

LOW-TEMPERATURE EXPERIMENTS ON THE FORMATION OF DEUTERATED $C_3H_3^+$

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ABSTRACT

Many deuterated molecules have been discovered in inter- and circumstellar regions. In some cases, the observed abundances can be explained with simple thermodynamic models; often, however, isotope enrichment is more complicated. This has been seen recently in detailed low-temperature experiments performed for the fundamental systems H_3^+/H_2D^+ and $CH_n^+/CH_{n-1}D^+$. An unsolved problem is to explain the large abundance of C_3H_2 and larger hydrocarbons and their deuterated variants observed in cold, dark interstellar clouds. In this work a variable-temperature 22 pole trap is utilized for closely scrutinizing various ion-molecule reactions that may contribute to the formation of $C_3H_2D^+$ or $C_3HD_2^+$ and, via dissociative recombination, C_3HD . The experimental study of the promising candidate $C_3H_3^+ + HD \rightarrow C_3H_2D^+ + H_2$, which has already been excluded by theory, corroborates that this exothermic H-D exchange does not occur at all. A careful analysis of the data reveals that the 15 K rate coefficient is smaller than $4 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$. In contrast, quite efficient routes have been found in the low-temperature experiments, starting with C_3^+ and proceeding via deuterated C_3H^+ to $C_3H_2^+$ and $C_3H_3^+$. Formation of C_3D^+ in $C_3^+ + HD$ collisions is 6 times faster than assumed in astrochemical models ($k = 9.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$). Surprisingly, direct production of C_3HD^+ via radiative association has also been observed ($k_r = 6.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$). Reactions of partly or fully deuterated $C_3H^+ + H_2$ collision system are strongly dependent on temperature and the hydrogen ortho to para ratio. In addition, it shows very complicated isotope effects. For example, in $C_3H^+ + HD$ collisions the formation of C_3HD^+ ($k = 4.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) dominates over the H-D exchange ($k = 5.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) and radiative association $C_3H_2D^+$ ($k_r = 3.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$). The reactions of $C_3H_2^+ + H_2$ are very slow for all isotope combinations. Although several questions remain open and more low-temperature experiments are needed, it is recommended that the new values are included in astrochemical databases, since they are fundamental to the correct description of the carbon chemistry in interstellar clouds.

Subject heading: astrochemistry — ISM: molecules — methods: laboratory

1. INTRODUCTION

1.1. Isotope Fractionation in General

A theoretical and experimental understanding of isotope fractionation is of central importance for modeling deuterium enrichment in molecules occurring in cold regions of interstellar space. Many singly and several doubly deuterated isotopomers have been detected in low-temperature interstellar clouds and meanwhile even fully deuterated ammonia has been found. There are molecules for which the DX/HX abundance ratio is a factor of 10^4 larger than the D/H elemental ratio, which is typically 2×10^{-5} in our galaxy (Roueff et al. 2000; Loinard et al. 2001; Millar 2002). Important in producing deuterium-containing species are exothermic exchange reactions between ions and HD or D. In addition, it is believed that D_2 molecules play a non-negligible role in the deuteration chemistry of cold, dark molecular clouds.

In general, the well-known difference in zero-point vibrational energy of the involved molecules determines the exothermicity of an H-D exchange reaction. Until recently it was generally accepted that, in the absence of an activation barrier, the reactions proceed much faster in the exothermic direction than in the opposite one and that the thermodynamic DX/HX ratio can be reached after an adequate time. However, dedicated low-temperature experiments have shown (Gerlich et al. 2002; Asvany et al. 2004a, 2004b) that there can be significant deviations from such simple models. This may be due to subtle details of the potential energy surfaces such as small barriers or bottlenecks that are not yet known with the accuracy required for low-temperature reactions. In addition, it is rather sure, al-

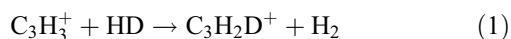
though not yet understood quantitatively with the exception of simple systems (Gerlich 1990), that symmetry selection rules play a pivotal role in replacing one or more atoms in a group of identical atoms by isotopes, or vice versa. The conservation of the total nuclear spin can have very restrictive consequences (Gerlich 2004). In this context it must be mentioned that traces of o- H_2 are of exceptional importance in deuteration, since they contribute not only rotational energy but also $I = 1$ to the total nuclear spin of the collision complex (Gerlich & Schlemmer 2002).

1.2. C_3H_2 Abundance and C_3HD/C_3H_2 Ratio

A variety of gas-phase and grain surface mechanisms processing hydrocarbon molecules and their deuterated analogues have been included in models of interstellar clouds (Millar et al. 1989; Roberts & Millar 2000a, 2000b; Millar 2002). For many species, including isotopomers, quantitative predictions have been made; however, there are several unsolved problems. A rather basic example is the large observed abundance of C_3H_2 and C_4H in photodominated regions. In a discussion of recent progress of interstellar carbon chemistry, Gerin et al. (2003) state that the currently known carbon inventory is not complete. The observed spatial correlations of various hydrocarbons are very critical tests of our understanding of the carbon chemistry. From the fact that in clouds, in contrast to models, more hydrogenated carbon species are present than pure carbon molecules, we conclude that important formation routes are ignored or that the used rate coefficients are inaccurate.

