Dissociative Proton Transfer Reactions of H_3^+, N_2H^+, and H_3O^+ with Acyclic, Cyclic, and Aromatic Hydrocarbons and Nitrogen Compounds, and Astrochemical Implications[†]

Daniel B. Milligan, Paul F. Wilson, Colin G. Freeman, Michael Meot-Ner (Mautner),* and Murray J. McEwan*

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8001, New Zealand

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A flowing afterglow-selected ion flow drift tube has been used to measure the rate coefficients and product ion distributions for reactions of H_3O^+, N_2H^+, and H_3^+ with a series of 16 alkanes, alkenes, alkynes, and aromatic hydrocarbons as well as acrylonitrile, pyrrole, and pyridine. Exothermic proton transfer generally occurs close to the collision rate. The reactions of H_3O^+ are mostly nondissociative and those of H_3^+ are mostly dissociative, but many reactions, especially those of N_2H^+, have both dissociative and nondissociative channels. The dissociative channels result mostly in H_2 and/or CH_4 loss in the small hydrocarbons and in toluene, loss of C_2H_2 from acrylonitrile, and loss of HCN from pyrrole. Only nondissociative proton transfer is observed with benzene, pyridine, and larger aromatics. Drift tube studies of N_2H^+ reactions with propene and propyne showed that increased energy in the reactant ion enhances fragmentation. Some D_3^+ reactions were also investigated and the results suggest that reactions of H_3^+ with unsaturated hydrocarbons B proceed through proton transfer that forms excited $(BH^+)^*$ intermediates. Pressure effects suggest that a fraction of the $(BH^+)^*$ intermediates decomposes too rapidly to allow collisional stabilization in the flow tube ($t < 3 \times 10^{-8}$ s). The other low-energy $(BH^+)^*$ intermediates are formed by the removal of up to 40% of the reaction exothermicity as translational energy, and these intermediates result in stable BH^+ products. The results suggest that, in hydrogen-dominated planetary and interstellar environments, the reactions of H_3^+ can convert C_2−C_6 hydrocarbons to smaller and less saturated molecules, but polycyclic aromatics are stable against decomposition by this mechanism. The dissociative reactions of H_3^+ can therefore favor the accumulation of small unsaturated hydrocarbons and aromatics in astrochemical environments.

Introduction

The unique physical conditions in the interstellar medium (ISM) of very low temperatures and number densities result in ion−molecule reactions as a main route for the formation of complex molecules.[1] Modeling of the ISM has motivated many studies of ion−molecule reactions, some by the selected ion flow (SIFT) method.

Any build-up of large molecules in this medium must be balanced against their dissociation to more simple species. This is the reason that complex molecules in the ISM are observed mainly in dark interstellar clouds, as the higher dust particle concentrations in these clouds shield the molecules from dissociation by photons and cosmic rays. These energy sources can cause dissociation of the molecules directly, or the ions can absorb some energy and will subsequently dissociate complex molecules via highly exothermic reactions.

One of the prime candidates for this dissociative role is the H_3^+ ion, which is formed readily when a hydrogen atmosphere is ionized. The H_3^+ ion has been observed in interstellar space, in both diffuse and dense molecular clouds,[2] as well as in the ionospheres of Jupiter, Saturn, and Uranus.[3] Hydrogen is abundant in these regions and as a result H_3^+ will be an important protonating agent. Hydrogen has an extremely low proton affinity (PA)[4] and therefore proton transfer from protonated hydrogen, i.e., H_3^+, to most other species is a highly exothermic and often dissociative process. In addition, such exothermic proton transfer reactions are usually fast, proceeding at collision efficiencies near unity.

Some of the reactions studied in this work have been investigated previously. Early studies of H_3^+ reactivity were done by Wexler,[5] by Munson et al.,[6] and by Aquilanti and Volpi,[7] where the last authors studied the reactions in a mass spectrometer with a radioactive ion source. Their pioneering work was done before the application of flow tubes to ion−molecule studies, and many of the rate coefficients and product assignments they recorded are questionable. The first flow tube investigation of H_3^+ reactions was by Burt et al.[8] in 1970, using a flowing afterglow technique. They reported that H_3^+ reacted with a number of simple molecules, mainly by proton transfer. The reactions of H_3^+ with oxygen-containing organics were later examined in some detail by Adams and co-workers.[9] They observed quite a number of product channels as a result of dissociative proton-transfer reactions. Spanel et al.[10] have examined the proton-transfer reactions of several protonated species with benzene, cyclopropane, and cyclohexane. Smith et al.[11] and Spanel et al.[12] have also studied the proton-transfer reactions of H_3^+ and H_3O^+ with a number of reagents.

Many dissociative charge and proton-transfer reactions produce both dissociation products and the undissociated molecular ions.[11−13] A basic question concerning these reactions is the cause of this distribution; in particular, why undecomposed products are formed when highly exothermic dissociation channels are available. For a fuller understanding of these dissociative reactions we need to consider the mechanism of

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* Corresponding authors: m.mautner@chem.canterbury.ac.nz and m.mcewan@chem.canterbury.ac.nz.

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the reactions. Dissociative proton transfer (DPT) may proceed first through sufficiently excited protonated intermediates $(BH^+)^*$, which subsequently decompose to a fragment ion F^+ and neutral or neutrals N. This reaction may occur in competition with the energy removal processes of collisional or radiative stabilization:

$$AH^+ + B \rightarrow (BH^+)^* + A \tag{1}$$

$$(BH^+)^* \xrightarrow{M, -h\nu} BH^+ \tag{2a}$$

$$\rightarrow F^+ + N \tag{2b}$$

The dissociative reaction is therefore composed of a proton-transfer reaction, for which the kinetics are well understood, and unimolecular dissociation, where the theory is also well established. However, the energy distribution in the population of the $(BH^+)^*$ intermediates is not as well characterized. In a fraction of the reactions, some of the proton-transfer exothermicity may be removed in inactive modes such as translation so that the $(BH^+)^*$ ions do not have enough energy to decompose, and this fraction always yields the stable BH^+ product. The other fraction of the $(BH^+)^*$ ions will have enough energy to decompose, but part of this population may be stabilized collisionally, and the yield of BH^+ vs F^+ products from this fraction should be pressure-dependent. The energy effects can be investigated by varying the internal energy of $(BH^+)^*$ by proton-transfer reactions of varying exothermicity with H_3O^+, N_2H^+, and H_3^+ reagent ions or by exciting the reagent ions by collisions in a drift tube. In the present work, we shall use both methods to examine energy effects on the product distributions.

Experimental Section

The results were obtained by use of the University of Canterbury flowing afterglow-selected ion flow-drift tube (FA-SIFDT). The main components are a flowing afterglow tube, where the reagent ions are generated by microwave discharge; a quadrupole mass filter and venturi injector, where ions from the FA are mass-selected and then injected into the reaction zone in the flow tube; and the flow drift tube, where the ions react with neutral molecules in a flowing He or H_2 carrier gas. The instrument has been described elsewhere.[14] All reactions are performed at room temperature (300 ± 5 K) and the ions are thermalized at this temperature, except when electric fields are applied in the drift tube. The pressure in the flow tube was typically 0.480 Torr with a helium carrier gas (corresponding flow rate = 254 atm $cm^3\ s^{-1}$ and flow velocity of 13 603 cm s^{-1}) and 0.340 Torr when hydrogen was used as the carrier gas (corresponding flow rate = 166 atm $cm^3\ s^{-1}$ and flow velocity of 12 359 cm s^{-1}).

A major consideration in the present experiments is the internal excitation of the reactant ions. The H_3^+ ions have large vibrational quanta, and vibrational excitation can contribute significant energy to the reactions. In addition, excited H_3^+ ions can also react with the He carrier gas to generate HeH^+ ions that can contribute additional dissociative proton-transfer reactions. The PA of helium is lower than that of hydrogen and thus the reactions of HeH^+ are expected to be more dissociative than those of H_3^+. The presence of more energetic ion species can significantly interfere with the determination of the products from H_3^+ reactions. To check these effects, the H_3^+ ions in this study were generated by two different methods that used either helium or hydrogen carrier gas in the SIFT reaction tube. The first method used a helium/hydrogen plasma in the flowing afterglow (FA) source to generate H_3^+ ions, which were then injected into a helium carrier in the SIFT reaction tube. The second method used helium with trace amounts of added krypton mixed in with the helium in the FA tube. The helium/krypton mixture was passed through the microwave discharge to generate Kr^+ ions, which were injected into a hydrogen carrier gas in the SIFT tube. The Kr^+ then reacts with the hydrogen carrier gas to generate H_3^+ ions.[15] Hereafter the methods will be denoted by the type of carrier gas in the SIFT reaction tube: viz., as the helium or hydrogen method, respectively.

