5^+$ Lifetime. The duration of time that a $C_2H_5^+$ ion, which is made through reaction of H_3^+ with ethylene, exists before undergoing dissociation to $C_2H_3^+$ and H_2 is fundamental to our understanding of the partitioning of excess energy among the various degrees of freedom of the $C_2H_5^+$ and H_2. The relative abundancies of $C_2H_5^+$ and $C_2H_3^+$ observed in the flowing afterglow instrument,[10] in a high pressure mass spectrometer,[11] in a conventional ICR apparatus[12] and in the present instrument are given in Table IV and provide definite limits on the $C_2H_5^+$ lifetime. All values have been chosen such that they are probably representative of reaction of very low energy H_3^+ ions.

The reaction of low energy H_3^+ ions with ethylene occurs according to the following

$$H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + H_2^* \tag{8}$$

$$\rightarrow C_2H_5^{+*} + H_2 + 2.5\,\text{eV} \tag{9}$$

$$\xrightarrow{M} C_2H_5^+ + M^* \tag{10}$$

$$\rightarrow C_2H_3^+ + H_2 \tag{11}$$

which can be used to rationalize the different product distributions given in Table IV. In the flowing afterglow apparatus, at a pressure of 0.5 Torr, the $C_2H_5^+$ accounts for 0.94 of the products. At the same pressure (same ion-neutral collision frequency) the fraction of products represented by $C_2H_5^+$ in the high pressure mass spectrometer is 0.7. Moreover, the qualitative effect of increasing the pressure increases the probability of observing the $C_2H_5^+$ product. Observation of much more $C_2H_5^+$ in the flowing afterglow apparatus results from the much longer reaction times (time between ion creation and observation of products) associated with this experimental method. This comparison suggests that reaction 12 also contributes to the product distribution.

$$C_2H_3^+ + H_2 \rightleftarrows C_2H_5^{+*} \tag{12}$$

$$\xrightarrow{M} C_2H_5^+ + M^* + 2.2\,\text{eV} \tag{13}$$

Since hydrogen was the bath gas in both experiments and since the total number of collisions was not varied at fixed pressures, contributions from (12) and (9) followed by (10) cannot be evaluated explicitly. In the high pressure mass spectrometry studies, source residence times were not measured and there is only the qualitative deduction that some of the ions must have lifetimes in the range of collision frequencies sampled by these experiments (4×10^{-7}–9×10^{-6} s).

It is interesting to note that (9) or (12) have very nearly the same excitation energy (2.5 or 2.2 eV, respectively), and thus should have approximately the same lifetimes. Consequently, independent of whether (9) or (12) dominates the product distribution, these experiments involve collisional stabilization of $C_2H_5^+$ ions, some of which must have lifetimes that are comparable to the ion-neutral collision time. Assuming that Langevin collision frequencies apply, competition between (9) and (10) and between (12) and (13) sets the limit that some $C_2H_5^+$ ions have lifetimes of this magnitude.

As discussed above, the tandem ICR instrument has been used to study the metastable decomposition of $C_2H_4D^+$ ions produced through the reaction of D_3^+, with ethylene; this experiment observes directly the unimolecular decomposition in the time interval from 3×10^{-6} s after formation to 3×10^{-3} s. Since the daughter ion ($C_2H_3^+$, $C_2H_2D^+$) relative abundance was 3 to 4% of the parent ion ($C_2H_4D^+$) relative abundance, it follows that, for those $C_2X_5^+$ ions which live as long as 3×10^{-6} s, the majority (96 to 97%) actually have lifetimes greater than 10^{-3} s. This result is consistent with the work of Kim, Theard, and Huntress[12] who used a pressure of the order of 10^{-5} Torr, intermediate between the high pressure flowing-afterglow results discussed above and the present low pressure results. Since they observed slightly more $C_2H_5^+$ than is observed in the present study, and since the ion-neutral collision time in their experiments is of the order of 10^{-4} s, it follows that some $C_2H_5^{+*}$ lifetimes fall in the range of 10^{-4} s. Increasing further the ion-neutral collision time to 10^{-2} using the present instrument causes only a small decrease in the relative abundance of the $C_2H_5^+$ ion.

