

Some Routes in Forming $C_3H_n^+$ Ions and Deuterated Variants under Interstellar Conditions

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Abstract. Laboratory experiments on hydrogenation and deuteration of C_3^+ , C_3H^+ and $C_3H_2^+$ in collisions with H_2 and HD have been performed from room temperature down to 15 K using a 22-pole ion-trap. At room temperature C_3^+ reacts slowly with H_2 but the reactivity increases with decreasing temperature. It has been shown that the association reaction $C_3^+ + H_2 \rightarrow C_3H_2^+ + hv$ can compete with the exothermic reaction $C_3^+ + H_2 \rightarrow C_3H^+ + H$. In collisions of C_3^+ with HD, formation of C_3D^+ is slightly favored over C_3H^+ formation. A pronounced competition between various channels has been detected for deuterated variants of the $C_3H^+ + H_2$ system. Most surprising is that formation of C_3HD^+ is over one hundred times faster than formation of $C_3H_2^+$ in collisions of C_3H^+ and HD. A tentative explanation is that the H-HD exchange takes place via an open-chain H_2CCCH^+ intermediate. Reactions of $C_3H_2^+$ and $C_3H_3^+$ with H_2 are very slow. The formation of $C_3H_2D^+$ or $C_3HD_2^+$ and finally C_3HD via dissociative recombination has been discussed. The reaction $C_3H_3^+ + HD \rightarrow C_3H_2D^+ + H_2$ can be ignored in astrochemical models since the reaction rate at 15 K is very small; however, quite efficient routes have been found starting from C_3^+ and proceeding via deuterated C_3H^+ to $C_3H_2^+$ and $C_3H_3^+$. The new reaction rate coefficients are recommended to be included in astrophysical databases. Nonetheless it is still unclear how to explain the large abundance of C_3H_2 and larger hydrocarbons and their deuterated variants observed in cold interstellar clouds.

Keywords: laboratory astrochemistry, low temperature collisions, hydrogenation, deuteration, ISM: molecules, ions, C_3H_2 , C_3HD , $C_3H_2D^+$

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INTRODUCTION

Within the last 30 years, different chemical models have been formulated for predicting the formation, processing and destruction of interstellar molecules. In all of them, gas phase reactions and surface processes are of key importance.

In general, gas phase ion-molecule reactions have no barriers [1] and due to the long range ion-induced dipole attraction their reaction rate coefficients are usually larger than those for neutral-neutral reactions. This is the reason why already early simulations (e.g. [2], [3]) of dense or diffuse clouds and accretion disks, using mainly ion-molecule reactions were quite successful in explaining the observed molecular abundances. The final step in the synthesis of neutrals coming from ion-molecule

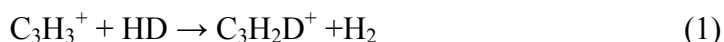
reactions is their recombination with electrons. Today's chemical reaction networks are very sophisticated, complex and specialized. In addition to ion-molecule reaction, they include a variety of other types of reactions. In order to numerically solve the problem one has to select the most important processes for predicting the evolution of interstellar clouds. For this precise reaction rate coefficients are needed and, therefore, dedicated measurements performed under conditions of astrophysical relevance are necessary.

For some ion-molecule reactions the rate coefficients are temperature independent but there are also many exceptions. Changes especially occur at low temperatures. Especially important for astrochemistry are radiative association reactions [4], near thermoneutral reactions and reactions slowed down by small barriers along the reaction path.

Almost 80 % of the detected interstellar molecules contain one or more carbon atoms. One problem in astrochemistry is to find chemical pathways leading from small molecules like C, C₂, C₃, C₂H or C₃H to those complex molecular structures which are suspected to be synthesized in inter- or circumstellar regions. It has been pointed out recently [5] that even for small molecules such as C₄H and C₃H₂ our present understanding of the chemical route is not sufficient to explain observations and that new formation routes must be found to explain abundances and correlations of molecules in PDRs.