By the helium method, a helium/hydrogen plasma is first generated in the FA source by a microwave discharge in the helium gas. This plasma was created by passing helium through a microwave discharge that generated a fraction of helium metastable atoms and ions. These metastable atoms and ions reacted subsequently with hydrogen added further downstream in the ion source flow tube. Many of the H_3^+ ions formed in this plasma have vibrational excitation. Some of this excitation will be quenched by collisions with the carrier gas before the ions exit the FA source, but a fraction of the ions may retain some vibrational excitation through the mass selection and injection process. The H_3^+ ions exiting from the FA are mass-selected by a quadrupole mass spectrometer and injected into the helium carrier gas. The process of injection has a significant effect on the energies of the H_3^+ ions. Some of these ions may gain enough energy to overcome the endothermicity involved in transferring a proton to the He carrier gas and thus generating HeH^+. With this in mind, the injection conditions were tuned to the lowest practicable energy by minimizing the amount of HeH^+ formed in the injection process and also by titrating the energy levels of the reactant ion with argon as the neutral reactant. Proton transfer to both helium and argon is endothermic from ground-state H_3^+, and only excited H_3^+ will proton transfer:

$$H_3^+ (\upsilon \neq 0) + He \rightarrow HeH^+ + H_2 \tag{3}$$

$$H_3^+ (\upsilon > 1) + Ar \rightarrow ArH^+ + H_2 \tag{4}$$

Reaction 3 is endothermic by 245 kJ mol^{-1} and can occur only when the H_3^+ ions are very excited, possibly due to the injection process itself. On the other hand, reaction 4 is endothermic for ground-state H_3^+ by only 53 kJ mol^{-1}, which can be overcome by excitation energy over any of the three lowest vibrational levels of H_3^+. Accordingly proton transfer to argon may occur unless the H_3^+ is in the ground state or either of the two $\upsilon = 1$ vibrational modes (bending or breathing). Consequently, when argon is added to the reaction flow tube, the magnitude of the ArH^+ signal gives a good indication of the excitation levels of the H_3^+ ions. This test was performed several times and the fraction of excited H_3^+ ions was generally less than 10% when the HeH^+/H_3^+ level was at a minimum due to optimized injection conditions.

A similar method was used for generating the D_3^+ reactant ions used for reactions with some of the small hydrocarbons. A moderately large flow of D_2 was introduced into the helium plasma at the FA nose cone and the D_3^+ (generated via the reaction of D_2^+ with D_2) was mass-selected and injected into the SIFT reaction tube. One complication for a D_3^+ reactant ion is that D_3^+ and HeD^+ ions (formed from energetic injection of D_3^+) are isobaric. As the reactions of excited D_3^+ and any HeD^+ with argon are exothermic, by comparing the D_3^+ and ArD^+ ion counts at high argon flows, we found that the energetic ions [HeD^+ and $D_3^+(\upsilon \neq 0)$] comprised ≤3% of the 6 amu signal.

The second method for generating H_3^+ was to inject a signal of Kr^+ from the FA into a hydrogen carrier in the SIFT reaction tube, forming H_3^+ through the reaction sequence 5 and 6:[15]

$$Kr^+ + H_2 \xrightarrow{k = 2.1 \times 10^{-10}\ cm^3\ s^{-1}} KrH^+ + H + 27\ kJ\ mol^{-1} \quad (5)$$

$$KrH^+ + H_2 \xrightarrow{k = 3.8 \times 10^{-11}\ cm^3\ s^{-1}} H_3^+ + H_2 - 2\ kJ\ mol^{-1} \quad (6)$$

The large number density of hydrogen molecules in the flow tube ensures the complete conversion of KrH^+ to H_3^+, despite the low rate coefficient for this process. The Kr^+ ions are generated by direct microwave discharge of the helium carrier gas in the FA to which a trace of Kr was added. This approach has several advantages over the helium method. First, as the H_3^+ is not injected into the SIFT tube, it cannot become excited by the injection process. Second, hydrogen is expected to be more effective at quenching any vibrationally excited H_3^+ ions through symmetric proton transfer reactions. Finally, the formation reaction 6 is slightly endothermic and thus should produce only ground-state H_3^+. This second method of generating H_3^+ should therefore effectively eliminate any vibrationally excited H_3^+ ions. However, this cannot be verified experimentally by an argon titration of excited H_3^+ ions, as the resulting ArH^+ ions will react with the hydrogen carrier to regenerate H_3^+.

The large number density of hydrogen molecules in the SIFT reaction tube can, however, create complications in the determination of the ionic products. Even slow association reactions with hydrogen (rate coefficients larger than 5×10^{-31} cm^6 s^{-1}) can have significant effects on the observed product distribution. Association reactions with hydrogen are especially problematical as they essentially reverse the dissociation reactions that involve H_2 loss. In these cases the product distributions in the hydrogen carrier gas will underestimate the amount of dissociation. For all these reasons, a combination of the two H_3^+ generation methods was required to determine accurately the product ratio produced by ground-state H_3^+ ions. Some small differences in product distribution are to be expected to arise from the different diffusion rates of the product ions in helium as compared with hydrogen. However, the substantial differences reported here in a few reactions are not due to differential diffusion.

There is one additional complication arising from trace neutral contaminants (particularly N_2 and H_2O) present in the carrier gas, as these two contaminants could not be completely eliminated. Because of the rapid reactions between H_3^+ and nitrogen (reaction 7) and between H_3^+ and water (reaction 8) and the similarly fast reaction between N_2H^+ and water (reaction 9),[16] even trace levels of these neutral contaminants will cause significant impurity ion signals at $m/z = 29$ and $m/z = 19$ to be observed. Typical water levels in helium in the flow tube after passage of the helium through a liquid nitrogen-cooled zeolite trap are about 150 parts per billion.

The ions thus formed in reactions 7 and 9 will react with the added neutral reactants via proton transfer and yield product distributions different than the reactions of H_3^+ alone. For a particular neutral reactant, these products are included in the detected product distribution and the products need to be deconvoluted to find the yields of the H_3^+ reactions themselves.

$$H_3^+ + N_2 \xrightarrow{k = 1.9 \times 10^{-9}\ cm^3\ s^{-1}} N_2H^+ + H_2 \quad (7)$$

$$H_3^+ + H_2O \xrightarrow{k = 5.3 \times 10^{-9}\ cm^3\ s^{-1}} H_3O^+ + H_2 \quad (8)$$

$$N_2H^+ + H_2O \xrightarrow{k = 2.6 \times 10^{-9}\ cm^3\ s^{-1}} H_3O^+ + N_2 \quad (9)$$

Reactions of H_3O^+ and N_2H^+ were included in this study for the purpose of deconvolution and for investigating the effects of reaction exothermicity.

To obtain accurate product distributions, the product ion counts generated by the ionic impurities were subtracted from each product channel. In most cases this correction was simply the branching ratio for the specific product channel multiplied by the number of counts intially due to the H_3O^+ or N_2H^+ ion. Where appropriate, a correction for mass discrimination was also applied.

A special case occurs when $C_2H_5^+$ is a product ion in any reaction. When this occurs, there is a mass overlap between $C_2H_5^+$ and the impurity ion N_2H^+ at $m/z = 29$. This complicates the estimation of the effect of contamination from N_2H^+ reactions. For these reactions, an estimate of the number of counts of N_2H^+ to be subtracted was computed from the measured flow of the neutral and the separately measured rate coefficient for the reaction between that neutral and N_2H^+.

The measurement of the flow rates of some of the neutrals added to the helium carrier gas in the SIFT tube was made difficult by their low vapor pressures or by their adsorption in the flow lines. In the case of naphthalene and methylnaphthalenes, the rate coefficients could not be determined due to these complications and only the products are reported to an accuracy of about 10%. With acrylonitrile, a mixture of acrylonitrile vapor in helium was required to prevent problems with adsorption of acrylonitrile to the system walls. The composition of this mixture of ∼10% acrylonitrile was calibrated by assuming that the reaction between H_3O^+ and acrylonitrile proceeded at the collision rate (5.1×10^{-9} cm^3 s^{-1}).[17] Since some of the reactions of H_3^+ reported in this study proceed more slowly than the collision rate, this assumption may slightly overestimate the reported rate coefficients for acrylonitrile reactions.

Results

The reactions of H_3^+, N_2H^+, and H_3O^+ have been investigated with a wide range of hydrocarbons as well as pyridine, pyrrole, and acrylonitrile. Most of the reactions of H_3^+ have been investigated with both helium and hydrogen carrier gases.

The rate coefficients for the reactions of H_3^+, N_2H^+, and H_3O^+ with the range of neutrals investigated are shown in Table 1, along with the theoretical collision rate coefficients.[17] The rate coefficients for the reactions of H_3^+ are considered to be slightly less accurate than most measured on the SIFT due to the increased uncertainties in measuring the small flows required for accurate rate coefficient determination in these fast reactions. The uncertainty of H_3^+ rate coefficients is assigned as ±20% rather than the usual uncertainties of ±15% in SIFT measurements that apply here to the H_3O^+ and N_2H^+ rate coefficients. The products observed for the three different ionic reactants, including the two different methods of H_3^+ formation, are shown in Table 2.

