Temperature variable ion trap studies of $C_3H_m^+$ with $H_2$ and HD

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Hydrogenation and deuteration of $C_3^+$, $C_3H^+$, and $C_3D^+$ in collisions with $H_2$ and HD has been studied from room temperature down to 10 K using a 22-pole ion trap. Although exothermic, hydrogenation of $C_3^+$ is rather slow at room temperature but becomes faster with decreasing temperature. In addition to the increasing lifetime of the collision complex this behavior may be caused by the floppy structure of $C_3^+$ and the freezing of soft bending modes below 50 K. For $C_3^+ + HD$ it has been shown that production of $C_3D^+$ is slightly favored over $C_3H^+$ formation. The controversy over which products are really formed in $C_3H^+ + H_2$ collisions and deuterated variants has a long history. Previous and new ion trap results prove that formation of $C_3H_2^+$ in non-endothermic but rather fast, in contradiction to erroneous conclusions from flow tube experiments and ab initio calculations. In addition the reaction shows a complicated isotope dependence, most probably caused by the influence of zero point energies in entrance and exit transition states. For example hydrogen abstraction with HD is faster than with $H_2$ while radiative association is slower. The most surprising result has been obtained for $C_3H^+ + HD$. Here $C_3HD^+$ formation is over one hundred times faster than $C_3H_2^+$. In addition to the details of the potential energy surface it may be that in this case an $H$–$HD$ exchange reaction takes place via an open-chain propargyl cation intermediate ($H_2CCH^+$). Reactions of $C_3H_2^+$ and $C_3H_3^+$ with $H_2$ are very slow but, due to the unique sensitivity of the trapping technique, significant rate coefficients have been determined. The presented results are of fundamental importance for understanding the energetics, structures and reaction dynamics of the deuterated variant of the $C_3H_m^+$ collision system. They indicate that the previous quantum chemical calculations are not accurate enough for understanding the low energy behavior of the $C_3H_m^+$ reaction systems. The laboratory experiments are of essential relevance for the carbon chemistry of dense interstellar clouds, both for formation of small hydrocarbons and deuterium fractionation.

1. Introduction

Astrochemistry, low temperature reactions

Low-temperature and low-density experimental studies of chemical processes in gas phase and on surfaces are of key importance for understanding how interstellar molecules are formed, processed and destroyed. For predicting the chemical evolution of inter- or circumstellar clouds, precise reaction rate coefficients are needed over a wide range of temperatures, and often state specific information is required. For many ion-molecule reactions, the rate coefficients are temperature independent and can be estimated with the simple Langevin model; however, there are also many exceptions. As shown by experiments performed in the last two decades, often unexpected changes occur at low temperatures. Of special importance for astrochemistry are radiative association reactions, near thermoneutral reactions, and collisions slowed down by small barriers along the reaction path.

In contrast to the early assumptions there are many important exothermic ion-molecule reactions which are not just determined by the long range ion-induced dipole capture but where the probability to form a specific product is very sensitive to tiny details of the potential energy surface. A well-understood example of a temperature dependent reaction is the hydrogen abstraction $NH_3^+ + H_2 \rightarrow NH_2^+ + H$, which has been measured by several groups with different techniques, covering the temperature range from 11 K to 800 K. A summary of results can be found in ref. 1. An important class of processes is isotope enrichment, since it is a very sensitive probe of chemical and physical conditions prevailing in space. Recently, it has been shown by several examples that H–D and D–H exchange is not only determined by differences in zero-point energy and simple statistical factors, but also by the fact that identical fermions ($H^+$) or bosons ($D^+$) are involved requiring proper quantum mechanical treatment of the exchange symmetry. Significant restrictions for isotope scrambling are imposed since the nuclear spin is so weakly coupled to the other degrees of freedom that, in all cases studied so far, it is conserved during the life time of the intermediate complex.6

$C_3H_m^+$ formation at low temperatures

Reactions of positive carbon or hydrocarbon ions with hydrogen have been studied quite often, in most cases at room temperature under (near-)thermal conditions. The techniques used in most experiments so far will be briefly mentioned in the experimental part. The wealth of interesting information, derived from the experimental and theoretical efforts, will be summarized in section 4 for discussing the new results. A detailed review of hydrogenation of carbon-cluster cations with molecular hydrogen has been given by Bohme and Wlodek.7 Scott et al.8 reported SIFT measurements using atomic hydrogen. A recent summary of rate coefficients and their inclusion in models of dense interstellar clouds can be found in ref. 9. Despite all experimental and theoretical efforts it has been stated in a recent discussion of the interstellar carbon chemistry10 that our knowledge is not complete and that new formation routes are needed, e.g. for explaining the large abundances of $C_2H_2$ and $C_2H$ observed in photon dominated regions. One obvious drawback is that few reliable low temperature rate coefficients are known. But even those which have been reported (see for example refs. 11 and 12 and the short overview below) did not find their way into the UMIST database for astrochemistry.11

Hydrocarbon chemistry starts with ions including only one carbon atom. As discussed in ref. 14, radiative association is

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required at the beginning of the reaction chain since, at energies below 0.4 eV, CH⁺ formation becomes very slow and the carbon ion can only react via C⁺ + H₂ → CH₂⁺ + hν. This association reaction has been studied several times. Finally, reliable experimental values have been reported at 10 K both for normal- and para-hydrogen. Also formation of the hypercoordinated carbocation C₂H⁺ requires stabilization of the complex formed in CH₃⁺ + H₂ collisions via emission of a photon. Early pioneering ion trap results have been corroborated by detailed studies at 10 K. As discussed recently in a low temperature study of the deuteration of CH₃⁺ (n = 3–5) in collisions with HD, the relaxation of the ions with para-hydrogen significantly reduces the deuteration efficiency. A negative temperature dependence and a significant isotope effect has been discovered for reactions of CH₄⁺ with H₂, HD and D₂. The first low temperature data have been measured for the reverse reaction CH₃⁺ + H with cold trapped ions exposed to a beam of hydrogen atoms.