Another example is the large deuterium fractionation of c- C_3H_2 in TMC-1. Values measured for the C_3HD/C_3H_2 ratio vary

from 0.08 to 0.16 depending on the position (Bell et al. 1988); Turner (2001) reports 0.048. Theoretical predictions are below 10^{-2} (Millar et al. 1989; Roberts & Millar 2000a). In order to increase the C_3HD/C_3H_2 abundance ratio resulting from the models, it was suggested by Howe & Millar (1993) that the reaction

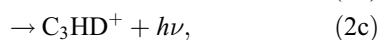
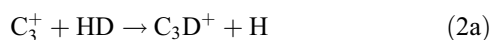


may occur rapidly at low temperatures and that the under-represented C_3HD is formed via dissociative recombination of $C_3H_2D^+$. This suggestion has been excluded later by Talbi & Herbst (2001) using quantum chemical calculations. Because of a very high transition barrier, the rate coefficient for $C_3H_2D^+$ formation is negligible at room temperature and below and, therefore, reaction (1) has been removed from modern models. However, it is always advisable for such rather complicated chemical systems to check independently whether there is really no low-energy pathway for H-D exchange. In this contribution, the theoretical conclusion is corroborated by a low-temperature trapping experiment.

1.3. New Routes in Forming Hydrocarbons and Deuterated Variants

Since deuteration via reaction (1) is completely negligible, there must be other ways leading to deuterated C_3H_2 in the observed abundances. In this context, one has to ask the general question of whether important pathways for producing hydrocarbons are unknown or ignored in general. Besides the gas-phase ion chemistry, the subject of this paper, there may be rather efficient neutral reactions involving radicals (Kaiser 2002). In addition, there is plenty of room for speculation about the chemistry occurring in and on grain ice mantles; there is observational evidence that deuterated carbonaceous species are released from the solid phase into the gas phase (Markwick et al. 2001, 2002). In order to explore in more detail astrochemically important reactions involving carbon atoms and molecules, a specific research program has been started in our laboratory based on ion trapping and atomic and molecular beams (Čermák et al. 2002; G. Borodi et al. 2005, in preparation). In addition to reactions with neutral carbons (Savić et al. 2005), new experiments with C_3^+ , C_3H^+ , and $C_3H_3^+$ interacting with hydrogen molecules have been performed (Savić & Gerlich 2005). In this contribution, selected experimental data are presented and discussed that are important for producing small deuterium-enriched hydrocarbons at low temperatures.

The exothermic reaction $C_3^+ + H_2 \rightarrow C_3H^+ + H$ is included in the UMIST database (Le Teuff et al. 2000) with a temperature-independent rate coefficient of only $k = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Experiments reveal that this basic process is strongly temperature dependent and that the reaction reaches a value of $k = 1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ below 50 K (Savić & Gerlich 2005). Also, the rate coefficients for deuteration via

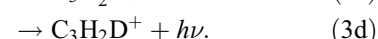
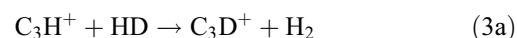


which are reported in this contribution, are fast at low temperatures.

The collision system $C_3H^+ + H_2$ is of central relevance for carbon chemistry, e.g., for synthesizing *c*- C_3H_2 (Adams & Smith 1987). The question of which products are directly formed has a long history. Early measurements that have been

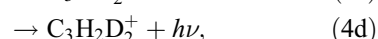
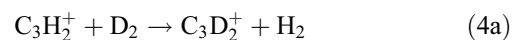
performed in a SIFT (selected ion flow tube) at 550, 300, and 80 K have been discussed in Herbst et al. (1983) and re-evaluated in Herbst et al. (1984). Difficulties in interpreting the results originated from the fact that, in the high-pressure flow tube, most collisions lead to $C_3H_3^+$ via saturated three-body association reaction and, therefore, hydrogen abstraction is almost completely suppressed. This hypothesis has been proven experimentally in an 80 K ion trap experiment (Gerlich & Horning 1992), which provided clear evidence that at low densities the $C_3H_2^+$ product prevails. The fact that in the flow tube less $C_3H_2^+$ was formed at lower temperatures has led to the erroneous conclusion that the formation of $C_3H_2^+ + H$ is endothermic by 4 kJ mol⁻¹ (Smith & Adams 1984). Several ab initio calculations later obtained the same value (Wong & Radom 1993), or an even higher one of 7 kJ mol⁻¹ (Maluendes et al. 1993a).

Many of the conclusions and assumptions are in conflict with experiments performed in a 22 pole trap at temperatures reaching down to 10 K and at buffer gas densities below 10^{12} cm^{-3} (Sorgenfrei & Gerlich 1994). The results obtained for a wide range of temperatures and densities clearly show that the hydrogen abstraction reaction increases with decreasing temperature down to 20 K, indicating a way to the products that is at least thermoneutral. The formation of $C_3H_3^+$ via radiative association shows a stronger temperature dependence and dominates finally at 10 K. Additional information on the energetics and dynamics has been obtained in Sorgenfrei & Gerlich (1994) by using *n*- H_2 and *p*- H_2 as a reactant and by studying the isotope combinations $C_3H^+ + D_2$ and $C_3D^+ + D_2$. Unfortunately, all these results have been ignored in the relevant literature, which has been summarized in Scott et al. (1997) and recently in McEwan et al. (1999). The data, e.g., the fundamental rate coefficient for the radiative association of $C_3H^+ + p\text{-}H_2$, also did not find its way into the UMIST database (Le Teuff et al. 2000). Because of the central importance of this collision system, the $C_3H^+ + H_2$ measurements have been reproduced and extended (Savić & Gerlich 2005) and, in addition, the following reaction channels have been studied at 15 K:



As outlined in the discussion section, reaction (3b) and the radiative association (3d) will play an important role in forming deuterated ions at low temperatures.