Discussion

(1) Alkanes. Five alkanes have been studied: two linear (propane and *n*-butane), one branched (*iso*-butane) and two cyclic (cyclopropane and methylcyclohexane).

(a) H_3O^+ Reactions. All the reactions of H_3O^+ with the acyclic alkanes have low rate coefficients, whereas the cycloalkane reactions are fast. The small rate coefficients for acyclic alkanes are due to the fact that their low proton affinities (PAs) make proton transfer slightly endothermic. The rate coefficient for propane is below the lowest limit that can be measured by

TABLE 1: Rate Coefficients Measured in This Work Compared with Calculated Collision Rate Coefficients from Ref 17 and Previous Measurements

	ionic reactant					
	H_3O^+		N_2H^+		H_3^+	
neutral	this work	ref 17	this work	ref 17	this work	ref 17
acetylene	0.01	1.3	1.4 (1.4[a])	1.2	2.6 (2.9,[a] 1.9,[b] 3.5[c])	2.8
ethylene	0.06 (0.06[d])	1.4	e	1.3	2.7 (2.0,[b] 3.6,[c] 2.8[f])	2.9
allene	1.4	1.4	1.4	1.7	2.9	3.4
propyne	1.8	2.0	1.5	1.7	3.0	4.2
cyclopropane	1.6 (1.5[g])	1.5	1.4 (1.3[h])	1.3	2.6 (3.0[h])	3.3
propene	1.7 (1.5[i])	1.7	1.4	1.5	3.1	3.7
propane	NR[j]	1.6	>0.63[k]	1.4	3.0	3.5
acrylonitrile[l]	5.1	5.1	4.4	4.4	9.1	11.3
2-butene	1.6	1.9	1.3	1.6	2.8	4.2
isobutane	<0.004	1.8	1.3	1.5	3.0	4.0
n-butane	<0.003	1.8	0.98	1.5	3.0	4.0
pyrrole	2.4	2.9	2.2	2.5	4.9	6.4
pyridine	2.5	3.4	2.3	2.9	3.5	7.9
benzene	1.3 (1.8[g])	1.9	1.5 (1.6[h])	1.6	3.3 (3.9[h])	4.4
toluene	1.3	2.2	1.3	1.8	3.9	5.8
methylcyclohexane	0.71	2.2	1.7	1.9	4.2	5.2

[a] Reference 18. [b] Reference 8. [c] Reference 19. [d] Reference 20. [e] The rate coefficient for this reaction could not be measured because of mass coincidence. On the basis of the difference in PAs, it should occur at close to the collision rate. [f] Reference 21. [g] Reference 12. [h] Reference 10. [i] Reference 22. [j] NR = no reaction; $k < 5 \times 10^{-13}$ cm^3 s^{-1}. [k] The rate coefficient for this reaction is believed to be close to the collision rate of 1.4×10^{-9} cm^3 s^{-1}; see text. [l] The rate coefficients for acrylonitrile are relative rate coefficients based on the collision rate being assumed for H_3O^+/acrylonitrile.

the SIFT technique, meaning that propane is essentially unreactive. An ionic product was observed at mass 43 ($C_3H_7^+$) but this is almost certainly due to a trace impurity, probably propene, in the reagent gas. The lowest energy $C_3H_7^+$ isomer (c-$C_3H_7^+$) possible in the reaction of H_3O^+ with C_3H_8 is 65 kJ mol^{-1} endoergic. The rate coefficients for *n*-butane and *iso*-butane were much higher than for propane and fall within the measurable range for the SIFT, although Spanel and Smith[24] did not report a reaction with *n*-butane. In both reactions, proton transfer is dissociative and produces $C_4H_9^+$, as the $C_4H_{11}^+$ ion that would correspond to nondissociative proton transfer is unstable. In addition, both reactions also yield the association product ($H_3O^+ \cdot C_4H_{10}$). Spanel and Smith[12b] noted this association of H_3O^+ with *n*-alkanes for *n*-pentane and larger homologues. The ion formed by the protonation of methylcyclohexane (C_7H_{14}), i.e., $C_7H_{15}^+$, must have a small barrier to further dissociation, as it is formed only when the difference in PAs between the proton acceptor and proton donor is small. The loss of one hydrogen molecule, $C_7H_{13}^+$, is more prevalent as an outcome from proton transfer. The rate coefficient for this process is higher than for either butane isomer and the product distribution we observe is in good agreement with the earlier measurement.[12]

(b) N_2H^+ Reactions. The reactions of N_2H^+ with the alkanes are more rapid than those of H_3O^+, and they become increasingly dissociative as the complexity of the neutral species increases. Propane appears to react at just under half the collision rate to give solely a $C_3H_7^+$ product. This process is exothermic by 51 kJ mol^{-1} to form n-$C_3H_7^+$ or 133 kJ mol^{-1} to form *iso*-$C_3H_7^+$, and the latter is the likely product. These energies and the fact that the proton affinity of propane is higher by 133 kJ mol^{-1} than that of nitrogen make the somewhat low reaction efficiency unexpected, as exothermic proton transfer usually proceeds at the collision rate.[25] It is almost certain that a significant fraction of reactions (>0.3) are dissociative and produce $C_2H_5^+ + CH_4$, where the product ion is isobaric with the N_2H^+ reactant ion. For this reason, we believe the true rate coefficient for the reaction with propane is close to the collision rate coefficient of 1.4×10^{-9} cm^3 s^{-1}.

(c) H_3^+ Reactions. The rate coefficients for the reactions of H_3^+ with the alkanes are all approximately 3×10^{-9} cm^3 s^{-1}, being marginally lower than the respective collision rates. The reaction with propane is relatively simple, and only the two dissociative channels with exothermicities greater than ~50 kJ mol^{-1} ($C_3H_7^+$ and $C_2H_5^+$) are observed. The formation of $C_3H_5^+$ is exothermic by 57 kJ mol^{-1}, but this product is not observed. The formation of this product would require the sequential loss of two H_2 molecules, and the first dissociation step may remove enough energy, preventing further dissociation of the $C_3H_7^+$ ion. The reactions of H_3^+ with the two butanes gave predominantly the ions $C_4H_9^+$, $C_3H_7^+$, and $C_2H_5^+$. For *n*-butane, the exothermic channels are shown in reaction 10. In calculating the thermochemistry, we assume that the unbranched structure has been retained.

$$H_3^+ + n\text{-}C_4H_{10}$$

$$\rightarrow CH_3CHCH_2CH_3^+ + 2H_2 + 271 \text{ kJ mol}^{-1} \tag{10a}$$

$$\rightarrow CH_3CHCH_3^+ + CH_4 + H_2 + 257 \text{ kJ mol}^{-1} \tag{10b}$$

$$\rightarrow C_3H_5^+ + CH_4 + 2H_2 + 110 \text{ kJ mol}^{-1} \tag{10c}$$

$$\rightarrow C_2H_5^+ + C_2H_6 + H_2 + 163 \text{ kJ mol}^{-1} \tag{10d}$$

The yields of the product ions generally follow the exothermicities, with $C_3H_7^+$, $C_4H_9^+$, and $C_2H_5^+$ being the main product ions observed. The other possible product ion, $C_3H_5^+$, is observed only as a minor product in the helium carrier gas, where it may be due to excited H_3^+ ions. With i-C_4H_{10} the relative energetics and product distributions are similar, and the yield of $C_2H_5^+$ formed is smaller than with n-C_4H_{10}, possibly because isomerization of i-C_4H_{10} is required to form this product.

(2) Alkenes and Cycloalkanes.

(a) H_3O^+ Reactions. In the reactions of H_3O^+ with the alkenes, the smallest alkene, ethylene, reacts at about 4% of the collision rate, since this proton transfer is endothermic by 11 kJ mol^{-1}, which also accounts for the competitiveness of the association channel. Proton transfer to the other alkenes is exothermic and proceeds near the collision rate, as was also noted by Spanel et al.[12] A fast reaction is also observed with cyclopropane, where $C_3H_7^+$ is the only product. This behavior is similar to the reactions of H_3O^+ with alkenes and may involve the ring opening of the neutral reactant in the reaction complex so that the reaction effectively involves the interaction of H_3O^+ with propene.

The only dissociative reaction of H_3O^+ observed in this work is in the reaction with methylcyclohexane. This is also the least exothermic dissociative reaction observed in this study. Spanel et al.[12] show a similar product distribution for this reaction.