The manifold of reactions with hydrogen involving two carbon atoms have not yet been studied thoroughly at low temperatures. The first hydrogenation step, the reaction C₂⁺ + H₂ → C₂H⁺ + H is fast at room temperature and most probably remains fast with decreasing temperature; however, the branching ratio in collisions with HD is not so easy to predict. There was an interesting discussion on the low temperature behavior of the C₂H⁺ + H₂ reaction. Formation of C₂H₃⁺ is slow at room temperature and the rate coefficient falls below the background of 6 × 10⁻¹⁸ cm³ s⁻¹ at 10 K, while radiative association with p-H₂ is rather fast, kₚ = 4.7 × 10⁻¹² cm³ s⁻¹. Evaluation of several measurements has lead to an endothermicity of 4.6 kJ mol⁻¹ for p-H₂ and 6.0 kJ mol⁻¹ for D₂. Interesting results indicating the role of rotation in low temperature collisions of C₂H₄⁺ with H₂ have been measured using the method of inducing reactions of cold ions via laser excitation. It is also interesting to note that C₂D₃⁺ has been observed to be formed at 10 K via radiative association of C₂D₄⁺ + D₂ with kₚ = 2.5 × 10⁻¹⁵ cm³ s⁻¹.

Reactions involving three carbon atoms are the central subject of this paper. New measurements became necessary since there were a lot of uncertainties and discrepancies between different experimental and theoretical results. For the simple C₂⁺ + H₂, the published room temperature rate coefficient of C₂H⁺ are only one or two tenths of the Langevin value and vary from experiment to experiment. The new temperature dependent data indicate that internal energy of the reactants reduces the reactivity explaining the experimental variations by non-thermalized reactants. The controversy over what products are formed in C₂H⁺ + H₂ collisions and the questionable theoretical prediction that formation of C₂H₂⁺ + H is endothermic has been discussed already by Sorgenfrei und Gerlich. Some aspects have been summarized recently in a paper on formation of deuterated C₂H⁺, the precursor of the smallest cyclic interstellar molecule, the c-C₃H₂⁺. More information about the earlier and the present data will be presented in the discussion section.

2. Experimental

It is a scientific and technical challenge to develop experiments for studying collisional processes between ions and neutrals at low temperatures. Three different classes of experiments have been developed in the past two decades utilizing beam methods, swarm techniques, and traps. In general, low temperatures are achieved by cryogenic cooling or by supersonic expansions and the reactants are thermalized via gas phase collisions, using predominantly cold buffer gas. Other methods such as laser cooling or radiative cooling during long storage times are not (yet) flexible enough for wider applications, e.g., in laboratory astrochemistry. In a recent review on mass spectrometry approaches to interstellar chemistry, low temperature methods have been mentioned only briefly and it has been emphasized that most rate coefficients used in astrochemical models have been measured at room temperature with traditional instruments, using either a flow tube (FT) or an ion cyclotron resonance (ICR) trap. Unfortunately the temperature variable multi electrode ion trap has not yet been recognized as an ideal tool for many applications in mass spectrometry, chemistry, spectroscopy etc.; however, there are certainly enough examples illustrating its potential. For example, some hints to applications in elemental analysis have been given recently. In addition a review is in preparation summarizing the versatility of rf ion traps (wide range of densities and temperatures, laser induced reactions, in situ synthesis, chemical probing, etc.).

2.1. The trapping machine

Most results presented in this contribution have been obtained with our standard variable temperature rf 22-pole ion trapping apparatus. A comprehensive description of the rf based technique used can be found elsewhere. The externally generated ions are mass selected in a first quadrupole mass filter which is operated here exclusively in the mass selective mode, and injected into a 22-pole ion trap. There, the ion cloud is confined in the radial direction by an effective potential created by applying two opposite phases of an rf generator (80 V, 17 MHz) to the two sets of 11 electrodes. In the axial direction the trap is closed by small potential barriers created by suitable voltages applied to the two gate electrodes. Due to the wide nearly field free region defined by the 22 poles, experiments at low collision temperatures are possible.

The temperature of the trapping region is defined by copper walls mounted onto a closed cycle refrigerator. In order to achieve low temperatures—5 K have been reached recently in a new trap—the cold part is surrounded by a second thermal shield held at about 50 K. Higher temperatures are obtained by electric heating of the trap holder. The temperature is usually measured using a carbon resistor, a calibrated diode or a hydrogen gas thermometer. Buffer and reactant gases are introduced by cooled tubes and are in thermal equilibrium with the cold walls surrounding the trap. As discussed in detail in previous descriptions of the rf trapping technique (see ref. 26, and references therein), the translational and internal degrees of freedom of the ions are coupled quite efficiently to the cold environment by inelastic collisions with buffer gas which can be introduced continuously or in pulsed mode. Experimental tests of the ion temperature include Doppler profile measurements, rotational distributions, formation of clusters, isotope enrichment and others. The present experiments have been performed at a nominal temperature of 15 K in order to avoid condensation of H₂ and HD. Note that, due to the mass ratio, the translational temperature of the heavy ions does not play a big role since the collision temperature is dominated by the motion of the light target gas.

Reaction rate coefficients are determined by operating the instrument in an iterative mode. First, a pulsed bunch of ions is injected into the 22-pole ion trap with low kinetic energy. They are cooled to the ambient temperature by the He buffer gas and stored for times varying from milliseconds to seconds. For avoiding space charge effects and saturation of the Daly detector, usually only a few hundred primary ions are trapped per pulse. After the selected reaction time, the remaining primary ions and the formed product ions are extracted by a pulse applied to the exit electrode. They are mass analyzed in...
the second quadrupole mass filter and counted using a Daly type detector. In order to improve the statistics and to average over fluctuation, the procedure (i) ion formation, (ii) trapping and reaction, and (iii) analysis is repeated rather often for each mass of interest and typically for ten different storage times.

The \( \text{H}_2 \) target gas used in the present experiments had a purity of 99.995% (Messer-Griesheim). The HD target gas has been purchased from Cambridge Isotope Laboratories Inc. The specified purity is 97%, the major contamination being \( \text{H}_2 \) and \( \text{D}_2 \). In situ tests have shown that both molecules contribute together less than 2%. The number density of the target gas is determined with an ion gauge calibrated with respect to a spinning rotor gauge. If there are no parasitic reactions complicating the data analysis, the error in determining absolute rate coefficients is mainly due to uncertainties in the number density of the target gas. If not otherwise stated, this results in an error of 20% at number densities above \( 10^{10} \text{ cm}^{-3} \). For determining radiative rate coefficients, usually the number density of hydrogen or He buffer gas is varied over several orders of magnitude.\(^{12,14} \) In this work association reactions have been studied at hydrogen number densities of some \( 10^{9} \text{ cm}^{-3} \). It has been checked in each case, that the second term can be neglected in the measured effective rate coefficient \( k^\ast = k_r + [\text{H}_2] k_s \) where \( k_r \) is the radiative and \( k_s \) the ternary rate coefficient.\(^{14} \)

2.2. Preparation of \( \text{C}_3\text{H}_4 \) ions

Since all ions containing three carbon atoms most probably have linear, cyclic and bent isomers, tests need to be performed in order to determine the possible presence of unrotated metastable states. In all experiments performed with the 22-pole trap, an rf storage ion source has been utilized. As described previously,\(^{25} \) the long storage time and the high number density of the neutral precursor gas or also of additional buffer gas usually leads to a significant reduction of internal excitation. Therefore it is also rather probable that ground state isomers are formed; however, this has not been tested extensively in each individual case. An important experimental hint in the trapping experiment is the mono-exponential decay of primary ions over several orders of magnitude. The chance that the reactivity of different isomers is the same over a wide range of temperatures is very low.

