Formation of biomolecule precursors in space

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Abstract. Alcohols and nitriles not only play an important role as templates for synthesis of larger molecules in the interstellar medium and planetary atmospheres, but they can also be regarded as precursors for biomolecules. Alcohols can form carbohydrates through reaction with HCO and nitriles can be hydrolysed to amino acids in aqueous solutions, which is the final step of the well-known Strecker synthesis. Therefore the question of the pathways of formation of alcohols and nitriles and the efficiency and the product distribution of their subsequent degradation reactions in the above-mentioned astrophysical environments is of great interest. In both processes dissociative recombination reactions of protonated nitriles and alcohols may play a major role and are included in models of interstellar clouds and planetary atmospheres. However, the reaction rate coefficients and product branching ratios for the majority of these processes are so far still unknown, which adversely affects the quality of predictions of model calculations. In this Contribution, we therefore present branching ratios and rate constants of the dissociative recombination of protonated methanol (CH₃OH⁺), as well as protonated acetonitrile (CH₃CNH⁺), acrylonitrile (C₂H₃CNH⁺) and cyanoacetylene (HC₃NH⁺). The impact of the obtained new data on model calculations of abundances of important interstellar molecules in dark clouds is discussed.
1. Introduction

For a long time, it has been accepted wisdom that the main building blocks of biomolecules (amino acids, carbohydrates and nucleobases) have been produced in a primeval soup under an atmosphere containing water, ammonia and methane. These conditions were reproduced to a certain extent by the famous Miller-Urey experiment [1]. Recent findings and uncertainties concerning the composition of the atmosphere of early Earth (biomolecule synthesis in the mentioned experiment is severely hampered by the presence of oxygen) have challenged this opinion and an extraterrestrial origin of amino acids, simple carbohydrates and nucleobases cannot be categorically excluded. Analysis of meteorites revealed the presence of quite a few amino acids and their hydrogen isotope distribution suggest an interstellar origin of these compounds [2]. Nevertheless, slightly more complex biomolecules like nucleobases or amino acids can hardly survive the strong UV field present under disk and planet formation in the early solar system [3], which makes a scenario, in which these compounds are generated in the interstellar medium and subsequently delivered to early Earth by comet or meteorite impact less likely. On the contrary, this may not hold for more UV-stable precursor molecules like alcohols, aldehydes, ethers and nitriles, which are present in considerable amounts in the interstellar medium. For example, laboratory investigations have shown that nitriles are destroyed by UV much more slowly than the corresponding acids [4]. Once delivered to Earth, nitriles could have been hydrolysed in aqueous solution to form amino acids. Amongst other precursor compounds, alcohols deserve a special interest, since they are able to form simple carbohydrates in the interstellar medium (ISM) by reaction with HCO [5]. Therefore, an important role of interstellar compounds in the formation of biomolecules on Earth cannot categorically be ruled out.

A crucial question concerns the formation and destruction pathways of all molecules in the interstellar medium. Three mechanisms are most common for generation of interstellar compounds: (a) processes on grain surfaces, (b) radical-neutral reactions and (c) ion-neutral reactions followed by dissociative recombination (DR). The latter process often involves formation of a protonated species, which then reacts to the final molecule by DR under ejection of a hydrogen atom. However, the high exoergicities of DR processes usually enable several pathways yielding different products and recent investigations on a multitude of such processes often lead to surprising and counter-intuitive results. These have sometimes severely challenged the feasibility of gas-phase ion reactions for production of important interstellar molecules, since, in some cases, gas-phase ion-neutral reactions, followed by DR of the produced ions, have been regarded as the only possible mechanism for production of interstellar molecules. If the DR of the latter ion, however, does not deliver the “desired product”, the invoked pathway becomes unfeasible.