(b) N_2H^+ Reactions. Dissociative channels are generally observed when N_2H^+ is the reactant ion, although the reaction

TABLE 2: Product Distributions in the Reactions of H_3O^+, N_2H^+, and H_3^+ with Neutral Molecules[a]

		H_3O^+		N_2H^+		H_3^+ (H_2 carrier)		H_3^+ (He carrier)	
neutral	products[a]	product ratio	$-\Delta H^{\circ\ b}$ (kJ/mol)	product ratio	$-\Delta H^{\circ\ b}$ (kJ/mol)	product ratio	$-\Delta H^{\circ\ b}$ (kJ/mol)	product ratio	$-\Delta H^{\circ\ b}$ (kJ/mol)
Alkanes									
C_3H_8	$C_3H_7^+ + H_2$	NR	−65	1.00	133	0.40		0.45	204
	$C_2H_5^+ + CH_4$		−93		−104	0.60		0.55	176
iso-C_4H_{10}	$C_4H_9^+ + H_2$	0.60[c]	−5	0.20	192	0.35		0.30	264
	$C_3H_7^+ + CH_4$		−19	0.80	178	0.60		0.50	250
	$C_2H_5^+ + C_2H_6$		−113		84	>0.05		0.20	155
n-C_4H_{10}	$C_4H_9^+ + H_2$	0.70[c]	2	0.25	199	0.35		0.35	271
	$C_3H_7^+ + CH_4$		−12	0.75	185	0.45		0.45	257
	$C_3H_5^+ + CH_4 + H_2$							0.05	110
	$C_2H_5^+ + C_2H_6$		−106		91	0.20		0.15	163
Alkenes and Cycloalkanes									
C_2H_4	$C_2H_5^+$	0.75[d]	−11	1.00	+187	1.00[e]		0.40	259
	$C_2H_3^+ + H_2$		−224		−27			0.60	45
$CH_2{=}C{=}CH_2$	$CH_2CHCH_2^+$ (allyl)	1.0	84	1.0	281				353
	$C_3H_3^+$ (cyclic) + H_2		−45		152	1.00[f]		0.3	224
	$C_3H_3^+$ (propargyl) + H_2		−150		48			0.7	120
$CH_3CH{=}CH_2$	$C_3H_7^+$ (isopropyl)	1.0	61	0.55	258				329
	$C_3H_5^+$ (allyl) + H_2		−86	0.45	110	0.70		0.65	183
	$C_3H_5^+$ (2-propenyl) + H_2		−108		89				161
	$C_3H_5^+$ (cyclopropyl) + H_2		−209		−12				59
	$C_3H_3^+$ (cyclic) + $2H_2$		−216		−18			0.10	53
	$C_3H_3^+$ (propargyl) + $2H_2$		−320		−122				−51
	$C_2H_3^+ + CH_4$		−181		16	0.30[g]		0.25	88
c-C_3H_6	$C_3H_7^+$ (isopropyl)	1.0	94	0.10	291				362
	(protonated cyclopropane)		59		257				328
	$C_3H_5^+$ (allyl) + H_2		−53	0.90	144	0.25		0.60	215
	$C_3H_5^+$ (2-propenyl) + H_2		−75		122				194
	$C_3H_5^+$ (cyclopropyl) + H_2		−177		21				92
	$C_3H_3^+$ (cyclic) + $2H_2$		−183		15				86
	$C_3H_3^+$ (propargyl) + $2H_2$		−287		−90				−18
	$C_2H5^+ + CH_2$		−396		−199				−127
	$C_2H_3^+ + CH_4$		−148		49	0.75		0.40	121
2-butene (C_4H_8)	$C_4H_9^+$	1.00	118	0.1	315	0		0	387
	$C_4H_7^+ + H_2$		−17	0.4	180	0.4		0.4	252
	$C_3H_5^+ + CH_4$		−43	0.5	155	0.35		0.35	226
	$C_2H_5^+ + C_2H_4$		−126		71	0.25		0.25	142
benzene	$C_6H_7^+$	1.00	59	1.00	257	1.00		1.00	328
toluene (C_7H_8)	$C_7H_9^+$	1.00	93	1.00	290	0.75		0.40	362
	$C_7H_7^+ + H_2$		40		237	0.20		0.50	309
	$C_6H_5^+ + CH_4$		−164		33	0.05		0.10	104
methylcyclohexane (C_7H_{14})	$C_7H_{15}^+$	0.10							
	$C_7H_{13}^+ + H_2$	0.90	29	0.40	226	0.60		0.35	298
	$C_6H_{11}^+ + CH_4$		50	0.30	247	0.25		0.20	319
	$C_4H_9^+ + C_3H_6$		−46	0.30	151	0.15		0.25	222
	$C_4H_7^+ + C_3H_8$		−56		141			0.10	213
	$C_3H_7^+ + C_4H_8$		−97		101			0.10	172
	$C_3H5^+ + C_4H_{10}$		−127		70				142
naphthalene	$C_{10}H_9^+$	1.00	112	1.00	309	1.00			381
1-methylnaphthalene	$C_{11}H_{11}^+$	1.00	144	1.00	341	1.00			413
2-methylnaphthalene	$C_{11}H_{11}^+$	1.00	143	1.00	340	1.00			412
Alkynes									
C_2H_2	$C_2H_3^+$	NR	−50	1.0	148	1.00[e]		1.00	219
$CH_3C{\equiv}CH$	$C_3H_5^+$ (allyl)	1.0	80	1.0	277				349
	$C_3H_5^+$ (propenyl)		58		255				327
	$C_3H_3^+$ (cyclic) + H_2		−50		148	1.0[g]		0.3	219
	$C_3H_3^+$ (propargyl) + H_2		−153		44			0.7	115
Nonhydrocarbons									
CH_2CHCN	CH_2CHCNH^+	1.00	94	1.00	291	0.90	362		
	$HCNH^+ + C_2H_2$		−160		37	0.10	109		
pyrrole	$C_4H_5NH^+$	1.00	184	1.00	382	0.75	453		
	$C_3H_5^+$ + HCN		−133		64	0.25	135		
pyridine	$C_5H_5NH^+$	1.00	239	1.00	436	1.00	508		
	$C_4H_5^+$ + HCN						121		

[a] Only the products formed from the reactant neutrals are shown; the deprotonated neutrals from the reagent ions, H_2O, N_2 and H_2, are omitted for clarity. [b] Exothermicity of the reaction channel, corresponding to the most stable ion and neutral isomers as products, unless otherwise indicated. Thermochemical data are from ref 23. [c] The remainder of the observed product was $C_4H_{10}{\cdot}H_3O^+$, which was formed via an association-type reaction. [d] The remainder of the observed product was $C_2H_4{\cdot}H_3O^+$, which was formed via an association-type reaction. [e] In H_2 carrier gas $C_2H_3^+$ was observed to associate with H_2, yielding $C_2H_5^+$. The product of the $H_3^+ + C_2H_2$ reaction in H_2 carrier was assigned after accounting for this reaction (see text). The product observed in $H_3^+ + C_2H_4$ in H_2 carrier was $C_2H_5^+$, which may originate in part from a $C_2H_3^+$ product associating with H_2. [f] A $C_3H_5^+$ product was also observed but was attributed to the association of $C_3H_3^+$ with the H_2 carrier gas, on the basis of observations in He carrier. [g] A $C_2H_5^+$ product was also observed but was attributed to the association of $C_2H_3^+$ with the H_2 carrier gas, on the basis of observations in He carrier.

with ethylene is nondissociative, as hydrogen loss is endothermic by 27 kJ mol^{-1}. Dissociative proton transfer to allene to form $C_3H_3^+ + H_2$ is exothermic by 48 kJ mol^{-1} to form linear $C_3H_3^+$, or by 152 kJ mol^{-1} for c-$C_3H_3^+$, but is not observed. The fact that the latter is not observed suggests that cyclization to form the c-$C_3H_3^+$ ion involves a significant barrier. The relationship between energy deposition and product distributions will be discussed later.

In 2-butene, H_2 loss and CH_4 loss have comparable energies and similar yields. Although both are significantly exothermic, the nondissociative channel is still observed, indicating that in 10% of the collisions, over 180 kJ mol^{-1} of the exothermicity is removed in nonreactive modes (see later discussion).

The reactions of N_2H^+ with cyclopropane and methylcyclohexane proceed near the collision rate and in both cases the dissociative channels dominate. We note that the dissociative channel is significantly more dominant in the reaction of N_2H^+ with cyclopropane than with its linear isomer, propene. This may be due to a lower barrier to H_2 loss from the cyclic isomer. Alternatively, protonation may result in ring opening, leading to the same lowest energy $[(CH_3)_2CH^+]^*$ intermediate but with more internal energy in the more exothermic c-C_3H_6 reaction, which leads to increased dissociation. Note that H_2 loss from the $(CH_3)_2CH^+$ ion may require a constrained four-center intermediate and possibly a significant barrier. The results for cyclopropane are in good agreement with those of Spanel et al.[10] Proton transfer to methylcyclohexane is also fast, possibly assisted by the availability of four dissociative channels and their corresponding transition states.