As reported in the literature, \( \text{C}_3^+ \) cations have been produced from many neutral gas precursors and also by laser ablation of carbonaceous material. In an early SIFT experiment,\(^{27} \) \( \text{C}_3^+ \) ions have been generated by electron impact ionization of methylacetylene \( \text{C}_3\text{H}_4 \). In a newer one, diacetylene has been used.\(^7 \) In the present work primary ions were produced in the storage ion source by bombarding allene (\( \text{CH}_2=\text{C}=\text{CH}_2 \), Aldrich, 97%) with electrons (energy \( \leq 40 \text{ eV} \)). The various attempts to correlate the reactivity of the ion with the precursors did not provide any conclusive information and it has been supposed that the deviation of the measured rate coefficients by a factor of up to 3 are caused by excitation of the internal degrees of freedom.\(^{28} \) Despite many experimental and theoretical efforts to determine the electronic structure of this simple ion, it is not clear how the \( \text{C}_3^+ \) ions really look like, especially if they are vibrationally excited. As discussed in detail in section 4 the present results may give a hint that the soft bending modes are only frozen if the ion becomes really cold. Does it have then a structure which is closer to linear?

In the case of \( \text{C}_3\text{H}_4^+ \) the cyclic form is \( 220 \text{ kJ mol}^{-1} \) higher than the linear one\(^{29} \) and none of the tests indicated the presence of excited ions in the present experiment in accordance with other experiences made with the storage ion source. The situation is less clear for \( \text{C}_3\text{H}_3^+ \) where some deviations from mono-exponential decay have been observed; however, it has been found that these ions always react very slowly, and therefore, no additional tests have been performed. For pre-paring \( \text{C}_3\text{H}_5^+ \) ions, allene \( \text{CH}_2=\text{C}==\text{CH}_2 \) (Aldrich, 97%) has been used as neutral precursor. Also \( \text{C}_3\text{H}_4^+ \) exists in two different isomeric forms, the cyclic one being the ground state while the \( \text{H}_2\text{C}_3\text{H}^+ \) structure is \( 106 \text{ kJ mol}^{-1} \) higher in energy.\(^{30} \) It is known from the literature\(^{31} \) that, under certain conditions, ionization of methyl-acetylene with \( 70 \text{ eV} \) electrons results in \( \sim 65\% \) \( \text{C}_3\text{H}_4^+ \) ions while \( \sim 35\% \) are \( \text{H}^+\text{C}_3\text{H}_3^+ \). Since the reactivity of the latter ones is much higher than that of \( \text{C}_3\text{H}_4^+ \), it is possible to quench them in suitable collisions.

3. Results

3.1. Reactions with \( \text{H}_2 \)

Fig. 1 shows a typical experimental result, the number of various trapped ions \( N_i \) as function of storage time \( t \), measured at \( 15 \text{ K} \) for a sequence of reactions. The number density of \( \text{H}_2 \) was rather low, \( 8.5 \times 10^9 \text{ cm}^{-3} \). The number of \( \text{C}_3^+ \) ions initially injected into the 22-pole (only 200 per filling) decays exponentially by forming two different products. Dominant is the hydrogen abstraction reaction

\[
\text{C}_3^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}^+ + \text{H}.
\]

In addition it can be seen that also \( \text{C}_3\text{H}_2^+ \) ions appear at early times. The pressure dependence clearly corroborates that they are formed by the bimolecular reaction

\[
\text{C}_3^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_2^+ + \text{H}_2.
\]

At the low \( \text{H}_2 \) number densities used in present experiments, ranging from \( 2.2 \times 10^9 \text{ cm}^{-3} \) to \( 8.5 \times 10^9 \text{ cm}^{-3} \), the probability for a ternary collision is negligible. This is complementary to the high pressure SIFT experiment\(^7 \) where \( \text{C}_3\text{H}_2^+ \) formation is completely dominated by ternary association \( \text{C}_3^+ + \text{H}_2 + \text{He} \rightarrow \text{C}_3\text{H}_2^+ + \text{He} \). Measurements in the intermediate pressure range have not been performed in this work. A detailed analysis of

![Fig. 1](image-url)

**Fig. 1** Typical experimental results showing the time dependence of the averaged number of primary and product ions trapped per filling, \( N_i \), as a function of storage time \( t \). By collisions with an intense pulse of He buffer gas, the injected \( \text{C}_3^+ \) primary ions are relaxed to the ambient temperature \( T = 15 \text{ K} \). They react with \( \text{H}_2 \) (number density \( 8.5 \times 10^9 \text{ cm}^{-3} \) via the reactions (1)–(5) and form \( \text{C}_3\text{H}^+ \), \( \text{C}_3\text{H}_2^+ \) and \( \text{C}_3\text{H}_3^+ \). The solid lines are solutions of an adequate reaction rate equation system using for the reactions the rate coefficients (1) \( 1.7 \times 10^{-9} \), (2) \( 8.5 \times 10^{-11} \), (3) \( 1.15 \times 10^{-10} \), (4) \( 6 \times 10^{-11} \), (5) 0 (all in cm³ s⁻¹). Note that the values for the subsequent reactions (3)–(5) deviate from those given in Table 1 for ground state ions since the intermediate ions are excited.
the data shown in Fig. 1 reveals that some C₃H₃⁺ ions are also formed via the hydrogen abstraction reaction

\[ \text{C}_3\text{H}^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_2^+ + \text{H}. \]  \hspace{1cm} (3)

In further steps the C₃H⁺ and C₃H₂⁺ products continue to react with H₂ forming finally C₃D³⁺ via

\[ \text{C}_3\text{H}^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{H}, \]  \hspace{1cm} (4)

\[ \text{C}_3\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{H}. \]  \hspace{1cm} (5)

The solid lines in Fig. 1 present the solutions of a rate equation system describing the chemical interaction of all trapped ions with H₂.