In contrast to the fast reactions measured for systems that were believed to be endothermic, almost no product formation has been observed for $C_3H_2^+ + H_2 \rightarrow C_3H_3^+ + H$, which is, without any doubt, exothermic for both isomers (Wong & Radom 1993). Experiments performed with different isotope combinations, e.g.,



have revealed that these reactions are so slow that they can be ignored in astrochemical models. An explanation for this is a barrier that has been calculated to be 9 kJ mol⁻¹ high (Wong &

TABLE 1
SELECTED REACTION RATE COEFFICIENTS

Reactions	k ($cm^3 s^{-1}$)	T (K)	Remarks
$C_3^+ + HD \rightarrow C_3D^+ + H$	9.3E-10	15	1
$C_3^+ + HD \rightarrow C_3H^+ + D$	7.6E-10	15	1
$C_3^+ + HD \rightarrow C_3HD^+ + h\nu$	5.9E-11	15	1
$C_3H^+ + HD \rightarrow C_3D^+ + H_2$	5.6E-11	15	1
$C_3H^+ + HD \rightarrow C_3HD^+ + H$	4.6E-10	15	1
$C_3H^+ + HD \rightarrow C_3H_2^+ + D$	3.0E-12	15	1
$C_3H^+ + HD \rightarrow C_3H_2D^+ + h\nu$	3.2E-11	15	1
$C_3H^+ + D_2 \rightarrow C_3D^+ + HD$	3.0E-13	10	2
$C_3H^+ + D_2 \rightarrow C_3HD^+ + D$	1.0E-11	10	2
$C_3H^+ + D_2 \rightarrow C_3D_2^+ + H$	2.7E-11	10	2
$C_3H^+ + D_2 \rightarrow C_3HD_2^+ + h\nu$	4.0E-12	10	2
$C_3D^+ + HD \rightarrow C_3HD^+ + D$	1.0E-10	15	1, 3
$C_3D^+ + HD \rightarrow C_3D_2^+ + H$	8.3E-11	15	1, 3
$C_3D^+ + HD \rightarrow C_3HD_2^+ + h\nu$	8.0E-12	15	1, 3
$C_3D^+ + D_2 \rightarrow C_3D_2^+ + D$	1.7E-10	10	2
$C_3D^+ + D_2 \rightarrow C_3D_3^+ + h\nu$	1.3E-10	10	2
$C_3H_2^+ + H_2 \rightarrow C_3H_3^+ + H$	1.7E-13	15	1
$C_3H_2^+ + D_2 \rightarrow C_3D_2^+ + H_2$	1.7E-14	10	2
$C_3H_2^+ + D_2 \rightarrow C_3HD^+ + HD$	3.0E-15	10	2
$C_3HD^+ + D_2 \rightarrow C_3HD_2^+ + D$	1.0E-14	10	2
$C_3D_2^+ + D_2 \rightarrow C_3D_3^+ + D$	1.0E-16	10	2
$C_3H_3^+ + HD \rightarrow C_3H_2D^+ + H_2$	<4E-16	15	1
$C_3H_3^+ + HD \rightarrow C_3H_4D^+$	1.5E-16	15	4

NOTES.—Selected reaction rate coefficients that are relevant for forming deuterated $C_3H_3^+$ at the indicated nominal temperatures. Remarks: (1) Results measured in the 22 pole trap at 15 K with pure HD (Savić & Gerlich 2005). (2) Data taken from Sorgenfrei & Gerlich (1994) and Sorgenfrei (1994). (3) Rate coefficients deduced from C_3D^+ intermediate products; for details, see Savić & Gerlich (2005). (4) Effective association rate coefficient measured at $[HD] = 10^{12} cm^{-3}$.

Radom 1993). Nonetheless, finite rate coefficients have been measured at low temperature for various isotope combinations, indicating that there must be some ways to circumvent the barrier or to tunnel through it.

In the next section a few short remarks concerning the experimental technology are made and three typical examples of raw data are given in order to provide evidence for the sensitivity, the reliability, and in some cases the complexity of the 22 pole trapping method. The results, which are put together in Table 1, are discussed in § 3. In this part more information on the reaction dynamics is added, which is mainly based on speculative details of the potential energy surfaces or on symmetry selection rules affecting the branching ratios in H-D scrambling. Some hints as to the astrochemical consequences of our low-temperature results are given.

2. EXPERIMENTAL AND TYPICAL RESULTS

2.1. 22 Pole Ion Trap

All laboratory measurements presented in this paper and the related work (Savić & Gerlich 2005) have been performed in the variable temperature radio frequency (RF) 22 pole ion trapping apparatus, most details of which have been described thoroughly in Gerlich & Horning (1992) and Gerlich (1995). Many additional hints can be found in other publications (Paul & Gerlich 1994; Schlemmer et al. 1999; Gerlich et al. 2002; Asvany et al. 2004a). In the trap, the ion cloud is confined in the radial direction by an effective potential that is created by the electric multipole field alternating in time and space. In the axial direction the storage volume is bordered by small potential

barriers created by suitable voltages applied to the gate electrodes located at the two ends of the trap. Each of the two sets of 11 electrodes is press-fitted into two copper electrodes that are mounted onto a closed cycle refrigerator. Thin sapphire plates are used for electric insulation and good thermal contact. The trapping volume is enclosed by copper walls. In order to achieve low temperatures (the present experiments have been performed at 15 K in order to avoid condensation; 5 K has been reached recently using a new cold head) the trap is surrounded by a second thermal shield held at ~ 50 K. The temperature is usually measured using a carbon resistor, a calibrated diode, or a hydrogen gas thermometer.