(c) H_3^+ Reactions. The reaction of H_3^+ with ethylene is interesting in that the nondissociative channel is exothermic by 259 kJ mol^{-1} while the dissociative channel to yield $C_2H_3^+$ is exothermic only by 45 kJ mol^{-1}, yet it is the major channel. In other words, the energetics means that H_2 loss from a ground-state $C_2H_5^+$ ion is endothermic by 214 kJ mol^{-1}, and this much energy must remain deposited in the internal modes of the $(C_2H_5^+)^*$ ion generated by proton transfer, to undergo the subsequent dissociation (see later discussion). Fiaux et al.[21] investigated this reaction with respect to the internal energy of the H_3^+ ions and showed that the amount of $C_2H_3^+$ observed increases with the internal energy of the H_3^+ ion. Interestingly, this is accompanied by a much more rapid decrease in the $C_2H_5^+$ ion product as direct charge transfer (CT) to form $C_2H_4^+$ begins to occur. Charge transfer is 132 kJ mol^{-1} endothermic for ground-state H_3^+. This observation indicates the amount of energy that it is possible to hold in vibrational excitation of H_3^+ and also shows that the ions used in this study are relatively thermalized as no CT products were seen. The ground-state product distributions of Fiaux et al. (70% $C_2H_3^+$, 30% $C_2H_5^+$)[21] also agree well with those obtained in the current study (60% $C_2H_3^+$, 40% $C_2H_5^+$). Note that this branching ratio could be obtained only from the helium carrier gas; $C_2H_5^+$ was the only product observed in a hydrogen carrier due to the association reaction of $C_2H_3^+$ with hydrogen.

The reaction with allene is relatively simple and forms only the dissociative product. The structure of the $C_3H_3^+$ product ion was investigated through its reactions with methanol. The reaction yielded a curved semilogarithmic decay of $C_3H_3^+$ ion signal with increasing CH_3OH flow, indicating that two different $C_3H_3^+$ species with different reactivities were present. A model using the rate coefficients of McEwan et al.[26] found that approximately 70% of these ions were the linear isomer and only 30% were the more energetically favorable cyclic one. Similar arguments to those made in the reaction of N_2H^+ with allene discussed above, where the exothermic reaction to produce c-$C_3H_3^+$ is not observed, suggest that there is an energy barrier for rearrangement to the cyclic ion.

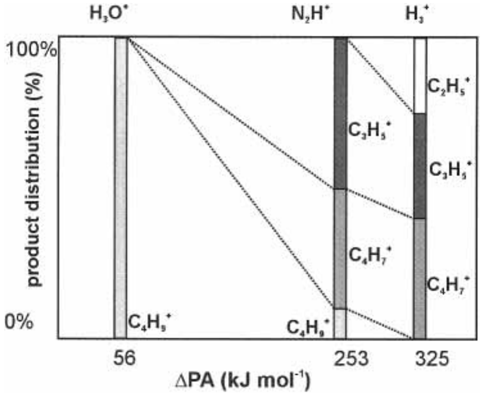

Figure 1. Observed product distribution for the reaction of 2-butene with H_3O^+, N_2H^+, and H_3^+. The proton affinity difference $PA(C_4H_8 - X)$, where $X = H_2O$, N_2, and H_2, is used as an indication of the energy contained in each ion. The curves show an interpolation between the available data points.

The reactions of both propene and 2-butene are relatively simple, giving the expected exothermic dissociative products. Propene reacts to give mostly $C_3H_5^+$ and $C_2H_3^+$. Some $C_3H_3^+$ was seen in the helium carrier but not in the hydrogen carrier, suggesting that it is produced by excited H_3^+ ions. Some of the $C_3H_5^+$ ions produced by the energetic reagent ions seem to retain enough energy to also lose H_2, although the overall process to form $C_3H_3^+$ by the reaction of ground-state H_3^+ is endothermic.

The final alkene studied was 2-butene, which gave only dissociative ion products in reaction with H_3^+, viz., $C_4H_7^+$ (0.40), $C_3H_5^+$ (0.35), and $C_2H_5^+$ (0.25). The only other dissociations possible energetically are those to give c-$C_3H_3^+ + CH_4 + H_2$, exothermic by 97 kJ mol^{-1}, and $C_2H_3^+ + C_2H_6$, exothermic by 65 kJ mol^{-1}. Both of these channels are only moderately exothermic and as such do not compete well with the observed channels that are exothermic by more than 200 kJ mol^{-1}. Formation of the cyclopropenyl ion is also apparently unfavorable due to the barrier discussed above. The change in product distributions from H_3O^+, N_2H^+, and H_3^+ with 2-butene illustrates the shift toward more dissociative processes as the energy of the reactant ion increases as shown in Figure 1. Only $C_4H_9^+$ is observed from H_3O^+ [$\Delta PA(C_4H_8 - H_2O) = 56$ kJ mol^{-1}], whereas *three* dissociative processes are found from H_3^+ [$\Delta PA(C_4H_8 - H_2) = 325$ kJ mol^{-1}].

With cyclopropane, as with propene, only dissociative products are observed. With both cyclopropane and propene in the helium carrier gas, the product ions $C_3H_3^+$, $C_3H_5^+$, and $C_2H_3^+$ are found, while in hydrogen only $C_3H_5^+$ and $C_2H_3^+$ are produced; the latter is observed as $C_2H_5^+$ due to association of $C_2H_3^+$ with the H_2 carrier gas. The $C_3H_3^+$ ion is a minor product and is likely to be the result of small amounts of more energetic ions in the helium carrier gas. Spanel et al.[10] reported 60% $C_3H_5^+$ and 40% $C_2H_3^+$ as the products of reaction with H_3^+ with cyclopropane, which is in good agreement with our findings in a helium carrier gas. By examining the dissociation products of eight proton donors, HX, reacting with cyclopropane, they also demonstrated that the dissociative product, $C_2H_3^+$, was produced only when the difference in PAs, $\Delta PA = PA(c\text{-}C_3H_6) - PA(HX)$, was greater than 292 kJ mol^{-1}. Their finding is consistent with our observations for 2-butene. As with N_2H^+, the reaction of H_3^+ with methylcyclohexane leads to extensive fragmentation. It is also interesting to note that the distribution of product ions is similar with N_2H^+ and H_3^+ despite the difference between the reaction exothermicities. We are unable to account for differences in the product ion distributions in the H_3^+ reaction with methylcyclohexane between the helium and hydrogen carriers.

The reactions of N_2H^+ and H_3^+ with cyclohexane were investigated by Spanel et al.,[10] who found the major channels to be $C_6H_{11}^+$ (H_2 loss) and $C_3H_7^+$ (C_3H_6 loss). There was also a shift to increased dissociative products for H_3^+ with respect to N_2H^+ that is similar to the present observations with methylcyclohexane.

(3) Alkynes.

(a) H_3O^+ Reactions. The reactions of H_3O^+ with the alkynes follow a similar trend to those of the alkenes. Proton transfer from H_3O^+ to acetylene is endothermic and only a slow association reaction is observed, while exothermic proton transfer to propyne undergoes proton transfer near the collision rate.

(b) N_2H^+ Reactions. Proton transfer from N_2H^+ to the alkynes is exothermic, and nondissociative proton transfer proceeds near the collision rate. In the case of acetylene this is the only possible exothermic reaction, but with propyne an additional exothermic dissociative channel is also possible.

$$N_2H^+ + CH_3C{\equiv}CH$$

$$\rightarrow CH_2CHCH_2^+ + N_2 + 277\ \text{kJ mol}^{-1} \qquad (11a)$$

$$\rightarrow l\text{-}C_3H_3^+ + N_2 + H_2 + 44\ \text{kJ mol}^{-1} \qquad (11b)$$

$$\rightarrow c\text{-}C_3H_3^+ + N_2 + H_2 + 148\ \text{kJ mol}^{-1} \qquad (11c)$$

The ion in reaction 11a has been assigned the allyl structure, as Fairley et al.[27] have shown that when enough energy is present to overcome the ~110 kJ mol^{-1} barrier to interconversion between the 2-propenyl and allyl structures, the allyl structure is the only product. Even though formation of c-$C_3H_3^+$ in reaction 11c would be exothermic by 148 kJ mol^{-1}, the reaction is not observed. This observation is consistent with the evidence noted earlier for a barrier to the formation of c-$C_3H_3^+$ ions.

(c) H_3^+ Reactions. The reactions of H_3^+ with alkynes are relatively simple. Proton transfer is exothermic in both cases. Acetylene gives only the exothermic product, $C_2H_3^+$; and propyne, only the dissociative product. A small amount of energetically impossible C_3H^+ was observed also in helium carrier gas, apparently from a small HeH^+ impurity ion and/or excited H_3^+. The $C_3H_5^+$ cation seen in the H_2 carrier gas may be formed by the association of $C_3H_3^+$ with H_2. For propyne the $C_3H_3^+$ ion was, as in the allene case above, formed in two isomeric structures. Approximately 70% of the products were l-$C_3H_3^+$ and 30% were c-$C_3H_3^+$, and again the formation of the energetically more favorable cyclic ion as the smaller product suggests a barrier.

An early investigation of this reaction by Aquilanti and Volpi[7] saw a mixture of $C_3H_3^+$ and $C_3H_5^+$ ions, with more $C_3H_5^+$ forming as the pressure was increased. Their observation is consistent with association of the $C_3H_3^+$ product ion with hydrogen. The fact that no $C_3H_5^+$ is observed in the helium carrier gas and that it apparently represents only ~30% of the products in the hydrogen carrier strongly suggests that $C_3H_5^+$ is not a primary product in this reaction.