The rate coefficients measured for the initial reactions (1) and (2) are listed in Table 1. All the results of this work are collected in this table in order to facilitate comparison with literature values and transfer into databases. The rate coefficients obtained for secondary reactions are not included, especially if the intermediate ions are formed via an exothermic reaction.

### Table 1  Measured reaction rate coefficients c for the indicated reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k/\text{cm}^3\text{ s}^{-1} ) or ( a/\text{cm}^3\text{ s}^{-1} )</th>
<th>( \beta )</th>
<th>( T/\text{K} ) or ( (T_1 - T_2)/\text{K} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃⁺ + n-H₂ → C₃H⁺ + H</td>
<td>1.7(−9)</td>
<td>0</td>
<td>15–44</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>4.7(−10)</td>
<td>−0.69</td>
<td>44–300</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>4.6(−10)</td>
<td>300</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>→ C₃H₂⁺ + hv</td>
<td>5.7(−12)</td>
<td>−1.02</td>
<td>20–44</td>
</tr>
<tr>
<td></td>
<td>8.5(−11)</td>
<td>15</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>→ C₃H⁺ + H</td>
<td>2.0(−9)</td>
<td>10</td>
<td>e</td>
</tr>
<tr>
<td>+ p-H₂</td>
<td>2.0(−9)</td>
<td>10</td>
<td>e</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.8(−10)</td>
<td>296</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5(−10)</td>
<td>300</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0(−10)</td>
<td>298</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ HD → C₃D⁺</td>
<td>9.3(−10)</td>
<td>15</td>
<td>b</td>
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<tr>
<td></td>
<td>→ C₃H⁺</td>
<td>7.6(−10)</td>
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<td>b</td>
</tr>
<tr>
<td></td>
<td>→ C₃HD⁺</td>
<td>5.9(−11)</td>
<td>15</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>→ C₃D₂⁺</td>
<td>1.3(−9)</td>
<td>10</td>
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<td></td>
<td>1.3(−10)</td>
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<td>1.8(−10)</td>
<td>300</td>
<td>32</td>
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<td></td>
<td>1.5(−10)</td>
<td>298</td>
<td>45</td>
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</tr>
<tr>
<td></td>
<td>C₃H⁺ + n-H₂ → C₃H₃⁺ + H</td>
<td>1.5(−10)</td>
<td>+0.09</td>
<td>15–44</td>
</tr>
<tr>
<td></td>
<td>1.4(−11)</td>
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</tr>
<tr>
<td></td>
<td>1.5(−11)</td>
<td>300</td>
<td>c</td>
<td></td>
</tr>
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<td>5.0(−11)</td>
<td>10</td>
<td>e</td>
<td></td>
</tr>
<tr>
<td>+ p-H₂</td>
<td>4.0(−11)</td>
<td>10</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ n.H₂ → C₃H₃⁺ + hv</td>
<td>2.3(−11)</td>
<td>−1.1</td>
<td>15–44</td>
</tr>
<tr>
<td></td>
<td>6.0(−11)</td>
<td>15</td>
<td>c</td>
<td></td>
</tr>
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<td></td>
<td>2.0(−10)</td>
<td>10</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>+ p-H₂</td>
<td>2.2(−10)</td>
<td>10</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.4(−12)</td>
<td>80</td>
<td>14</td>
<td></td>
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<tr>
<td>+ HD → C₃D⁺</td>
<td>5.6(−11)</td>
<td>15</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>→ C₃HD⁺</td>
<td>4.6(−10)</td>
<td>15</td>
<td>b</td>
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<tr>
<td></td>
<td>→ C₃H₂⁺</td>
<td>3.0(−12)</td>
<td>15</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>→ C₃H₂D⁺ + hv</td>
<td>3.2(−11)</td>
<td>15</td>
<td>b</td>
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<tr>
<td>+ D₂</td>
<td>3.0(−13)</td>
<td>10</td>
<td>c</td>
<td></td>
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<tr>
<td></td>
<td>→ C₃HD⁺ + H</td>
<td>1.0(−11)</td>
<td>10</td>
<td>c</td>
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<td></td>
<td>→ C₃D₂⁺ + H</td>
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<td></td>
<td>→ C₃HD₂⁺ + hv</td>
<td>4.0(−12)</td>
<td>10</td>
<td>c</td>
</tr>
<tr>
<td>C₃D⁺ + HD → C₃HD⁺</td>
<td>1.0(−10)</td>
<td>15</td>
<td>d</td>
<td></td>
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<tr>
<td></td>
<td>→ C₃D₂⁺</td>
<td>8.3(−11)</td>
<td>15</td>
<td>d</td>
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<td>→ C₃HD₂⁺</td>
<td>8.0(−12)</td>
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<tr>
<td>+ D₂</td>
<td>1.0(−14)</td>
<td>15</td>
<td>c</td>
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<tr>
<td></td>
<td>→ C₃D₂⁺ + D</td>
<td>1.7(−10)</td>
<td>10</td>
<td>c</td>
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<tr>
<td></td>
<td>→ C₃D₂⁺ + hv</td>
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<td>10</td>
<td>c</td>
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<tr>
<td>C₃H₂⁺ + n-H₂ → C₃H₃⁺ + H</td>
<td>1.7(−13)</td>
<td>15</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0(−13)</td>
<td>10</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>+ p-H₂</td>
<td>5.0(−13)</td>
<td>10</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ D₂</td>
<td>1.0(−14)</td>
<td>10</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>→ C₃D₂⁺ + hv</td>
<td>1.0(−14)</td>
<td>10</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>→ C₃HD⁺</td>
<td>3.0(−15)</td>
<td>10</td>
<td>e</td>
</tr>
<tr>
<td>C₃H₂⁺ + D₂ → C₃H₂D₂⁺ + D</td>
<td>1.0(−14)</td>
<td>10</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>C₃D₂⁺ + D₂ → C₃D₂⁺</td>
<td>1.0(−16)</td>
<td>10</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>C₃H₂⁺ + p-H₂ → C₃H₂⁺ + H</td>
<td>1.0(−14)</td>
<td>10</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ HD → C₃H₂D⁺ + H₂</td>
<td>&lt; 4(−16)</td>
<td>15</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>→ C₃H₂D⁺</td>
<td>1.5(−16)</td>
<td>15</td>
<td>b</td>
</tr>
</tbody>
</table>