2.2. Measuring Procedure

Primary ions $C_3H_n^+$ ($n = 0-3$) have been produced by electron bombardment in a differentially pumped RF storage ion source using different precursors. The extracted ions are mass selected in an RF quadrupole optimized for an adequate mass resolution in the range from 36 to 39 amu on one side and for transferring the selected ions efficiently into the trap on the other side. Already in the storage ion source, several methods have been employed for chemically quenching those ions that have the same mass as the chosen $^{12}C_3H_n^+$ but contain ^{13}C or D isotopes. Adding small amounts of hydrogen gas to the hydrocarbon used as precursor has been found to work in certain cases (concerning isomers; see below). The selected ions are injected into the trap, where they are stored for times varying from a few milliseconds to tens of seconds. Directly after injection they are cooled down rapidly to the wall temperature by using a short (≈ 10 ms), intense He pulse. The neutral reactant gas is let into the trapping region via precooled tubes. The HD used (Cambridge Isotope Laboratories Inc.) has been tested in situ (Asvany et al. 2004a) to have a purity of 98%, with 2% of H_2/D_2 . After a given 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. The sequence of ion formation, injection, relaxation, reaction, and analysis is repeated many times for each mass and typically for 10 different storage times. As previously discussed, 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 maximum.

2.3. Preparation of Primary Ions and Isomers

Since C_3H^+ , $C_3H_2^+$, and $C_3H_3^+$ have cyclic and noncyclic isomers, several tests based on reactions in the trap have been performed in order to determine the possible presence of excited isomers. In the case of C_3H^+ the cyclic form is 220 kJ mol $^{-1}$ higher than the linear one and none of the tests indicated the presence of excited ions in the present experiment. It is a general experience with the storage ion source that ions are quenched quite efficiently to the ground state. The situation is less clear for $C_3H_2^+$; however, it has been found that these ions always react very slowly, and therefore no additional tests have been performed. For preparing $C_3H_3^+$ ions, allene $CH_2 = C = CH_2$ (Aldrich, 97%) has been used as neutral precursor. Also, $C_3H_3^+$ exists in two different isomeric forms, the cyclic one being the ground state while the $H_2C_3H^+$ structure is 106 kJ mol $^{-1}$ higher in energy (Wyss et al. 2001). It is known from the literature (Smith & Adams 1987) that, under certain conditions, the ionization of methyl acetylene with 70 eV electrons results in $\sim 65\%$ c- $C_3H_3^+$ ions, while $\sim 35\%$ are “l”- $C_3H_3^+$. Since the

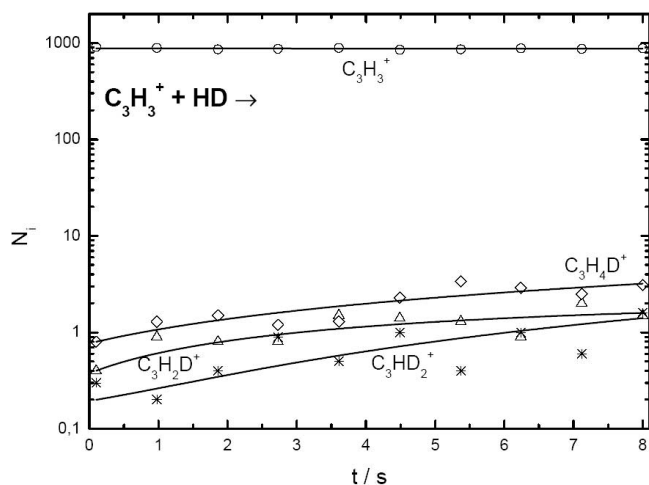


FIG. 1.—Average number of $C_3H_3^+$ and product ions as a function of storage time t ($T = 15$ K, $[HD] = 3.5 \times 10^{12}$ cm $^{-3}$). Even after $t = 8$ s, the number of injected primary ions (~ 1000 per filling) is almost unchanged, despite the rather large number density of the target gas. Minor traces of products are detected on the masses 40–42 amu. Details concerning the assignment to association ($C_3H_4D^+$), deuteration ($C_3H_2D^+$), and sequential deuteration ($C_3HD_2^+$) are discussed in the text. The solid lines are solutions of a system of coupled differential equations describing the reaction system.

reactivity of the linear ions is much higher than that of $c-C_3H_3^+$ (Auslos & Lias 1981; McEwan et al. 1994), it is possible to quench them in suitable collisions. In most trapping studies performed in our lab with ions produced in the storage source, only mono-exponential decays have been observed, one exception being $C_3H_2^+$. This is taken as an indication that this type of ion source produces predominantly the lowest energy isomer. The chance that the reactivity of both isomers is the same over a wide range of temperatures is very low.

2.4. Typical Results

A set of data for reaction (1) that is typical for our trapping experiments is shown in Figure 1. Every 8 s a well-prepared number of $C_3H_3^+$ ions was injected into the trap, in average about $N_{i=1} = 1000$ per filling. Without any further analysis it becomes clear that the H-D exchange in $C_3H_3^+ + HD$ collisions is extremely slow, since the number of primary ions does not change from 1 to 8 s, although they undergo some 10^4 collisions with the abundant HD gas ($[HD] = 3.5 \times 10^{12}$ cm $^{-3}$). A careful analysis of the time dependence indicates a minor decay of $C_3H_3^+$. Since this loss may not be only due to reactions, it is more reliable and also more sensitive to evaluate the increase of product ions. As can be seen from Figure 1, traces have been found on masses 40–42 amu. Note that less than three ions per filling are produced in the 8 s from the initially injected $C_3H_3^+$. The ions found on mass 42 amu are assigned to $C_3H_4D^+$ formed by radiative and ternary association. The masses 40 and 41 amu can be associated with $C_3H_2D^+$ produced via reaction (1) and $C_3HD_2^+$ produced via a second deuteration step, respectively. A simple evaluation of the $C_3H_2D^+$ and $C_3HD_2^+$ products formed within the storage time from the primary ions (less than 3 from 1000) leads immediately to a rate coefficient of 1×10^{-16} cm 3 s $^{-1}$. This small value is already sufficient for completely excluding reaction (1) from astrochemical models; however, it is certainly a question of fundamental importance whether the H-D exchange in reaction (1) is completely forbidden or whether there are paths to form the exothermic deuterated product, e.g., via tunneling.