It has been observed that in cold ISM environments the DX/HX abundance ratio can be a factor of 10⁴ larger than the D/H elemental ratio. Understanding isotope fractionation is of central importance for modeling deuterium enrichment in interstellar molecules. It is generally accepted that most important ways in producing deuterated molecules are collisions between ions and HD, D or D₂. The difference in zero-point vibrational energy of the molecules determines the endo- or exothermicity of an H-D exchange reaction. Usually reactions proceed much faster in the exothermic direction than in endothermic one; however, an activation barrier can complicate the situation. New low-temperature measurements [6], [7], [8] have shown that there can be significant deviations from simple models, due to small barriers or bottlenecks of the potential energy surfaces. In addition, symmetry selection rules play a central role in replacing one or more atoms in a group of identical ones by isotopes and vice versa [9]. This together with conservation of the total nuclear spin can have a huge influence [10].

A typical example for an unsolved problem in today's reaction models is the very large deuterium fractionation of c-C₃H₂ in TMC-1. For the C₃HD/C₃H₂ ratio, a value of 0.048 has been reported in [11]; other observations lead to ratios between 0.08 and 0.16, depending on the position [12]. Theoretical predictions stay below 0.01 [13], [14], [15]. In order to reproduce observed C₃HD/C₃H₂ ratio, it has been proposed in [16] that the reaction



may occur rapidly at low temperatures and that C₃HD is formed via dissociative recombination of C₃H₂D⁺. This has been excluded by quantum chemical calculations [17] since high transition barrier have been found.

The detailed understanding of reaction dynamics at very low energies is very important from a fundamental point of view. It is interesting what happens if the total

energy varies by a small amount near zero. One consequence is that the number of partial waves contributing to the collision complex formation becomes smaller and smaller and finally only s-waves need to be considered. In reactions where H atoms are involved this effect play a role already at collision energies in the meV range. In this limit, quantum-mechanical calculations (but also statistical models) become simplified. Dynamical effects such as resonances may play a role. At low energy collision energies, other effects can occur because excitation of rotational or fine structure states can be the dominant contribution to the total energy. In general, a low total energy leads to long collision complex lifetimes enabling very unlikely processes to occur like radiative association, rearrangement via internal tunneling, or non-adiabatic mixing.

EXPERIMENTAL AND TYPICAL RESULTS

The results presented in this paper have been obtained using a variable temperature rf 22-pole ion trapping apparatus. The machine is fully described in [18] and here only a brief description is given. Primary ions are generated externally in a storage ion source [19]. Then a pulsed bunch of ions is mass selected in a first quadrupole mass filter (operated in this work in the mass selective mode) and injected into a 22-pole ion trap with low kinetic energy. In the 22-pole trap, ions are confined in radial direction by an effective potential. This is created by applying two opposite phases of an rf generator to the two sets of 11 electrodes. In the axial direction the trap can be closed by small potential barriers created by voltages applied to the gate electrodes at both ends of the trap. In order to achieve temperatures as low as 5 K, the trap is mounted onto a closed cycle refrigerator and 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. Buffer and reactant gases introduced by cooled tubes are in thermal equilibrium with the surrounding walls. The stored ions are efficiently coupled to the temperature of the buffer gas via collisions. In the present case a short and intense pulse of He is introduced into the trap. The ions can be stored for times varying from milliseconds to seconds. During this time, they react with the neutral target gas. Usually only few thousands primary ions are used per pulse in order to avoid space charge effects and saturation of the Daly detector. After a given reaction time, the remaining primary and the newly formed product ions are extracted from the trap by a pulsed voltage applied to the exit electrode. They are mass analyzed in the second mass filter and finally counted using a Daly type detector. For improving the statistics and eliminating fluctuations, the procedure of ion formation, trapping, reaction and analysis is repeated very often for each mass of interest and for typically ten different storage times.

All primary ions were produced in the storage ion source by electron bombardment (collision energy ≤ 40 eV) of allene ($\text{CH}_2=\text{C}=\text{CH}_2$, Aldrich, 97 %). Until recently it was unclear how C_3^+ really looks like. Recent calculations [20] indicate a cyclic structure with the lowest states being perturbed by the Jan-Teller effect. 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. The reactivity of the linear and cyclic ions is usually different. In most studies

performed with ions produced in the storage ions source, only mono-exponential decay have been observed, one exception being $C_3H_2^+$. This indicates that the storage ion source produces predominantly the lowest energy isomer.