* Rate coefficients \( k = a \times 10^{-b} \) are presented as \( a/(−b) \). The values are given at the indicated temperature \( T \) or the temperature dependence is represented by the function \( k = a(T/300\text{ K})^b \). This work, 15 K or fitted temperature dependences, see Figs. 2 and 3. These values might slightly deviate from thermalized ones. For details see the text. \( \text{C}_3\text{D}^+ \) has not been injected from the source, the rate coefficients have been deduced from Fig. 2. Data published in ref. 2 and unpublished results from ref. 33. Effective association rate coefficient measured at \([\text{HD}] = 10^{−8} \) cm⁻³.
reaction. As discussed in more detail in the next section for hot intermediate ions collisional relaxation competes with secondary reactions. Therefore results deviate from thermal rate coefficients measured by directly injecting these intermediates, e.g. C$_3$H$^+$, and thermalizing them with the intense pulse of buffer gas.

By repeating the measuring procedure described above at different temperatures, reaction rate coefficients between 15 K and 300 K have been obtained. They are presented in Fig. 2 for reactions (1) and (2) and in Fig. 3 for reactions (3) and (4). Rate coefficients for reaction (5) are not included in the figures because, between 15 K and 100 K, they are only 5 $\times$ 10$^{-13}$ cm$^3$ s$^{-1}$ and become smaller than 10$^{-14}$ cm$^3$ s$^{-1}$ at higher temperatures. In modeling the measured time dependence, reaction (5) can be ignored without changing the outcome of the other rate coefficients. Inspection of the two figures reveals that hydrogen abstraction, i.e. reaction (1) and (3) is nearly temperature independent below 50 K and falls off by about one order of magnitude going up to room temperature. The two radiative association reactions (2) and (4) show a much steeper fall off. For extending the evaluation radiative association toward higher temperatures, the traces of $^{13}$C$^{12}$C$^{12}$C$^+$ or $^{13}$C$^{12}$C$^{12}$CH$^+$ isotopes in the primary beam would have to be accounted for. It is surprising that the association reaction (2) can compete with the exothermic reaction (1). At 20 K almost 5% of the collision complexes are stabilized by emission of a photon! The competition between abstraction reaction and stabilization is more pronounced for the C$_3$H$^+$ + H$_2$ system; below 50 K the sum of both rate coefficients leads to a temperature independent value, indicating that the minor decrease of reaction (3) is not due to a small barrier or endothermicity but, as discussed below, more due to the fact, that at low temperatures the collision complex emits a photon before it decays towards the C$_3$H$_2$ product.

For applications in reaction networks the measured temperature dependence has been approximated with the function $k = a(T/300K)^b$ used in the UMIST database. The parameter $\gamma$ which is mainly for endothermic reactions, has been set to 0. As can be seen from Fig. 2 and Fig. 3 it was

![Fig. 2](image1.png)  
**Fig. 2** Temperature dependence of measured rate coefficients for the reactions C$_3^+$ + H$_2$ $\rightarrow$ C$_3$H$^+$ + H (filled circles) and C$_3^+$ + H$_2$ $\rightarrow$ C$_3$H$_2^+$ + $\nu$ (stars). The error bars indicate only that statistical uncertainties can be made very small, for systematic errors (e.g. for radiative association) see text. The lines are fits of the data using the function $k = a(T/300K)^b$ with different parameters describing the low temperature ($T<50$ K) and the high temperature dependence. At 300 K additional experimental points for C$_3$H$_2^+$ formation are included (taken from the literature: triangle: ref. 27, square: ref. 32, triangle pointing down ref. 7).

![Fig. 3](image2.png)  
**Fig. 3** Temperature dependence of the reaction rate coefficients for the reactions C$_3$H$^+$ + H$_2$ $\rightarrow$ C$_3$H$_2^+$ + H (filled circles) and C$_3$H$^+$ + H$_2$ $\rightarrow$ C$_3$H$_2^+$ + $\nu$ (solid diamonds). Literature values are from ref. 12 (open symbols). The solid lines are fits to the data using the function $k = a(T/300 K)^b \exp(-\gamma/T)$ used in the UMIST database. The parameter $\gamma$ which is mainly for endothermic reactions, has been set to 0. As can be seen from Fig. 2 and Fig. 3 it was
necessary to determine sets of parameters (α, β) for selected temperature intervals in order to get better agreement with the data. The resulting parameters are listed in Table 1.

### 3.2. Reactions with HD

In addition to H₂ also HD has been used as target gas under otherwise identical experimental conditions. It is obvious from Fig. 4 where primary and product ions are plotted as a function of trapping time, that the situation is more complicated than in Fig. 1 due to the various isotopes. In the experiment minor traces of mass 42 (most probably C₃D₃⁺) have also been observed; however, they are not presented in the figure since the signal is at the lower limit of the scale. The initially injected and relaxed C₃⁺ ions react with HD which is present in the trap with a number density of 7.9 × 10⁻⁹ cm⁻³. A detailed explanation of the complex chemical interplay is not easy since, in addition to H and D atom abstraction and radiative association, also H-D exchange reactions are possible. Since there are a variety of different ions having the same mass, one has to be very careful in the interpretation of the data.

In order to explain the measured ion abundances, a coupled rate model has been developed. The processes included in this model are shown schematically in Fig. 5. Also information from the non-deuterated C₃⁺ + H₂ reaction is used to unravel the complex interplay. In the first collision with HD, C₃⁺ abstracts predominantly an H or a D atom with an overall rate coefficient k₁ and a probability p or 1 − p, respectively. A few percent of the primary ions form C₃HD⁺ via radiative association (k₃). The C₃H⁺ products undergo further reaction with HD and form (i) C₃H₂⁺ via H atom abstraction (k₄), (ii) C₃D⁺ via H - D exchange (k₄), (iii) C₃DHD⁻ by D atom abstraction (k₅), and finally (iv) C₃H₂D⁺ via radiative association (k₆).