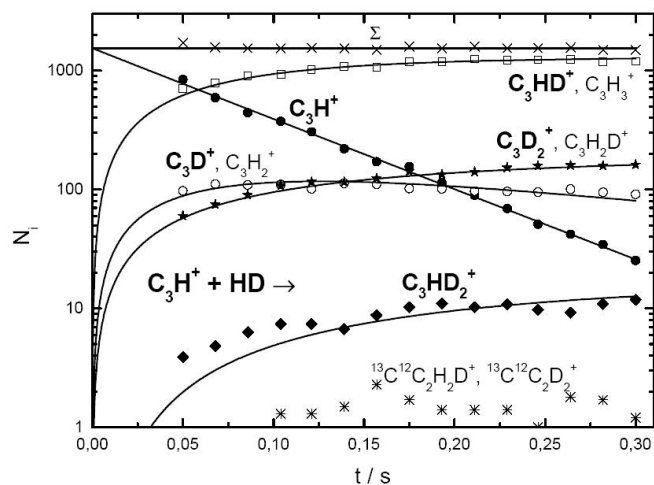


FIG. 2.—Time dependence of the average number of trapped ions as a function of storage time t ($T = 15$ K, $[HD] = 2.6 \times 10^{10}$ cm $^{-3}$). The injected primary C_3H^+ ions undergo a mono-exponential decay over 2 orders of magnitude. As can be seen from the indicated products, a rich chemistry is started with $C_3H^+ + HD$. The dominant product is deuteration leading to C_3HD^+ . Hydrogen abstraction leads to $C_3H_2^+$, which has the same mass as the H-D exchange leading to C_3D^+ . Another important channel is the formation of $C_3H_2D^+$ via radiative association. The solid lines are solutions of a system of coupled differential equations describing primary and secondary reactions also resulting in doubly deuterated products.

In order to determine more precisely such small rate coefficients, a complicated analysis of the data is required. There are several other reactions possible, e.g., the production of $C_3H_4^+ + D$. This channel and several others have been excluded from playing a role by injecting externally produced and mass-selected $C_3H_4^+$ ions into the trap and monitoring their reactions with HD under similar conditions. Other perturbations are due to minor traces of $^{13}CC_2H_2^+$, $^{13}C_2CH^+$, $^{13}C_3^+$, or C_3HD^+ mixed into the mass 39 amu primary beam, since some of them can react with HD via H-D exchange or hydrogen abstraction with rate coefficients that are 10^6 times larger. In addition, one must account for H_2 , D_2 (2%), and other impurities in the target gas. It is obvious that most of these effects actually reduce the reaction rate coefficient for reaction (1), derived from the measured data. Accounting quantitatively for a variety of such processes, the time dependence of the recorded masses has been modeled with an adequate system of coupled differential equations. A typical set of solutions is shown in Figure 1 as solid lines. The resulting rate coefficients are included in Table 1. Selecting the best quality measurements from various measurements performed under different conditions, we conclude that the rate coefficient for deuteration of $C_3H_3^+$ in collisions with HD is smaller than 1×10^{-16} cm 3 s $^{-1}$.

Figure 2 shows the time dependence of a variety of ions that are produced from initially injected C_3H^+ ions in sequential reactions with HD at 15 K. In comparison to Figure 1, a target density 2 orders of magnitude lower has been used, $[HD] = 2.6 \times 10^{10}$ cm $^{-3}$. Nonetheless, the primary ions disappear with a time constant of ~ 70 ms, indicating that fast reactions play a role. As already mentioned above, the mono-exponential decay over 2 orders of magnitude provides evidence that only ground-state isomers come out of the storage ion source. As can be seen from the various products indicated in the figure, a rich chemistry is started with the $C_3H^+ + HD$ collisions. Comparing the two initially dominant channels, deuteron abstraction, C_3HD^+ , and hydrogen abstraction, $C_3H_2^+$, shows that an incredible isotope effect has been discovered favoring deuteration. This is

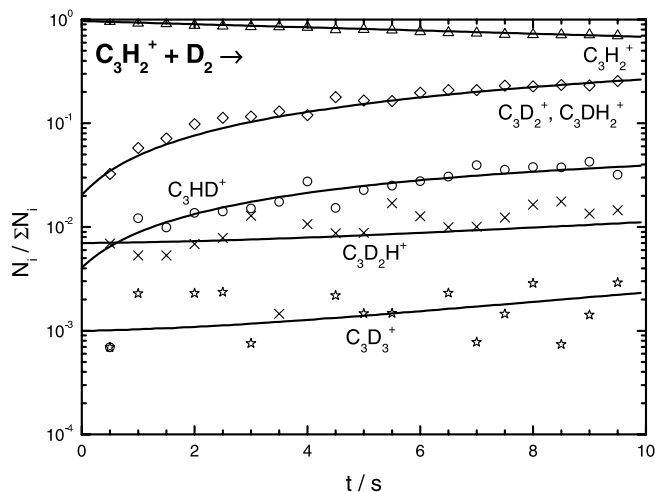


FIG. 3.—Average normalized number of $C_3H_2^+$ and product ions as a function of storage time t ($T = 10$ K, $[D_2] = 1.7 \times 10^{12}$ cm^{-3}). Despite the high number density and long storage times, only 30% of the primary ions react. The dominant product, mass 40 amu, is $C_3D_2^+$, formed via an H_2 - D_2 switching reaction. H-D exchange is significantly slower. Solutions from numerical simulation of the reaction system are shown as solid lines; the resulting rate coefficients can be found in Table 1.

especially obvious, since on mass 38 amu the dominant product is C_3D^+ , formed via H-D exchange. All relevant primary and secondary reactions have been modeled with a system of coupled differential equations. The solutions are shown in Figure 2 as solid lines; the resulting rate coefficients are included in Table 1.