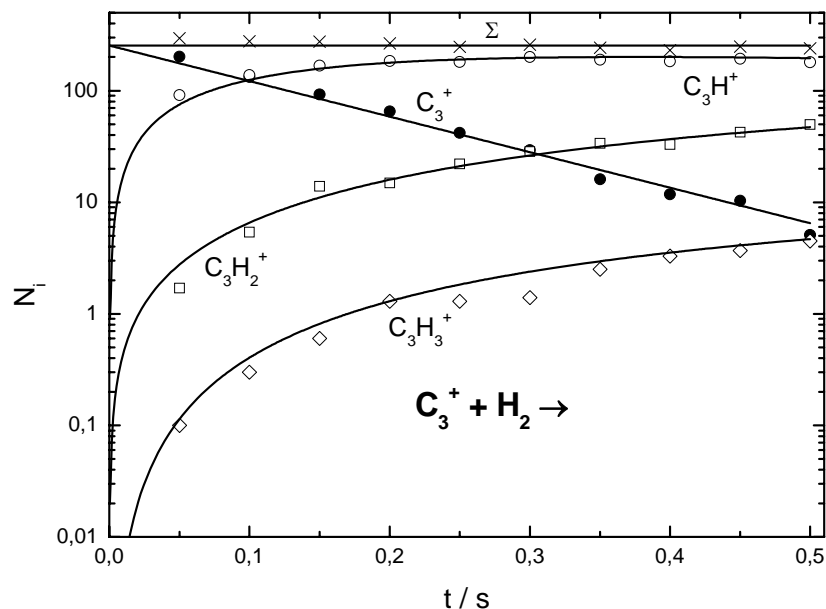


FIGURE 1. Typical experimental results. Shown is the averaged number of primary and product ions trapped per filling, N_i , as function of the storage time t . Within less than 100 ms the C_3^+ ions are cooled to the ambient temperature. They react with H_2 (number density $4.1 \times 10^9 \text{ cm}^{-3}$) via a cascade of reactions forming C_3H^+ , $C_3H_2^+$ and $C_3H_3^+$. The solid lines are solutions of an adequate reaction rate system.

In the present experiments, both H_2 and HD has been used as neutral reactant. The H_2 had a purity of 99,99990 % (Messer-Griesheim) while HD (Cambridge Isotope Laboratories Inc.) had a purity of 98 % with 2 % of H_2 and D_2 [7]. The number density of target gas is determined with an ion gauge calibrated with respect to a spinning rotor gauge. In the present work the error of the absolute rate coefficients is estimated to be 20%, mainly caused by fluctuations of the density.

Fig. 1 shows a typical experimental result measured at 44 K. Plotted is the number of trapped ions, N_i , as a function of the storage time t which is identical with the reaction time. The analogue reactions with HD are more complex. Typical experimental results for these reactions are presented in [21] and [22].

RESULTS AND DISCUSSION

Ion-molecule reactions between hydrocarbons and H_2 have been studied often. The reaction



is exothermic by 197 kJ mol^{-1} [23]. Therefore, the reaction rate coefficients measured at room temperature, 1.8×10^{-10} [24], 2.5×10^{-10} [23], 3×10^{-10} [25] and $4.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [21] are surprisingly low. In addition, a value of $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ has been measured at 10 K [26]. Our recent temperature dependent measurements [21] have approved that the reaction becomes faster with decreasing temperature. Below

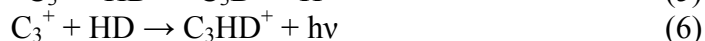
44 K a constant value of $1.7 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ is reached. Within our experimental error of 20 %, this is in accordance with the Langevin capture rate coefficient. The temperature dependence of the rate coefficient can be approximated with the function $k = \alpha (T/300\text{K})^\beta$ with the parameters $\alpha = 4.7 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ and $\beta = -0.69$ for temperatures between $T = 44$ and 300 K .

It is surprising that the association reaction



competes with the exothermic reaction (2). At 20 K almost 5 % of the collision complexes are stabilized by emission of a photon. For the temperature range $T = 20 - 44 \text{ K}$ the coefficients are $\alpha = 5.7 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ and $\beta = -1.02$ while reaction rate coefficient $k = 8.5 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ have been measured at temperature of 15 K [21].