From these several experiments, we may conclude that $C_2H_5^+$ ions produced by the reaction of collisionally relaxed H_3^+ with C_2H_4 exhibit a range of lifetimes from $<10^{-7}$ to $>10^{-3}$ s. This is readily rationalized in terms of a distribution of energy deposited in $C_2H_5^{+*}$ and a strong energy dependence of the ethyl ion decomposition reaction 11. The present experimental results show that approximately 30% have lifetimes greater than 10^{-3} s and 3-4% decay in the time interval from 3 μs to 3 ms and require that most of the $C_2H_5^{+*}$ initially formed (>60%) have lifetimes shorter than microseconds.

This conclusion is consistent with statistical theories of unimolecular dissociation such as the quasi equilibrium theory of mass spectra. In fact, for $C_2H_5^+$, one calculation[29] suggests that the rate of dissociation will change by six orders of magnitude as the internal energy is increased by 0.1 eV. Since both the internal energy and the translational energy of the reactants (H_3^+ and C_2H_4) are well defined, the manner in which the heat of reaction is partitioned among the degrees of freedom of the products depends on the kinematics of the reaction.

Energy Partitioning. In the present experiment, the reaction time is about 10^{-3} s and the average time between collisions is of the order of 10^{-2} s. If we assume that those $C_2H_5^+$ ions which live longer than 10^{-3} s do not have enough energy to dissociate, we may obtain information about the partitioning of the exothermicity in the reaction of H_3^+ with ethylene. Figure 4 shows that reaction of the lowest energy H_3^+ ions gives 0.31 $C_2H_5^+$. Since formation of $C_2H_3^+$ is 0.5 eV exothermic, we conclude that 0.31 of the collisions result in the hydrogen molecule carrying away at least 0.5 eV of energy either as internal or translational energy.

The energy limit of 0.5 eV assumes that the activation energy barrier is given by the standard heats of formation of the reactants and products. Since the reverse of such reactions may have energy barriers of several tenths of an electron volt, the energy of the hydrogen molecule could be much less than 0.5 eV. Elwood and Cooks[30] have measured the kinetic energy release for this reaction and found that the barrier to the reverse reaction is 0.019 ± 0.002 eV. Consequently we conclude that 0.31 of the hydrogen molecules produced in the reaction of H_3^+ with ethylene do carry away at least 0.5 eV of excitation energy.

While the idea that reaction exothermicity is divided statistically among the products has often been invoked, it cannot explain the present results. The ion, $C_2H_5^+$, has a large number of degrees of freedom and, furthermore, the quanta within these degrees of freedom are very small when compared to the vibrational quantum for the hydrogen molecule and the density of ion states is correspondingly much higher. If the reaction exothermicity were randomly divided among the possible states of the products, essentially all would appear in the $C_2H_5^+$ ion.

It has been shown that the hydrogen molecule resulting from the initial protonation reaction typically contains large amounts of energy. To show whether this energy is relative translational energy of the products or is vibrational excitation energy in H_2, the reaction of KrH^+ with ethylene was studied. This is a unique substitution since Kr and H_2 have identical proton affinities; thus the reaction exothermicities remain unchanged. While these results will be discussed elsewhere,[31] it is noted that reaction of stabilized KrH^+ gives essentially the same product distribution as is observed for reaction of stabilized H_3^+ ions. It follows that 30% of the krypton atoms must also carry away a minimum of 0.5 eV. If both KrH^+ and H_3^+ react with ethylene through the same mechanism, we may surmise that the hydrogen molecule carries away the excess energy as translation and not as vibration.