A third example for reaction sequences occurring in the trap is shown in Figure 3 for $C_3H_2^+$ reacting with D_2 at 10 K. Various experiments have shown that the hydrogen abstraction reaction $C_3H_2^+ + H_2 \rightarrow C_3H_3^+ + H$ is very slow at room temperature (Smith & Adams 1984; Hansel et al. 1989; McEwan et al. 1999), while it becomes faster at elevated ion kinetic energies. The conclusion of an endothermicity of 17 $kJ\ mol^{-1}$ (Smith & Adams 1984) is in contradiction to a rate coefficient of 6×10^{-12} $cm^3\ s^{-1}$ measured at 80 K (Gerlich & Horning 1992) and to ab initio molecular orbital calculations (Wong & Radom 1993), which predict exothermicities of 8 and 91 $kJ\ mol^{-1}$ for forming l - $C_3H_3^+$ and c - $C_3H_3^+$ in collisions of l - $C_3H_2^+$ and c - $C_3H_2^+$ with H_2 , respectively. Obviously, the slow rates observed are due to a barrier of several $kJ\ mol^{-1}$. This is also in accordance with the results plotted in Figure 3. Despite the high number density of deuterium, $[D_2] = 1.7 \times 10^{12}$ cm^{-3} , only 30% of the $C_3H_2^+$ primary ions have been converted into products. Solutions from numerical simulation of the reaction system are shown as solid lines, the resulting rate coefficients can be found in Table 1. Note that the dominant product, mass 40 amu, is first produced via an H_2 - D_2 switching reaction; H-D exchange and reactions leading to $C_3H_mD_{3-m}^+$ are significantly slower.

3. DISCUSSION AND ASTROCHEMICAL CONSEQUENCES

The chemistry of hydrocarbon ions has been the object of many experimental and theoretical efforts until the early nineties; however, inspection of the relevant literature reveals that there was a certain stagnation in the last 10 yr. This is in contrast to the progress made in observations and therefore it is not surprising that chemical reaction networks are not (or not any more) able to describe the details of measured abundances. For observed molecules such as C_4H and C_3H_2 , Gerin et al. (2003)

wonder whether important reaction paths are missing or whether the relevant reaction rates are incorrect. The results reported in this work and for C_3^+ and $C_3H^+ + H_2$ in Savić & Gerlich (2005) provide a partial answer to these questions: our understanding of hydrocarbon reaction under interstellar conditions must be revised. In the following discussion several aspects of the hydrogenation or deuteration of $C_3H_n^+$ are discussed, going from $n = 0$ to 3. It has already been mentioned in the experimental section that all these ions have different isomers including cyclic, bent, and linear arrangements of the three carbon atoms. There is experimental evidence that the storage ion source produces ground-state isomers; however, no information has been obtained on the structure of the products, although the method of chemical probing could be used.

3.1. $C_3^+ + HD$

Hydrogenation of carbon clusters has been studied rather often. Despite an exothermicity of 195 $kJ\ mol^{-1}$ (Hansel et al. 1989), C_3^+ reacts with H_2 surprisingly slowly at room temperature. Published values vary between 1.8×10^{-10} and 4.6×10^{-10} $cm^3\ s^{-1}$, indicating that the reactivity may depend quite strongly on the way the experiments are performed. McEwan et al. (1999) report a value of $k = 2.4 \times 10^{-10}$ $cm^3\ s^{-1}$ in an overview summarizing the most recent knowledge concerning ion molecule reactions between $C_mH_n^+$ and hydrogen molecules and atoms. Our recent temperature dependent study (Savić & Gerlich 2005) has shown that C_3H^+ formation occurs with a rate coefficient of 1.7×10^{-9} $cm^3\ s^{-1}$ at temperatures below 50 K, a value that is, within our experimental error of 20%, in agreement with the capture rate coefficient. As discussed in detail in (Savić & Gerlich 2005), this temperature dependence may be due to the complicated ground-state potential energy surface of C_3^+ , which may lead to a linear structure if the ions are getting cold.

In addition, experiments have been performed for C_3^+ reacting with HD at number densities below 10^{10} cm^{-3} . The time dependence of the composition of the trap content (see Fig. 4 of Savić & Gerlich 2005) is very complicated, since even in the first step H or D atom abstraction competes with radiative association. As discussed in detail in Savić & Gerlich (2005), the evaluation of the kinetics is also complicated by the fact that the intermediate products formed in exothermic processes react with slightly different rate coefficients because of their internal excitation. In order to get precise information on the initial unperturbed C_3D^+/C_3H^+ branching ratio, extremely small amounts of HD have been used with partial pressures similar to the background gas.