(4) Aromatic Hydrocarbons. The aromatic hydrocarbons studied were benzene, toluene, naphthalene, and 1- and 2-methylnaphthalene. Because of their low vapor pressures, the latter three were only studied in a dilute mixture in a helium carrier gas and rate coefficients were not obtained, although it is anticipated that proton transfer or dissociative proton transfer will occur at close to the collision rate.

The reactions of H_3O^+ and N_2H^+ with all the aromatics gave only nondissociative proton transfer and had rate coefficients that were close to the collision rate, in good agreement with the findings of Spanel et al.[10,12] The reactions of H_3^+ with all the aromatics, except toluene, yielded only the protonated parent ions. Since these molecules have large polarizabilities, the calculated rate coefficients are high but the experimental rate coefficients are somewhat smaller.

The reactions of toluene are interesting. The reaction is nondissociative with N_2H^+, although H_2 loss would be exothermic by 237 kJ mol^{-1} to form the tropylium ion or by 187 kJ mol^{-1} to form the methylenebenzyl cation. Increasing the exothermicity by 72 kJ mol^{-1} in going to H_3^+ leads to a significant H_2 loss channel and a smaller CH_4 loss channel. The exact extent of this dissociation is difficult to gauge in the H_3^+/toluene reaction, however, as the product ratios in the helium and hydrogen carrier are quite different. In the helium carrier the observed products were $C_7H_9^+$ (0.40), $C_7H_7^+ + H_2$ (0.50), and $C_6H_5^+ + CH_4$ (0.10), whereas in the hydrogen carrier the ratios were 0.75, 0.20, and 0.05. There are two possible reasons for this observed difference in branching ratio: either the H_3^+ in the helium carrier was vibrationally excited and amplified the hydrogen loss channel, or $C_7H_7^+$ reacts with hydrogen (possibly very slowly) to generate $C_7H_9^+$. The product ion due to methane loss observed in the hydrogen bath gas was actually $C_6H_7^+$. However, the $C_6H_5^+$ ion cannot be observed in the presence of a hydrogen carrier, as Ausloos et al.,[28] Giles et al.,[29] and Scott et al.[30] have shown that $C_6H_5^+$ associates rapidly with hydrogen to give $C_6H_7^+$. Direct formation of $C_6H_7^+$ requires either the energetically unfavorable elimination of CH_2 (162 kJ mol^{-1} endothermic) or the unlikely insertion of the hydrogen molecule into the ionic reactant followed by loss of CH_4. We have therefore assigned the products of the reaction with H_3^+ as $C_6H_5^+$, which then rapidly associates with hydrogen to give the observed $C_6H_7^+$. Several groups have demonstrated that the open or cyclic isomers of $C_6H_5^+$ react quite differently with hydrogen, with the reactions of the cyclic ion being faster.[29,30] The $C_6H_5^+$ ions observed in this study were completely converted to $C_6H_7^+$ by the end of the flow tube, and therefore we tentatively assign the cyclic structure to the $C_6H_5^+$ ions formed in this reaction.

(5) Nitrogen Compounds. Three neutrals containing nitrogen were also investigated: pyridine, pyrrole, and acrylonitrile. Of these molecules, only acrylonitrile, CH_2CHCN, has been observed in the interstellar medium at this time.[31] The H_3O^+ and N_2H^+ ions reacted with all three species by simple proton transfer. The rate coefficients obtained for acrylonitrile were measured by use of a mixture of the vapor in helium, where the concentration of acrylonitrile was calibrated relative to the rate coefficient observed from H_3O^+. The reactions with N_2H^+ also all proceeded via nondissociative proton transfer with rate coefficients near the collision rate.

The reactions with H_3^+ were more complex. Nondissociative proton transfer was still the only product observed for pyridine, but dissociative channels were observed with pyrrole and acrylonitrile.

$$H_3^+ + C_4H_5N$$

$$\rightarrow C_4H_5NH^+ + H_2 + 453\ \text{kJ mol}^{-1}\ (0.75) \quad (12a)$$

$$\rightarrow C_3H_5^+ + HCN + H_2 + 135\ \text{kJ mol}^{-1}\ (0.25) \quad (12b)$$

$$H_3^+ + CH_2CHCN$$

$$\rightarrow CH_2CHCNH^+ + H_2 + 362\ \text{kJ mol}^{-1}\ (0.90) \quad (13a)$$

$$\rightarrow HCNH^+ + C_2H_2 + H_2 + 109\ \text{kJ mol}^{-1}\ (0.10) \quad (13b)$$

Reaction 12b requires considerable rearrangement and loss of the aromaticity of pyrrole but is still significantly exothermic. A similar channel for pyridine leading to $C_4H_5^+ + HCN + H_2$ is 121 kJ mol^{-1} exothermic but it is not observed, possibly due to a barrier resulting from the significant aromaticity of the molecule.

(6) Reaction Mechanisms. The mechanisms of dissociative proton-transfer reactions, including those of H_3^+, were investigated extensively by Futrell and co-workers[21,32−35] and more recently by Spanel et al.[10] The discussion below follows similar arguments.

The loss of H_2 can occur by two basically different mechanisms. One mechanism involves proton transfer to form an excited protonated intermediate, followed by the dissociation of this intermediate. If the intermediate is sufficiently long-lived, scrambling can occur among the hydrogen atoms in the intermediate, which can be tested by deuterium labeling. The second mechanism involves direct reaction by hydride abstraction or protonation of a carbon atom followed by rapid loss of the incoming proton without scrambling. The hydride abstraction or rapid loss mechanisms are indistinguishable by deuterium labeling. These reactions are shown below.

Proton transfer:

$$XH^+ + C_xH_y \rightarrow (C_xH_{y+1}^+)^* + X \quad (14)$$

$$(C_xH_{y+1}^+)^* \rightarrow C_xH_{y-1}^+ + H_2 \quad (15)$$

Hydride abstraction or rapid loss:

$$XH^+ + C_xH_y \rightarrow C_xH_{y-1}^+ + H_2 + X \quad (16)$$

In the present work we examined the reactions of D_3^+ with several of the small hydrocarbons. First, the results showed an almost complete lack of any product ions containing two deuterium atoms. This finding is consistent with practically all other investigations that have attempted isotopic labeling and is independent of whether the labeling was present in the reactant ion or the neutral.[10,21,32−35] In other words, if H_3^+/D_3^+ was reacted with C_xD_y/C_xH_y, at most one of the hydrogen isotopes from the reactant ion was seen in the ionic products. This observation suggests that proton transfer proceeds though long-range polarization stripping in a loose intermediate where the H_2 and hydrocarbon moieties retain their identities.

To distinguish between the proton transfer and direct mechanism, we note in Table 3 that in all the reactions of D_3^+ in this work, except the reaction with propane, all the product ions retained one D atom. The loss of H_2 vs HD or CH_4 vs CH_3D from the excited reaction intermediates produced by the initial D^+ transfer intermediates followed a statistical distribution showing full hydrogen scrambling.

TABLE 3: Ratios of Observed vs Statistical HD/H$_2$ Loss or CH$_3$D/CH$_4$ Loss[a] from ($C_XH_YD^+$)* Formed from the Reaction of D_3^+ with a C_XH_Y Hydrocarbon

neutral hydrocarbon	product ion	hydrogen/deuterium ratio	
		experimental	statistical
ethylene	$C_2H_3^+$	0.50	0.67
propene	$C_3H_5^+$	0.44	0.40
	$C_2H_3^+$	1.30	1.32
propyne	$C_3H_3^+$	0.57	0.67
propane	$C_2H_5^+$	3.0	0.80
	$C_3H_7^+$	<4.0	0.28

[a] Equivalently, D loss vs D retention.

A special case in this work is that of propane, where the ion formed upon initial protonation, $C_3H_9^+$, is not a stable species. In this reaction there is essentially no isotope scrambling and almost no deuterium is retained in the products. The results suggest a direct mechanism. Note that hydride abstraction constitutes attack of the incoming proton on a hydrocarbon hydrogen, while the fast dissociation mechanism involves protonation of a carbon atom or of a C−H bond followed by rapid H_2 loss. Since the C−H bonds in propane are similar to those in the alkyl groups of the other hydrocarbons and the hydrogen atoms carry similar partial charges, it is unlikely that hydride abstraction is easier here than in the other hydrocarbons and the rapid dissociation mechanism is more likely. This is also consistent with the observations of Futrell and co-workers[21,32−35] of increased direct reaction products with increasing ion energy, which also facilitates rapid dissociation. Spanel et al.[10] also found a nonstatistical distribution of $C_3H_5^+/C_3H_4D^+$ in the reaction of ArD^+ with cyclopropane and concluded that the more direct process of dissociative hydride ion transfer, rather than proton transfer, was responsible.