In analogy C₃D⁺ products react with HD and form (i) C₃HD⁺ via H atom abstraction (k₇), (ii) C₃D₂⁺ via D atom abstraction (k₈), and (iii) C₃HD²⁻ via radiative association (k₉). Since it has been shown that C₃H₂⁺ and C₃H₃⁻ react very slowly with H₂, it has been assumed that also reactions of their isotope equivalents, C₃HD⁺, C₃D₂⁺, C₃H₂D⁻, C₃HD²⁻, can be ignored. Isotope scrambling in C₃H₂⁺ + HD has been studied carefully in a separate experiment and found to be slower than 4 × 10⁻¹⁶ cm³ s⁻¹.

Since the model contains ten fitting parameters (p, k₁ - k₉) it has been decided to perform additional independent measurements. For determining the branching ratio the HD number densities have been reduced to such low values that secondary reactions finally can be neglected. Using partial HD pressures down to the background pressure, a reliable value p = 0.45 have been determined. A complete new reaction network has been examined by preparing externally C₃H⁺ instead of C₃⁺. After mass selection these ions are injected into the trap containing HD under similar conditions. A selection of reactions in Table 2 together with the rate coefficients needed for fitting the data in Fig. 4. Comparison of the two rows reveals that the parameters needed to describe the C₃⁺ + HD network are different from those determined from the C₃H⁺ + HD studies. In some cases, the rate coefficients become larger, in others smaller. The changes are in accordance with the general temperature dependence of the competing channels. Hydrogen abstraction (k₃) and k₉) is faster with the excited C₃H⁺ ions produced in C₃⁺ + HD reactions than with the thermalized ones. In analogy it is not surprising that radiative association of C₃H⁺ with HD is slower for hot C₃H⁺ ions.

**Table 2** Comparison of rate coefficients² of thermalized and excited ions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Thermal</th>
<th>Excited</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H⁺ + HD → C₃D⁺ + H₂</td>
<td>5.6(–11)</td>
<td>4.0(–11)</td>
</tr>
<tr>
<td>→ C₃HD⁺ + H</td>
<td>4.6(–10)</td>
<td>2.7(–10)</td>
</tr>
<tr>
<td>→ C₃H₂⁺ + D</td>
<td>3.0(–12)</td>
<td>9.0(–12)</td>
</tr>
<tr>
<td>→ C₃H₂D⁻ + hν</td>
<td>3.2(–11)</td>
<td>—</td>
</tr>
<tr>
<td>C₃D⁺ + HD → C₃HD⁺ + D</td>
<td>1.0(–10)</td>
<td>6.0(–11)</td>
</tr>
<tr>
<td>→ C₃D₂⁺ + H</td>
<td>8.3(–11)</td>
<td>2.3(–10)</td>
</tr>
<tr>
<td>→ C₃HD²⁻ + hν</td>
<td>8.0(–12)</td>
<td>4.1(–12)</td>
</tr>
</tbody>
</table>

² Rate coefficients k = a × 10⁻ᵇ are presented as (a-b). These data have been obtained by producing externally the hydrogenated ions and using a He pulse for relaxation. 'C₃D⁻' has been produced by D-H exchange with C₃H⁺. This may not lead to fully thermalized ions; however, the exothermicity is much lower than starting with C₃⁺. Rate coefficients, needed for fitting the measurements shown in Fig. 4. In this case the injected C₃⁺ are cold, however, the subsequent products are formed in very exothermic reactions and are therefore excited. This can be seen from the significantly deviating results.
Although in principle possible, it has not been attempted to get information on the relaxation process or answering the question, how the excess energy of 197 kJ mol\(^{-1}\) provided by reaction (1) is distributed between internal excitation and kinetic energy. Also the results entered for \(C_3D\) ions in the left row in Table 2 may not be completely thermalized since they are formed by \(H-D\) exchange; however, energy is gained only from the differences in zero point energy which leads to rather cold ions. Therefore these values have been included into Table 1. Note that the influence of excited intermediate products also has been observed and discussed in the stepwise hydrogenation of \(N^+\) stored in \(H_2\).

4. Discussion

4.1. \(Cs^+ + H_2\) and HD

Previous results. The hydrogenation of carbon-cluster ions has been studied rather often. As mentioned above a number of methods and neutral precursors have been used to create the ions; however, no conclusive information on any specific isomer or on metastable excited states has been obtained. Inspection of Fig. 2 and Table 1 reveals that the room temperature values vary between 1.8 and 4.6 \(\times\) \(10^{-10}\) \(cm^3\) s\(^{-1}\). Taking a closer look at all data it can be supposed that internally excited ions react slower and that the same holds for kinetic energy. Rate coefficients obtained with ICR cells are all rather small indicating that the ions remain in this experiment more or less excited depending on the production mechanism. Flow systems usually reach thermal conditions; however, it has been noted in ref. 11 that vibrational quenching of \(C_3^+\) may not be efficient enough in helium carrier gas and that other molecules such as \(N_2\) should be added for relaxation. This may partly explain why our 300 K trap rate coefficient is larger than the SIFT results. Trapping experiments are especially simple to perform if the excited ions react slower. In such a case one can follow the exponential decay of the primary ions at rather high number densities over very long times leading finally to thermal conditions. The so far unanswered question, why, despite the large exothermicity of 197 kJ mol\(^{-1}\), \(C_3\) reacts with \(H_2\) only at a fraction of the Langevin rate coefficient, \(k_L = 1.5 \times 10^{-12}\) \(cm^3\) s\(^{-1}\), will be discussed below.

The importance of determining temperature dependent rate coefficients for carbon-cluster cation has been emphasized by Bohme and Wlodek;\(^7\) however, there have been no experiments published with \(C_3^+\) below 300 K. For \(C_4^+\) a steep temperature increase, \(k \approx T^{-1}\), was found by Giles et al.\(^{11}\) cooling the SIFT down to 80 K. The fact that \(C_3^+\) reacts at 10 K with the Langevin rate or may be slightly faster was observed in the previous 22-pole ion-trap experiment\(^{13}\) focusing on the reactivity of \(C_3H^+\). The error of the absolute values, included in Table 1, are somewhat larger than the standard uncertainty of 20% since the measurements have been performed at densities of a few \(10^9\) \(cm^3\) only. An important result from these 10 K studies is that there is no influence of the rotation of hydrogen: \(p\)-\(H_2\) and \(n\)-\(H_2\) react with the same rate coefficient. As far as they can be compared, all previous results are in accord with our data for \(C_3H^+\) formation. New and surprising is the increase \(k \approx T^{-0.69}\) up to 50 K reaching then the Langevin capture rate coefficient, within our experimental error of 20%. For the collision system \(C_3^+ + D_2\) and also for \(C_3^+ + HD\) similar observations have been made. The measured rate coefficients are slightly smaller; however, the decrease is in full accordance with the mass dependence of the capture cross section. Therefore, the use of deuterated target does not give additional hints to the reaction mechanisms, especially tunneling seems to play no role. An interesting observation is the isotope anomaly in \(H\) or \(D\) abstraction for \(C_3^+ + HD\) collisions. The measured isotope ratio, \(\frac{C_4D^+}{C_3H^+} = 1.22\), is in contradiction to a simple classical picture which is based on the anisotropy of the interaction potential and which orients the HD such that \(H\) abstraction would be favored in a direct reaction. For more details on deuteration see ref. 5.