As can be seen from the rate coefficients given in Table 1, formation of C_3D^+ via deuteron abstraction is slightly faster than hydrogen abstraction. This is in contradiction to a simple classical picture, which is based on the orientation of HD because of the anisotropy of the interaction potential. The separation of the center of charge and the center of mass orients the HD, especially if it is not rotating, such that the H atom is preferentially pointing toward the ion. This would lead to a branching ratio C_3D^+/C_3H^+ smaller than 1, while the measured value is 1.22. Therefore, it can be concluded that hydrogen abstraction does not occur in a direct way. This is corroborated by the temperature dependence of hydrogen abstraction, which may be explained with the formation of a collision complex, the lifetime of which must be long enough for rearrangement. Inspection of possible $(C_3H_2^+)^*$ structures (Wong & Radom 1993) reveals that the hydrogen molecule is first loosely attached to the C_3^+ ion, which may have to go through a special geometry

(may be linear) in order to break the hydrogen bond and to form the linear C_3H^+ product. A hint that the initially formed intermediate state has only a small binding energy is the fact that the reaction probability approaches unity only below 50 K. Another hint that some of the collision complexes are really long lived is that radiative association also contributes with more than 3%.

3.2. $C_3H^+ + HD$

In their paper on the competition between association and reaction for $C_3H^+ + H_2$, Maluendes et al. (1993a) have discussed some serious discrepancies between their theoretical results and measurements from an 80 K ring electrode trap experiment (Gerlich & Horning 1992). They proposed that studies between 10 and 300 K should be undertaken to give some further guidance to *ab initio* calculations. This has been done utilizing the first version of our temperature-variable 22 pole ion trap; however, the important results have been overlooked in later publications as discussed in the introduction.

The obvious difference between flow tube and trapping experiments is the density and temperature range, the interaction time and, perhaps, difficulties in preparing thermalized ions. In a trap, most problems can be avoided or accounted for by systematically varying the pressure over many orders of magnitude and changing the storage times from milliseconds to minutes. Thermalization of the primary ions can be achieved efficiently by intense buffer gas pulses filling the trap for short times. All experiments presented in Sorgenfrei & Gerlich (1994) and the new ones published in Savić & Gerlich (2005) clearly prove that hydrogen abstraction in $C_3H^+ + H_2$ collisions is not endothermic and that the temperature dependence observed in flow tubes is only due to the saturated stabilization of the long-lived collision complexes as already pointed out in Gerlich & Horning (1992). Also, the effective rate coefficients reported in McEwan et al. (1999) have to be reconsidered.

Less obvious to us is why all high-quality calculations (Maluendes et al. 1993a, 1993b; Wong & Radom 1993) predict thermochemical values in contradiction to our experimental findings. It should be possible today to get energies with the required accuracy. More demanding and challenging for *ab initio* calculations is to find the detailed features of the potential surface, which are needed to explain experimental observations such as competition between radiative association and hydrogen abstraction and especially the very complicated isotope effects reported for reactions with D_2 in Sorgenfrei & Gerlich (1994) and for HD in this contribution. Note, for example, that the rate coefficient for radiative association of C_3H^+ in collisions with D_2 is 50 times smaller than with H_2 . The model potential that has been used to understand qualitatively the data presented here and in Savić & Gerlich (2005) is based on shallow wells in the entrance and exit channel and barriers or bottle necks hindering the transition to and from the strongly bound intermediate (see Fig. 4 of Sorgenfrei & Gerlich 1994).

The results obtained now for $C_3H^+ + HD$ collisions are very surprising. As can be seen directly from Figure 2, formation of C_3HD^+ is by far the dominant channel for this astrochemically important isotope combination. Inspection of the rate coefficients, given in Table 1, reveals that H-D exchange and radiative association leading to $C_3H_2D^+$ is already 10 times less efficient while the rate coefficient for $C_3H_2^+$ formation is 100 times smaller. One possible explanation for that is an efficient switching reaction, i.e., the addition of the HD target molecule on one side of the linear chain and the loss of the H on the other side. This mechanism is partly supported by the results obtained for $C_3D^+ + HD$

and $C_3H^+ + D_2$ (see Table 1). However, it can also be seen from the large rate coefficients measured for $C_3D^+ + D_2$ that in reality the reaction dynamics are more complicated. Since in all the various isotope combinations of the $C_3H^+ + H_2$ system the same potential surface plays a role, it must be assumed that either the zero-point energies in the transition states are responsible for the remarkable differences or restrictions due to symmetry selection rules.

Most important for the production of deuterated hydrocarbons in interstellar chemistry is that $C_3H^+ + HD$ leads to deuterated products with almost 50% of the collision rate. Note, however, that the product is C_3HD^+ , which cannot be so easily converted into $C_3H_2D^+$.

3.3. $C_3H_3^+ + HD$ and $C_3H_2^+ + D_2$

From a point of their reactivity, collisions of $C_3H_3^+$ or $C_3H_2^+$ with HD or D_2 can most probably be ignored in astrochemical models, since they are very slow. Nonetheless, they are interesting from a fundamental point of view, since in both cases exothermic reactions are possible. The potential surface of $C_3H_3^+ + HD$ has been discussed in detail by Talbi & Herbst (2001). The *ab initio* results show a well in the entrance channel that is 1.7 kJ mol⁻¹ below reactants and that corresponds to a long-distance c- $C_3H_3^+ - HD$ van der Waals molecule. The exit channel $C_3H_2D^+ - H_2$ lies 6 kJ mol⁻¹ below reactants. As a consequence, long-lived complexes can be formed only at very low energies, if at all. Moreover, the calculations indicate that the reaction can only proceed via a transition state that can be associated to a complex formed from c- C_3H_2 and H_2D^+ . Since this barrier is 320 kJ mol⁻¹ above reactants it is clear, without any further calculations, that no exchange will become observable. The experimental result presented in Table 1 is in accord with this conclusion. The data indicate an overall deuteration rate coefficient of 10⁻¹⁶ cm³ s⁻¹, which is most probably due to radiative or partly due to ternary association. More conclusive results would require additional measurements; however, they are not necessary for the present purpose.