Another question about the mechanism is whether collisional stabilization, reaction 2a above, is significant. Information on this point can be obtained by pressure effects, especially from a comparison with the results of Smith and Futrell.[21,32−35] The product ratios in their experiments, obtained at low pressures ($<10^{-5}$ Torr), are very similar to the results obtained in the SIFT. Thus one can conclude that the lifetime of the excited ions, i.e., the time required for unimolecular dissociation, is less than the time between collisions in the SIFT at 0.5 Torr ($\sim 3 \times 10^{-8}$ s). The presence of the carrier gas does not appear to significantly alter the product distribution. This suggests that reaction 2a above is not significant for the reactions observed both here and in the ICR experiments.

(7) Energy Effects. The main energy effect observed in the present reactions is the increasing dissociation with exothermicity in the reactions of H_3O^+, N_2H^+, and H_3^+ with a given neutral. To investigate further the role that energy plays in these reaction systems, we examined the reactions of N_2H^+ with propene and propyne in the drift tube. The product ratios at different collision energies were obtained in a 0.34 Torr helium carrier gas with drift tube voltages ranging from 0 to −275 V. The voltage of −275 V is the maximum voltage applied over 50 rings uniformly spaced over 50 cm with a constant potential gradient between each ring. The graph obtained for propene is shown in Figure 2.

When the drift tube results for the N_2H^+/propene branching ratios in Figure 2 are compared to the branching ratio for an H_3^+ reactant, it is apparent that the increased energy of the reactant ions increases dissociation and narrows the gap between the two product distributions. While the $C_2H_3^+$ product is not seen in the N_2H^+ reaction at thermal energies, it constitutes ~12% at −275 V, about half the value observed with the H_3^+

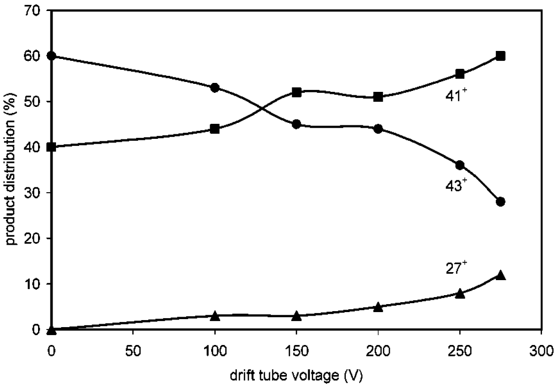

Figure 2. Variation of branching ratio for the N_2H^+/propene reaction as the voltage of the drift tube is altered. The line marked 43^+ is for the $C_3H_7^+$ ion, the line marked 41^+ is for the $C_3H_5^+$ ion, and the line marked 27^+ is for the $C_2H_3^+$ ion. The results were obtained in 0.34 Torr of helium.

ion. The $C_3H_5^+$ product is, as expected, less important at the higher energies, while the $C_3H_3^+$ product channel increases. This indicates that the differences observed between the N_2H^+ and H_3^+ proton-transfer products of C_3H_6 in Table 2 may be eliminated if sufficient energy is placed in the N_2H^+ ion. The N_2H^+/propyne system was also investigated by use of the drift tube. As the voltage on the drift tube was increased, the $C_3H_3^+$ ion was found to increase from ~3% at thermal energies up to 12% at −250 V, which corresponds to 5 V cm^{-1} at 0.34 Torr. Again this appears to show that energy in the N_2H^+ reactant ion, possibly both as translation and vibration, can contribute to dissociation. These observations are complementary to those of Figure 1 and the results reported by Spanel et al.[10] Both of these sets of results show more dissociative channels as the difference in PA between the proton acceptor and proton donor increases.

(8) Energy Deposition and Product Distribution. In many of the present reactions, and many other exothermic dissociative reactions, a large fraction of the product ions do not decompose, although the exothermicity can deposit more than enough energy in the intermediate $(BH^+)^*$ than is required for dissociation. For example, 25−35% of the products of the reaction of H_3^+ with cyclopropane remain as $C_3H_5^+$, although dissociation to c-$C_3H_3^+$ is 86 kJ mol^{-1} exothermic. Similarly, in the H_3^+/2-butene reaction, 35% of the ion products do not dissociate although dissociative channels exist that are 252 and 226 kJ mol^{-1} exothermic.

The lack of dissociation may result from the release of a fraction of the exothermicity of proton transfer in modes that are not available for the dissociation of the $(BH^+)^*$ intermediate. Smith and Futrell examined this aspect of proton transfer by comparing the reactions of KrH^+, H_3^+, and O_2H^+, whose neutral components have very similar proton affinities of 424.6, 422.3, and 421.0 kJ mol^{-1}, respectively, with the hydrocarbons CH_4, C_2H_4, and C_2H_6. In the most relaxed states of the reactant ions, the product ratios for all ions are very similar. This indicates that no significant energy is carried away in the vibrational modes of H_2 and O_2, as krypton is an atomic species. The exothermicity seems to be removed primarily as relative translation between the product hydrogen molecule and carbonium ion.[35]

The distribution of energy may be estimated more quantitatively, along the lines applied by Fiaux et al.[21] to the reaction of H_3^+ with ethylene. The lack of pressure effects on the product distributions suggests that collisional stabilization in reaction 2a is not significant. For the present considerations, we also assume that radiative stabilization is not significant, at least for the small ions with few vibrational modes. If stabilization of $(BH^+)^*$ is in fact negligible, then all the complexes with sufficient energy to dissociate do dissociate. Conversely, the observed nondissociated BH^+ products are due to low-energy $(BH^+)^*$ intermediates that were formed with too little energy to dissociate. These low-energy intermediates are formed by the removal of the proton transfer exothermicity in inactive modes, especially translation.[35]

For these reasons, the distribution of energy released by proton transfer is of central interest. The internal energy of a $(BH^+)^*$ intermediate formed in reaction 1 can be calculated from the energy balance of reaction 1 above:

$$E_{\mathrm{vib,rot}}(BH^+)^* + E_{\mathrm{trans}}(BH^+)^* + E_{\mathrm{vib,rot}}(A) + E_{\mathrm{trans}}(A) = E_{\mathrm{thermal}}(AH^+) + E_{\mathrm{thermal}}(B) + E_{\mathrm{PT}} \quad (17)$$

Here E_{PT} is the exothermicity of the proton-transfer reaction at 0 K (i.e., ΔH_0°), and the other terms on the right-hand side are thermal energies of the reactants. The sum $E_{\mathrm{trans}}(BH^+)^* + E_{\mathrm{vib,rot}}(A) + E_{\mathrm{trans}}(A)$ represents E_{inactive}, the energy in modes that $(BH^+)^*$ cannot access for dissociation. For the present estimates, we assume that, for small reactants with few vibrational modes and for highly exothermic proton transfer, the thermal energies of the reactants are negligible compared with E_{PT}.

Neglecting the thermal energies $E_{\mathrm{vib,rot}} + E_{\mathrm{trans}}$ of the reactants AH^+ and B and $E_{\mathrm{vib,rot}}(A)$, the energy in the active modes of the intermediate ion is given by

$$E_{\mathrm{vib,rot}}(BH^+)^* = E_{\mathrm{PT}} - E_{\mathrm{inactive}} \quad (18)$$

Referring to Figure 3, the excess internal energy in the active modes of $E_{\mathrm{ex}}(BH^+)^*$ is the energy over $E_{\mathrm{dissoc}}(BH^+) + E_{\mathrm{barrier}}$, where $E_{\mathrm{dissoc}}(BH^+)$ is the energy of dissociation of BH^+ to form the fragments $F^+ + N$ at 0 K. This excess energy is given by subtracting $E_{\mathrm{dissoc}} + E_{\mathrm{barrier}}$ from both sides of eq 18:

$$E_{\mathrm{ex}}(BH^+)^* = E_{\mathrm{vib,rot}}(BH^+)^* - E_{\mathrm{dissoc}}(BH^+) - E_{\mathrm{barrier}} = E_{\mathrm{PT}} - E_{\mathrm{inactive}} - E_{\mathrm{dissoc}}(BH^+) - E_{\mathrm{barrier}} \quad (19)$$

Note also that the overall dissociative proton transfer (reactions 1 + 2b) is equivalent thermochemically to proton transfer to form BH^+, followed by dissociation. Therefore the energy, E_{DPT}, of the overall dissociative proton-transfer reaction is given by

$$E_{\mathrm{DPT}} = E_{\mathrm{PT}} - E_{\mathrm{dissoc}}(BH^+) \quad (20)$$

Therefore from eqs 19 and 20

$$E_{\mathrm{ex}}(BH^+)^* = E_{\mathrm{DPT}} - E_{\mathrm{inactive}} - E_{\mathrm{barrier}} \quad (21)$$

In the absence of a barrier, the excess energy of $E_{\mathrm{ex}}(AB^+)^*$ is equal simply to the exothermicity of dissociative proton-transfer reaction minus the energy removed in the inactive modes. According to the above considerations, $(BH^+)^*$ dissociates if $E_{\mathrm{ex}}(BH^+)^* > 0$; i.e., if $E_{\mathrm{inactive}} < E_{\mathrm{DPT}} - E_{\mathrm{barrier}}$. Conversely, the reaction yields the undissociated proton-transfer product BH^+ if $E_{\mathrm{ex}}(BH^+)^* < 0$; i.e., if $E_{\mathrm{inactive}} > E_{\mathrm{DPT}} - E_{\mathrm{barrier}}$. If the barrier is negligible, the amount of energy removed in the inactive modes to yield BH^+ can be found simply from the reaction thermochemistry, i.e., $E_{\mathrm{inactive}} > E_{\mathrm{DPT}}$. The fraction of reactions where this amount of energy is removed can be found