Herman, Kerstetter, Rose, and Wolfgang[32] have studied the conversion of internal energy into translational energy in ion–neutral beam studies and explained their results at low relative energy by invoking a "modified stripping" model. This model, later generalized and now known as the "polarization reflection"[33] or "impulsive reaction"[34] model, considers the effects of the long range polarization forces in both the approach and retreat trajectories on the kinetic energy of the products. It is appropriate to consider this model in conjunction with the present study performed at very low kinetic energy such that long-range attractive forces dominate. Moreover, in the case of H_3^+, isotopic studies show that the reaction intermediate is best characterized as a $C_2H_5^+ \cdot H_2$ species and not a $C_2H_7^+$ ion, consistent with proton transfer occurring via an impulsive mechanism.

According to this model, reaction commences as the ion and the neutral are drawn together by the long-range ion-induced dipole force. While less than 0.1 eV initially, the relative kinetic energy at the point of closest approach is of the order of 1 eV. At this point, the $H^+–H_2$ bond breaks, a $H^+–C_2H_4$ bond is formed simultaneously, and the neutral H_2 is elastically scattered off the repulsive barrier of the $C_2H_5^+$. As the H_2 leaves the collision center, its kinetic energy decreases due to the polarization forces. Since the basic assumptions of this model have been adequately described,[33,34] only the results will be given here.

Using the same notation as Hierl, Herman, and Wolfgang, the final energy of the products of the center-of-mass system, T_4, is given by

$$T_4 = [(X)(Z)P/(X + Y)(Y + Z)] - P' \qquad \text{(VI)}$$

where Y is the mass of the transferred particle, X and Z are the masses of the other two particles, P is the potential energy which is converted into kinetic energy as the reactants are brought from infinite separation to the distance of closest approach, and P' is the translational energy of the products which is converted into potential energy as the products separate from the point of closest approach to infinity. The quantities P and P' are assumed to be given by

$$\begin{aligned} P &= e^2\alpha(C_2H_4)/2r^4 \\ P' &= e^2\alpha(H_2)/2r^4 \end{aligned} \qquad \text{(VII)}$$

where α is the polarizability of ethylene and hydrogen, respectively, e is unit charge, and r is the distance of closest approach. If an arbitrary but reasonable value of r of 2 au (2.1 Å) is chosen, (VI) predicts a relative kinetic energy of the products of 1.2 eV which is in accord with the present experimental results.

Table IV. Product Distributions for the Reaction of H_3^+ with Ethylene as Observed Using High Pressure Mass Spectrometry,[11] Flowing Afterglow,[10] ICR,[12] and the Present Tandem Instrument

Method	Pressure, Torr	Product distribution	
		$C_2H_5^+$	$C_2H_3^+$
Flowing afterglow[10]	0.1–0.3	0.94	0.06
High pressure ms[11]	0.05	0.51	0.49
	0.10	0.56	0.44
	0.20	0.67	0.33
	0.30	0.68	0.32
ICR[12]	3×10^{-4}	0.40	0.60
Present results ICR	10^{-6}	0.31	0.69
High pressure MS	0.5	0.7	0.3

A more severe test of the applicability of this model to the present results lies in comparison of the H_3^+ and KrH^+ results since the relative kinetic energies of the products, according to the polarization reflection model, are functions of the mass and polarizabilities of hydrogen and krypton. Without actually specifying r, the final kinetic energies of the products, $T_4(KrH^+)$ and $T_4(H_3^+)$, are $T_4(KrH^+) = 11.0/r^4$ eV Å^4 and $T_4(H_3^+) = 14.0/r^4$ eV Å^4. Thus, if the distance of closest approach is the same for both reactions, the model predicts that the products of both reactions will have approximately the same kinetic energy. This prediction is required and is in agreement with the present experimental results which show that $C_2H_5^+$ is produced with the same internal energy in both reactions. This correlation constitutes a rather severe test of the applicability of the model because H_2 and Kr have very different polarizabilities ($\alpha(H_2) = 5.4$ au, $\alpha(Kr) = 16.7$ au) and masses.