Long-lived complex: association, isomerization? The first argument always used for explaining the increase of reactivity with decreasing temperature is the increase of the mean lifetime of the collision complex. In \(C_3^+ + H_2\) collisions, long-lived intermediates can be formed since there are several strongly bound \(C_3H_2^+\) ions with various stable structures\(^{14}\) including the cations of cyclopentenylidene, propargylidene, propadienylidene, and propadienylidene, the cyclic one being the most stable. For getting a net effect for the reaction outcome, other time dependent mechanisms must play a role. An obvious example is the radiative association process, where the emission of a photon occurs usually very slowly, especially if only infrared transitions are involved. This can be presupposed in the present case. Assuming a typical upper limit for the radiation rate, \(10^3\) s\(^{-1}\), it can be concluded from the number of \(C_3H_2^+\) produced at low temperatures that there must be \(C_3^-\)\(-H_2\) collision complexes living longer than \(5 \times 10^{-3}\) s. Similar arguments could be used for explaining the \(5\% \ C_3H_2^+\) products, formed in the high pressure SIFT environment via ternary association, even at 300 K! Within such a, certainly oversimplified, model one could try to explain the \(C_3H^+\) formation. For this one first has to find out why the internal reorganization and isomerization steps, leading finally to hydrogen abstraction, require an interaction time of \(\mu\)s. Secondly one has to search for arguments, why a significant fraction of the formed collision complexes really live so long at temperatures of 50 K and below although there must be a classically open pathway towards the very exothermic product channel. The fact that the reaction finally occurs with the collision rate allows the assumption that no substantial barrier has to be overcome by the reactants to reach the long-lived collision complex. In detail, however, such a speculative reaction model has to be founded on details of the potential energy surface such as small barriers, bottleneckes, small sub-spaces of the phase space, dynamical constraints etc. A similar discussion follows below for abstracting the second hydrogen atom.

Structure of \(C_3^+\). A slightly different approach in finding some explanations for the low temperature behavior of \(C_3^+\) interacting with \(H_2\) is based on the structure of this ion. But also in this case only speculative conclusions can be drawn since the ground state potential energy surface is not known with the required accuracy. The past 20 years have seen many theoretical and experimental efforts aiming to determine the structures of carbon clusters and cluster ions. In the case of \(C_3^+\) both linear and bent geometries were in the discussion as briefly mentioned in ref. 35. Grev et al.\(^{36}\) stated in the title of their publication that “the \(C_3^+\) cation is bent”. This statement was corroborated in most of the later \(ab\) \(initio\) quantum mechanical studies of the \(C_3^+\) molecular structure, see for example refs. 37 and 38, and references therein. In general the reported bond angles are 5° to 10° larger than in an equilateral triangle and the \(C-C-C\) distance increases by only a few hundreds of an Å going from the linear to the bent structure, reaching values slightly above 1.3 Å. More important than this facts is for our experiments that the relative energies are very close to each other and allow for a very facile isomerization, probably also below room temperature. As can be found for example in the Table 3 of ref. 37, the linear form of \(C_3^+\) \((\Sigma_u^+, \Omega_{2v}^\text{1h}, \text{symmetry})\) lies just 4 kJ mol\(^{-1}\) above the bent structure \((\Omega_u^0, \Omega_{2v}^\text{1h}, \text{symmetry})\) and the transition state \((\Omega_u^0, C_3\text{ symmetry})\) for interconversion between these two isomers is just 5 kJ mol\(^{-1}\) high.

As already discussed above, there have been many experimental approaches to get structural information on this simple
triatomic ion. All approaches to use various production mecha-
nism including laser evaporation of solid state material or
dissociative electron ionization of linear, cyclic or branched
molecules did not lead to any correlation, e.g. with the
reactivity of the ions. Also more sophisticated mass spectro-
metric approaches such as collisionally activated dissociation
(CAD) or neutralization-reionization of C3+ did not provide
any conclusive information on the structure. It is rather certain
that all techniques used, including also Coulomb explosion,
suffered from “hot” or “warm” ions. The result shown in
Fig. 2 may be taken as an indication that the ions have to be
cooled down below 50 K if one wants to see a stable structure
and that at higher temperatures soft bending modes are excited
to large amplitude motions avoiding most time the optimum
configuration for breaking the hydrogen bond. If one follows
the arguments given in ref. 7 that the arrangement of the three
carbons in a ring reduces the reactivity, one may conclude that
the probability to find the C3+ ion in a near-linear structure
with carbene character at each end may become larger if
one approaches the ground state. In order to predict this, more
precise potential surfaces and exact zero point energies are
required. Also 13C isotope substitution may lead to additional
hints37 how this floppy molecule really looks like in the ground
state; however, experiments must be performed at low tem-
peratures.