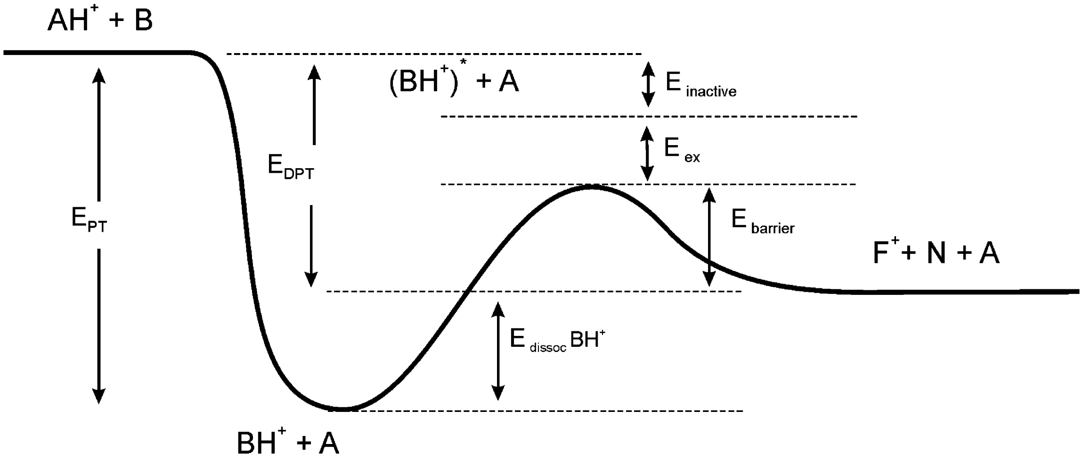

Figure 3. Schematic energy diagram for dissociative proton-transfer reactions $AH^+ + B \rightarrow (BH^+)^* \rightarrow F^+ + N$. The energy terms are defined in the text.

from the ratio $[BH^+]/([BH^+] + [F^+])$ when the product distributions are known.

For example, in the reaction of N_2H^+ with $CH_3CH{=}CH_2$, the dissociative reaction is exothermic by 110 kJ mol^{-1} but 55% of the $(C_3H_7^+)^*$ ions do not dissociate. Therefore, in 55% of the reactions, more than 110 kJ mol^{-1}, i.e., 42% of the 258 kJ mol^{-1} proton-transfer exothermicity, is removed in the inactive modes. Similar estimates may be made for other reactions in Table 2 where both dissociative and nondissociative channels exist. In the reactions of N_2H^+ with *c*-C_3H_6, >49% of the exothermicity is removed in 10% of the reactions; with 2-butene, >57% is removed in 10% of the reactions.

Similar considerations can be applied to reactions where only nondissociative reactions are observed although exothermic dissociation channels exist. However, they may overestimate the removed energy. For example, in the reaction of N_2H^+ with toluene, which is 100% nondissociative, >82% of the exothermicity would need to be removed in all the reactions to prevent H_2 loss. This seems unlikely and suggests that the lack of dissociation is due to an energy barrier.

Where barriers to dissociation exist, the excess energy required for dissociation reflects the difference between ground-state BH^+ and the energy required for its dissociation including the barrier (see Figure 3). Clearly, if a barrier exists, then less energy needs to be removed in the inactive modes to prevent dissociation. Therefore, the examples give a lower limit to the energy retained in $(BH^+)^*$ and an upper limit to the energy removed from the dissociating population. For example, the dissociation of $C_3H_7^+$ to $C_2H_5^+ + H_2$ was found by several investigators to involve a barrier (reverse activation energy)[36−38] of 70 kJ mol^{-1}.[39] Therefore, only 40 kJ mol^{-1}, rather than 110 kJ mol^{-1}, needs to be removed in 55% of the reactions of $N_2H^+ + CH_3CHCH_2$ to obtain the $C_3H_7^+$ ion.

The other approximation above was neglecting the energy of $(BH^+)^*$ resulting from the thermal energies of the reactants. This correction has the reverse effect on the considerations of energy distribution and increases the energy that must be removed in the inactive modes to prevent dissociation. This correction can be significant: for example, a significant fraction of the $C_3H_7^+$ population at 300 K has vibrational energy up to 20 kJ mol^{-1}.[39]

A more quantitative calculation of the energy deposited in $(BH^+)^*$ may be obtained if the potential energy surfaces are known. If the potential energy surfaces and transition-state parameters are known, RRKM calculations can relate the energy content of $(BH^+)^*$ to the observed product ratios. These calculations can be useful when there are competitive dissociation channels whose ratio is sensitive to the energy. Examples are the reactions in Table 2 where several dissociation channels exist and the product distribution changes in going from N_2H^+ to H_3^+ reactions. In such cases RRKM calculations can match the observed product distributions to the energy distribution in the $(BH^+)^*$ population and from this can identify the distribution of E_{PT} in the active and inactive modes.

Conclusions

Exothermic proton-transfer reactions from H_3O^+, N_2H^+, and H_3^+ to hydrocarbons are dissociative to various extents, producing stable protonated ions, BH^+, and fragments F^+. Common dissociation pathways following exothermic proton transfer are hydrogen loss, methane loss, and the loss of other small alkanes or alkenes, with the dissociative channels increasing with increasing exothermicity of proton transfer. The main question in such reactions is the distribution of the reaction exothermicity in the reaction intermediates, which control the product distributions.

Deuterium labeling in this and preceding work[10,21,32−35] shows that most reactions in this paper are best characterized by proton transfer to form excited $(BH^+)^*$ intermediates. A fraction of these intermediates dissociates at a rate that allows hydrogen scrambling. A lack of pressure effects on product distributions suggest that the decomposing fraction of $(BH^+)^*$ is not stabilized by collision and dissociates faster than the collision time in the SIFT ($\sim 3 \times 10^{-8}$ s). The lack of collisional stabilization indicates that the intermediates $(BH^+)^*$ that do not dissociate within the time frame of the SIFT experiment contain too little energy to do so. On this basis the energy distribution upon proton transfer can be estimated, showing that up to 40−60% of the reaction exothermicity may be removed in several reactions (less if barriers exist) as translational energy, in agreement with the conclusions of previous workers.[21,32−35] In reactions where no stable protonated ion exists, as is the case for propane, unimolecular decay occurs instantaneously without allowing for hydrogen scrambling. RRKM calculations on reactions with competing channels may define the energy distributions more quantitatively.

For smaller hydrocarbons including alkanes, alkenes, alkynes, and cyclic species, dissociative reactions are usually observed if the exothermicity of a particular channel exceeds 100 kJ mol^{-1}. In some cases, more highly exothermic channels are less prominent unless there is no other available exothermic reaction pathway.

In aromatic hydrocarbons, as the molecules increase in size, the tendency for dissociative proton transfer decreases as the energy in $(BH^+)^*$ is distributed in many vibrational modes. The aromatic hydrocarbons observed, such as benzene and the polycyclic aromatics naphthalene and methylnaphthalenes, exhibit no dissociation channels. Notably, while the reaction of H_3^+ with toluene is partly dissociative, the reaction with methylnaphthalene is not, showing the stabilizing effect of the larger molecular size. The lack of dissociation may be due to radiative stabilization of (methylnaphthaleneH^+)* or alternatively, its longer lifetime allowing collisional stabilization. Both of these stabilization processes are facilitated by the large number of active modes. We also note that the $C_7H_7^+$ ion formed by H_2 loss from toluene may have the tropylium structure, but in methylnaphthalene a tropylium ion would be fused to a benzene ring, which may be destabilizing. In any event, the lack of dissociation of methylnaphthalene suggests that H_3^+ may not be able to dissociate alkylated or unalkylated PAHs.

The interstellar medium and the atmospheres of Jovian planets are dominated by hydrogen, and ionizing radiation rapidly produces H_3^+ that is likely to be the major ionic reagent. The dissociative reactions of H_3^+ with nonaromatic hydrocarbons can be a major mechanism for converting more-saturated to less-saturated species by H_2 loss and for converting larger to smaller molecules by the loss of CH_4 or other small hydrocarbons. On the other hand, aromatics are observed to be stable against decomposition by H_3^+ and also by other protonating ions where proton transfer is less exothermic. We also note that these processes are paralleled by electron impact ionization, where the unsaturated hydrocarbons fragment more readily while PAHs yield significant amounts of molecular ions. Ionizing reactions, including dissociative ion−molecule reactions of H_3^+, therefore favor the accumulation of unsaturated and aromatic molecules in ionizing and hydrogen-dominated astrochemical environments.

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