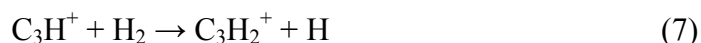
The reaction of C_3^+ with HD has one more product channel since formation of C_3H^+ , C_3D^+ and C_3HD^+ is possible:



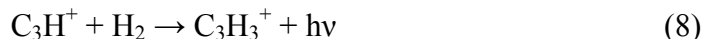
The reaction rate coefficient for reaction (4) is $9.3 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ at 15 K. It is slightly higher than the value for reaction (5) of $7.6 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$. For the reaction (6) $5.9 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ has been measured [21]. As can be seen, reaction of C_3^+ with HD is slightly slower than reaction with H_2 and even slower with D_2 ($1.3 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ [27]). This is in accordance with the mass dependence of the capture cross section.

Within a simple classical picture, reaction between an ion and HD favors H abstraction because the separation of the center of charge and the center of mass orients HD such that the H atom preferentially points toward the ion (especially in the rotational ground state). The rate coefficients measured for reactions (4) and (5) are in contradiction with this simple model. Therefore, it can be concluded that hydrogen abstraction does not occur in a direct way. This conclusion can be corroborated by the temperature dependence of reaction (2). Namely, the observed hydrogen abstraction temperature dependence can be explained by formation of a long-lived collision complex since several stable strongly bound C_3H_2^+ ion isomers exist. The lifetime of such complex must be long enough for rearrangement. The possible structures of $(\text{C}_3\text{H}_2^*)^+$ [28] indicate that the hydrogen molecule is first weakly connected 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. The fact that the reaction probability is much smaller at room temperature than at low temperatures can be taken as a hint that the initially formed intermediate state has only a small binding energy. Indication that some of the collision complexes are really long lived is that the radiative association also contributes with more than 3 %.

The first results using flow tube technique on reactions between C_3H^+ and H_2 have been discussed in detail in [25], [29], [30], [31]. The high pressure flow tube conditions lead to saturated three-body association and significant suppression of hydrogen abstraction. This strong competition in C_3H_3^+ and C_3H_2^+ formation has been verified by pressure dependent measurements over a wide range of pressures in an 80 K ion trap [4]. Since the lifetime of intermediate complex is temperature dependent, decrease of C_3H_2^+ products with decreasing the temperature has led to the wrong conclusion that the reaction

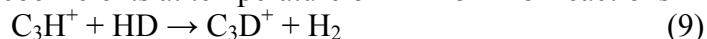


is endothermic by 4 kJ mol^{-1} [30]. Later ab initio calculations got the same value [28] or an even higher endothermicity of 7 kJ mol^{-1} [32]. It has been proposed in [32] that more studies between 10 and 300 K are needed to give some guidance to ab initio calculations and that has been done in the 22-pole trapping machine [27], [21]. The results on reaction (7) and reaction



at temperatures between 10 and 50 K and with n-H₂ and p-H₂ have been reported in [27] and within the range 15 – 300 K for n-H₂ in [21]. There is a good overall agreement between these experiments. At 300 K rate coefficients for reactions (7) and (8) sum up to 2 % of collision rate but they reach almost 20 % at 20 K. For the hydrogen abstraction reaction (7), the parameters α and β are $1.5 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ and + 0.09 respectively in the the temperature range 15 – 44 K while for 44 – 300 K they are $1.4 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ and – 1.05 [21]. The rate coefficient for radiative association (8) increases from $1.5 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ at $T = 72 \text{ K}$ to $6 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ at $T = 15 \text{ K}$. The use of p-H₂ instead of n-H₂ speeds up radiative association but it slows down hydrogen abstraction due to competition between these two channels. This is mainly due to the colder conditions prepared with the non-rotating H₂. Therefore, all results [27], [21] clearly show that hydrogen abstraction in $\text{C}_3\text{H}^+ + \text{H}_2$ collisions is not endothermic.