4.2. C3H+ + H2 and HD

Previous results. Due to its relevance to carbon chemistry in
space and in combustion, the collision system C3H+ + H2 has
been studied rather often. Early measurement31,39 which have
been performed in a SIFT at various temperatures have been
discussed in refs. 27 and 40. The data are not included here
since the high pressure flow tube environment has lead to
saturated three-body association and hydrogen abstraction
has been suppressed significantly. This competition has been
verified by pressure dependent measurements performed over a
wide range in an 80 K ion trap.14 The increase of the He
number density leads to an increasing production of C3H+ at
the expense of C3H2+, the sum of both channels remaining
nearly constant up to [He] = 1018 cm−3. Due to the tempera-
ture dependence of the lifetime of the intermediate complex,
the suppression of C3H2+ formation increases with decreasing
temperature. This has lead to the erroneous conclusion that
formation of C3H2+ + H is endothermic by 4 kJ mol−1.39 Ab
initio calculations52 obtained later the same value, or an even
higher endothermcity of 7 kJ mol−1.39 It has been realized that
the theoretical results are in obvious discrepancy with an 80 K
ring electrode trap experiment14 and it has been proposed by
Maluendes et al.30 that more studies between 10 K and 300 K
should be undertaken to give some further guidance to ab initio
calculations. This has been done in the 22-pole ion trap
apparatus used also in the present work.12 Unfortunately, the
important results have been overlooked in later publications,
e.g. in the compilation reported by McEwan et al.97 Results
reported in ref. 12 are included in Fig. 3 with open symbols. These experiments have been performed both with p-H2 and n-H2 while in the present work, the measurements
have been repeated only with n-H2 target gas. As can be
seen, there is a good overall agreement. The previous data go
down to 10 K while in the present work the temperature range
has been extended up to 300 K. It is obvious that cold
conditions favor both channels. At 300 K both rate coefficients
sum up to only 2% of the collision rate while this fraction
remains almost 20% at 20 K. Above 50 K hydrogen abstraction
varies proportional to 1/T while radiative association shows a
much steeper dependence. All relevant parameters can be
found in Table 1. The low temperature branching ratio be-
tween the two channels has been proven to be independent on
the hydrogen number density between 109 and 1015 cm−3. As

![Fig. 6 Assumed potential energy curves along the reaction path for various isotope combinations of the reaction C3H+ + H2 → C3H2+ + H. The aim of this plot is to illustrate schematically energy shifts caused by the zero point energies in the transition barriers.](image-url)
either a slow transition towards the strongly bound intermediate or a decay back to the reactants leads to the observed result, that the rate coefficient for product formation is a only fraction of the Langevin value. It also can explain the strong temperature dependence. In the strongly bound complexes, decay toward products, stabilization by association or also dissociation competes. Within this model, the isotope effects are caused not only by the differences in zero point energies in the reactants and products but also by the assumed mass dependent shifts in the transition states.

**Reverse reactions.** In order to get additional information on this complicated interplay, it is interesting to study the reverse processes of reactions (3) and (4). C\(_3\)H\(_2\)+ + H has been studied several times, some results are presented in refs. 9 and 41. Since these results are from high pressure SIFT studies, ternary processes prevail. In addition, the energy content of the ions at 300 K is higher than the barriers or endothermicities which are needed to explain the results from this work. Studies with cold trapped ions interacting with a slow beam of hydrogen atoms are in progress in this laboratory, first results for CH\(_3\)+ + H have been obtained.\(^3\) The VUV photochemistry of the propargyl radical, C\(_3\)H\(_2\), has been investigated recently using synchrotron radiation.\(^4\) At photon energies above 15.5 eV only traces of C\(_3\)H have been detected in dissociative photoionisation and it has been concluded that formation of C\(_3\)H\(_2\)+ + H is kinetically strongly favored. This supports our observation that reaction (3) is slightly exothermic from the left to the right. Table 1 also contains some results for reactions of C\(_3\)H\(_2\)+ with n > 1. They are all rather slow but measurable with the present instrument. These observations are in accordance with calculations\(^5\) which predict, despite the large exothermicity, a significant barrier. In room temperature measurements\(^6\) products from C\(_3\)H\(_2\)+ + H\(_2\) have not been detected. The same holds for the C\(_3\)H\(_2\)+ + D\(_2\) collision.\(^7\) It has been shown that products from C\(_3\)H\(_2\)+ + H\(_2\) interactions appear only at elevated kinetic energy.\(^8\)

5. **Conclusions**

In order to study in more detail the formation of small hydrocarbons at low temperatures, a dedicated research program has been started in our laboratory based on ion trapping and atomic and molecular beam methods.\(^3,4,21,43\) In addition to results obtained for reactions between stored ions and neutral carbon atoms and clusters, the present work has focused on the interaction of C\(_n\)H\(_n\)+ ions with hydrogen and deuterated variants. The experiments have been performed in the variable temperature 22-pole ion trap (TV–22PT). The observed temperature dependences are tentatively explained with the complex lifetime which may depend on the total or specific energies, with barriers or bottle necks and competition between various decay channels. The studies provided many surprising results which are, among others, of central importance for astrochemical applications.\(^7\)

For obtaining information on the structure of the involved ions and for better understanding the reaction dynamics, more precise quantum-chemical calculations are needed. It should be possible today to get the asymptotic energies, e.g. of reaction (3), with the required accuracy or to make a significant step forward to determine the features of a C\(_3\)\(^+\) ion thermalized at 50 K. More demanding and challenging for ab initio calculations is to find and characterize, with meV accuracy, the critical regions of the potential surface which have been introduced in the discussion section in a speculative way for explaining the present experimental observations, especially the complicated isotope effects. Provided that all details of the potential energy surface are available, detailed dynamical calculations would be needed. In the present situation, dealing with low temperature ion-molecule reactions with long lived and strongly interacting collision complexes, statistical theories may be a suitable or most probably a necessary alternative.

It has been concluded in several papers,\(^11,7,8\) summaries\(^9\) that reactions of carbon and hydrocarbon ions with hydrogen have been well studied, but it has to be emphasized that this holds only for energies at room temperature and above. The present work clearly indicates the need of a systematic study of these clusters over a wide range of temperatures. Several general conclusions have been made for C\(_n\)H\(_n\)+ as a function of n and m. For example the reactivity of pure carbon clusters decreases as n increases up to 9 or 10 where it becomes non-measurable using an ICR trap. Is this also true at 10 K? The statement that C\(_n\)H\(_n\)+ ions via radiative association. An interesting but even more complex project is the in situ synthesis of branched carbon structures by adding carbon atoms to cold trapped ions. The first tests performed into this direction indicate the feasibility of such experiments.\(^4\) Very interesting from a dynamical point of view is also the C\(_3\) elimination, observed for C\(_4\)+ and C\(_5\)+ + D\(_2\).\(^45\)

Another class of reactions which is of huge importance for astrochemistry is the addition of CO molecules to hydrocarbon ions since atom abstraction from this strongly bound molecule is endothermic for all C\(_n\)H\(_n\)+. The results reported so far from SIFT measurements show partial saturation and as indicated in the present work, the extrapolation of such measurements to the low temperature and low density conditions of interstellar clouds is very uncertain. Preliminary ion trap results for CH\(_3\)+ + CO have been reported recently.\(^46\)

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**References**