Since KrH^+ has an internuclear separation which is about twice as large as the internuclear separation in H_3^+, the present results suggest that the effective distance of closest approach depends primarily on the $C_2H_5^+$ and not on the incoming ion geometry. If one breaks r up into two parts, one part representing the distance of closest approach between the proton and the ethylene molecule and another part representing the distance of closest approach between the proton and the outgoing neutral product (Kr or H_2), the difference in the bond lengths in KrH^+ and H_3^+ effectively decreases the H_2 kinetic energy relative to that of the Kr atom. This prediction, while certainly speculative, is consistent with the present results. Note, however, that Chang and Light[34] found the best fit by using the same r for both reactants and products.

Conclusions

Both the rate of reaction and the product ion distribution were measured as an explicit function of the average number of H_3^+-H_2 collisions occurring prior to reaction with ethylene. The present results indicate that the reaction is very fast; within experimental error it proceeds at the ion-neutral collision rate as calculated using the Langevin ion-induced dipole theory. The present results also show that the rate of reaction is independent of the H_3^+ vibrational excitation energy.

The observed product distribution shows that at least 14% of the H_3^+ ions are formed initially with a minimum of 1.1 eV of excitation energy and that collisions with hydrogen molecules rapidly deactivate the excited ions. Coupled with other experimental and theoretical studies from this laboratory,[5,9,24,28] we conclude that H_3^+ ions are initially formed with a rather broad distribution of excitation energies and with an average energy of 1.5 to 2.0 eV. While 5 to 10 collisions with H_2 are required to completely deactivate the H_3^+ ion, only 2 or 3 of these are reactive collisions.

Results obtained using isotopically substituted reactants show that H_3^+ reacts under the present low energy and low pressure conditions by transferring a proton to the ethylene which, if energetically possible, will randomly eliminate a hydrogen molecule. This reaction scheme is illustrated by (8), (9), and (10). The present results, coupled with previous studies[2,14,15] of the $C_2H_7^+$ ion, strongly suggest that the intermediate in the first step of the reaction is best described as $C_2H_5^+ \cdot H_2$ and not as a $C_2H_7^+$ ion.

A critical analysis of past and present results on the reaction of H_3^+ with ethylene shows that those $C_2H_5^+$ ions which have enough energy to decompose to $C_2H_3^+$ and H_2 do so with lifetimes in the time interval from 10^{-8} to 10^{-6} s. Isotope effects for elimination of H_2, HD, and D_2 by the $C_2X_5^+$ ions are much less than the isotope effects observed for the same reaction in the special case where the $C_2X_5^+$ ions live at least 10^{-6} s. This result further supports our contention that the majority of the $C_2H_3^+$ are produced from $C_2H_5^+$ ions which have lifetimes less than 10^{-6} s.

One especially interesting result of the present study is the formation of stable ethyl ions in a two-body process which do not require stabilization by a third body. This situation is possible only if the hydrogen molecule carries away a substantial portion of the exothermicity of the reaction. Thus the many previous studies which have assumed that all of the reaction exothermicity is deposited in the particle with the higher density of states (in this case, $C_2H_5^+$) should be reconsidered. Parallel studies performed in this laboratory on reactions of H_3^+ with methanol[9] as well as of KrH^+ with ethylene[30] support the hypothesis that at least 31% of the H_2 neutrals produced in the reaction of vibrationally relaxed H_3^+ with ethylene are produced with at least 0.5 eV of translational energy.

The "polarization stripping" model as described by Hierl, Herman, and Wolfgang[33] has been applied to the reaction of H_3^+ and KrH^+ with ethylene to predict the relative translational energy of the products of the reactions. This model predicts that the products will have approximately the same translation energy in both reactions. This result correlates very well with the present results which show that the $C_2H_5^+$ ions formed with the same excitation energy and thus the kinetic energy of the products is the same in both reactions. Since Kr and H_2 have very different polarizabilities and masses, and since the KrH^+ and the H_3^+ are geometrically very different, we feel that this correlation between theory and experiment strongly supports the applicability of the "polarization stripping" model to these reactions.

Ion-neutral crossed beam studies, presently in progress in our laboratory, are measuring angular and energy distributions of the products of the reactions as a function of the translational energy of the reactants. These results, coupled with the present thermal energy results, will provide further insight to the dynamics of these reactions.

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