Using HD instead of H₂ in collisions with C_3H^+ has revealed a lot of unexpected results. Measured reaction rate coefficients at temperature of $T = 15 \text{ K}$ for reactions



are $5.6 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$, $4.6 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$, $3 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$, and $3.2 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$, respectively [21]. In comparison with reactions with H₂ [27], [21], and D₂ [26], the overall fastest reaction is $\text{C}_3\text{H}^+ + \text{HD}$, reaching almost 50 % of the collision rate at 15 K. That can be explained by the fact that HD is a more efficient cooler than the homonuclear hydrogen molecules where nuclear spin restrictions restrict rotational transitions. In addition it has to be emphasized that $\text{C}_3\text{H}^+ + \text{HD}$ collisions lead almost exclusively to deuterated hydrocarbons, a very important results for interstellar chemistry. Note however that the major product, C_3HD^+ , cannot be easily converted into $\text{C}_3\text{H}_2\text{D}^+$.

For reaction (10) and (11) an incredible large isotope effect has been discovered. Formation of C_3HD^+ is 150 times more probable than formation of C_3H_2^+ ! That fact can not be explained based on differences in zero point energies. It is probably caused by an H-HD switching reaction. In this case the addition of the HD on one side of the linear intermediate complex leads to the loss of the H atom bound on the other side. In order to explain qualitatively the competition between hydrogen abstraction and radiative association, the isotope effect and total reactivity a simple model potential has been proposed in [27] and [21].

Careful measurements on reaction (1) have been performed recently [22]. It has been found that the rate coefficient for deuteration of C_3H_3^+ in collisions with HD is smaller then $1 \times 10^{-16} \text{ cm}^3\text{s}^{-1}$. The reaction rate coefficient of $5 \times 10^{-13} \text{ cm}^3\text{s}^{-1}$ has been measured for the reactions $\text{C}_3\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{H}$ and $\text{C}_3\text{H}_2^+ + \text{D}_2 \rightarrow \text{C}_3\text{HD}^+ + \text{HD}$

at 10 K, while value of $1.7 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ have been obtained for the $\text{C}_3\text{H}_2^+ + \text{D}_2 \rightarrow \text{C}_3\text{D}_2^+ + \text{H}_2$ reaction [27], [26]. Collisions of C_3H_3^+ and C_3H_2^+ with HD or D_2 are not of importance for astrochemical models since these reactions are very slow. On the other hand they are interesting from fundamental point of view since exothermic reactions are possible. Small but finite rate coefficients measured at low temperature indicate that there must be some ways to circumvent the barrier or to tunnel through it.

CONCLUSIONS

In the focus of this contribution are low-temperature ion trap measurements of reactions involving C_3H_n^+ ($n = 0 - 3$) ions and hydrogen and deuterated variants. The relevance for the carbon chemistry of interstellar clouds has been discussed. We conclude that chemical reaction networks have to be revised since important reactions are missing or are included with wrong rate coefficients especially concerning their temperature dependence. Since branching ratio in distributing the hydrogen or deuterium atom from and HD molecule is almost 1:1 for $\text{C}_3^+ + \text{HD}$ collisions and completely different ratios are obtained for the competing products in $\text{C}_3\text{H}^+ + \text{HD}$ collisions, branching ratios have to be checked individually for each reaction. Including the new rate coefficients into models, especially those for reactions with C_3^+ at low temperature will increase the number density of hydrocarbons in dense interstellar clouds. The data presented in [21], [22] and here are not yet complete for correctly describing the correlations between different hydrocarbons and their deuterated variants. Therefore more dedicated experiments on this subject have to be done. It is sure that the most interesting reactions are $\text{C}_3\text{HD}^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_2\text{D}^+ + \text{H}$ or $\text{C}_3\text{HD}^+ + \text{H} \rightarrow \text{C}_3\text{H}_2\text{D}^+ + h\nu$ since on this way C_3HD^+ can be again pushed into the game. In the addition to the low temperature reactions with H_2 , HD and D_2 , experiments on collisions of C_mH_n^+ with H and D atoms have to be performed. With this aim, a special trapping apparatus has been constructed in our laboratory [33].

From the failure of the related theory we conclude that a much higher accuracy must be postulated from the quantum chemical calculations, especially in the vicinity of asymptotic regions or at transition states. Of special interest for the deuteration are zero-point energies in all critical regions. Assuming that all the details of the potential energy surface are accurately known, detailed dynamical calculations can be performed.

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