It is certain that reaction (1) does not play any role in low-temperature astrochemistry. It is not completely definite whether the same statement holds for the deuterated variants of $C_3H_2^+ + H_2$. Also in this case, it is known from calculations (Wong & Radom 1993) that hydrogen abstraction is quite exothermic (91 kJ mol⁻¹) but hindered by a barrier of 9 kJ mol⁻¹. Qualitatively, the small rate coefficient measured for reaction (4) (see Table 1) is in accord with this; however, it is rather clear, e.g., from Figure 3, that here deuterated products are really formed. The speculation that this may be due to tunneling is supported by a larger rate coefficient of 5×10^{-13} cm³ s⁻¹, which has been measured for the reaction $C_3H_2^+ + H_2 \rightarrow C_3H_3^+ + H$ for both n- H_2 and p- H_2 (Sorgenfrei & Gerlich 1994).

4. CONCLUSIONS

In the center of this contribution are new low-temperature ion trap measurements that are of general relevance for the carbon chemistry of interstellar clouds. The presented experimental results have been selected according to simple hydrocarbon reactions that many of them contribute to the production of C_3HD . We conclude that the chemical reaction networks have to be revised, since important reactions are either missing or are included with erroneous rate coefficients, especially concerning their temperature dependence. The detailed data show that the use of simple statistical branching ratios in distributing the hydrogen or deuterium atom from an HD target molecule has to be checked in each case; for $C_3^+ + HD$, the experimental reality

is close to 1:1, while completely different ratios are obtained for the competing products in C₃H₃⁺ + HD collisions.

There is no doubt that the new rate coefficients, especially the large reactivity of C₃⁺ at low temperatures, will increase the number density of hydrocarbons in dense interstellar clouds. Less obvious is the influence of the presented data on deuteration. First test calculations using the results from this paper in the UMIST database show some interesting trends (A. J. Markwick 2004, private communication). The large rate coefficient for reaction (3b) significantly suppresses formation of neutral C₃HD, since product ions with two H (or D) atoms are trapped there. Only reactions such as



or radiative association with atoms may bring them back into the reaction chain toward C₃HD. It is surprising that the calculations indicate that a rate coefficient of a few 10⁻¹³ cm³ s⁻¹ leads to an increase of the C₃HD/C₃H₂ ratio by a factor of almost 4! Unfortunately, reaction (5) has not yet been studied at low temperatures and predictions are problematic, since the isotope effects of this type of reaction are as complicated as those of reaction (3).

The data set presented here and in Savić & Gerlich (2005) is certainly not complete for correctly describing the correlations between different hydrocarbons and their deuterated variants as reported from observations (Gerin et al. 2003). From a fundamental point of view there are many reactions that are of basic interest and a challenge for low-temperature trapping experiments; for example, reactions starting with C⁺ colliding with deuterated variants of hydrocarbons, e.g., C⁺ + C₂H₃D → C₃H₂D⁺ + H, or reactions involving CH₂D⁺ or DCO⁺. Certainly of importance are collisions of H₂D⁺ with carbon clusters or hydrocarbons, one example being the direct deuteration of C₃H₂ in collisions with H₂D⁺. For D₃⁺ + C₃, first experiments have been reported (Savić et al. 2005). The results confirmed the theoretical predictions (Fischer et al. 2005) that deuteron transfer is by far the dominant reaction channel; nonetheless, it may be possible at low temperatures that H₂D⁺ + C₃ can associate via photo emission. An example which also still belongs to the class of C₃H_n⁺ reaction systems is the reaction H₃⁺ + CH₂CCH₂ → c-C₃H₃⁺ + 2H₂. If, at low temperatures, hydrogenation of carbon molecules occurs at a reasonable rate via radiative association with H atoms, this reaction can also be regarded as an efficient way to produce hydrogen molecules.

The near thermoneutral reactions involving hydrocarbon ions and the complicated role zero-point energy plays in transition states indicate the need for very sensitive low-temperature and low-density experiments as realized with the trapping technique, while the traditional methods of ion chemistry seem to fail to provide the necessary information. The result measured for C₃H₃ + HD and similar observations made for CH₅ + HD (Asvany et al. 2004b) prove the sensitivity of the trapping method. The determination of rate coefficients smaller than 10⁻¹⁶ cm³s⁻¹ are important for finding routes with low probabilities. In addition to the reactions with HD or D₂, experiments with condensable molecules, radicals, and atoms such as H, D, or N must be performed at low temperatures. For example, all reactions C_mH_n⁺ + D → C_mH_{n-1}D⁺ + H are exothermic; however, it is not straightforward to predict the reactivity at low temperatures from 300 K measurements (McEwan et al. 1999). In a new special trapping apparatus constructed in our laboratory, such studies are in progress (G. Borodi et al. 2005, in preparation).

Finally, we must conclude from the failure of the related theory that, in addition to low-temperature experiments, quantum chemical calculations are needed that have “astrochemical accuracy.” It is supposed that this is more demanding than spectroscopic accuracy, in which one needs to be precise only in the vicinity of the ground-state configuration, while in a chemical reaction a variety of asymptotic regions and critical transition states have to be known with accuracies much better than 1 kJ mol⁻¹. Very important, especially for deuteration, are zero-point energies in all critical regions. Provided that all details of the potential energy surface are available, detailed dynamical calculations have to be performed or, alternatively, statistical theories may be used. This is often applicable to low-temperature ion-molecule reactions with long-lived and strongly interacting collision complexes. In these cases, special attention has to be paid to the restrictions imposed by symmetry selection rules, which are especially important in the case of D–H exchange and if o-H₂ is participating.

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