For example, interstellar methanol has been thought to be produced by the following processes:

\[
\text{CH}_3^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}^+ + \text{hv} \\
\text{CH}_3\text{OH}_2^+ + e^- \rightarrow \text{CH}_3\text{OH} + \text{H}
\]  

An analogue synthesis pathway also exists for nitriles:

\[
R^+ + \text{HCN} \rightarrow \text{RCNH}^+ + \text{hv} \\
\text{RCNH}^+ + e^- \rightarrow \text{RCN} + \text{H}
\]

DR also functions as a crucial step in the destruction of molecules in the interstellar medium and planetary ionospheres. Proton acceptors like nitriles and alcohols might be protonated (e.g. by H$_3^+$ in dark interstellar clouds). Subsequent DR might then in many cases lead only to a small extent to the unprotonated species. Fragmentation processes of the intermediate formed neutral product of the DR into several reactive species can turn protonation followed by DR into an efficient destruction mechanism for molecules in such environments. Conversely, if DR exclusively leads to the
unprotonated species, it constitutes an efficient recycling mechanism for species lost through protonation. Therefore, not surprisingly, DR reactions are included in model calculations of planetary ionospheres as well as dark and diffuse interstellar clouds. Since the quality of the predictions of such computations is largely dependent on the quality of the input data, they are likely to be substantially affected by the DR rates and product branching ratios that are used. Most importantly, these data have to be applicable for the relevant astrophysical conditions (ultra-high-vacuum, low collision energies), which are non-trivial to obtain in experiments. Unfortunately few laboratory measurements of interstellar DR reactions are available and the rate constants and branching ratios used as input in model calculations are often just educated guesses. Fortunately, the application of storage rings allows determination these numbers at vacuums excluding three-body processes (which are prohibited in the interstellar medium due to the low particle densities) and with collision energies down to several meV, which is similar to dark cloud conditions.

Very recently, protonated nitriles reemerged as a focus of interest due to the Cassini-Huygens mission. In the higher layers of Titan’s ionosphere, the Ion-Neutral Mass Spectrometer on board the Cassini spacecraft detected much larger abundances of protonated nitriles than predicted by previous model calculations [6]. Since DR is a crucial destruction process of ions in this environment, branching ratios and reaction rates of DR of protonated nitriles are substantial as input in state-of-the-art models of the ionosphere of this satellite, whose atmosphere is argued to resemble that of early Earth.

In this Contribution, we present measurements of branching ratios and rate constants of the dissociative recombination of protonated methanol (CH$_3$OH$^+$), protonated acetonitrile (CH$_3$CNH$^+$), acrylonitrile (C$_2$H$_3$CNH$^+$), and cyanoacetylene (HC$_3$NH$^+$) using the CRYRING storage ring located at Stockholm University, Sweden. The impact of our DR data for CH$_3$OH$^+$ on model calculations of abundances of important interstellar molecules in dark clouds will be discussed.

2. Experimental section
The DR experiments have been performed at the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory, Stockholm University. The experimental procedure has been described in detail elsewhere [7] and is therefore summarised only briefly here. For technical reasons related to the data analysis (better resolution on the detector using deuterated compounds) fully deuterated compounds were used in the case of protonated acetonitrile and protonated methylacetylene. For protonated methanol, measurements of both the light hydrogen and fully deuterated isotopomers were undertaken. In the case of CH$_3$OH$^+$, CD$_3$OD$^+$, CD$_3$CND$^+$ and C$_2$H$_5$CNH$^+$ the ions were produced in a hollow cathode pulsed discharge ion source (voltage 1–2 kV) from a mixture of the undeuterated/unprotonated species (methanol, methanol-d$_5$, acetonitrile-d$_3$ and acrylonitrile) with hydrogen/deuterium in excess, probably through the following process:

$$\text{H}_3^+ + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}_2^+ + \text{H}_2$$ (5a)

$$\text{D}_3^+ + \text{CD}_3\text{OD} \rightarrow \text{CD}_3\text{OD}_2^+ + \text{D}_2$$ (5b)

Deuteronated cyanoacetylene (DCCCN$^+$) was produced in the same ion source from a mixture of fully deuterated acrylonitrile in deuterium. It should be mentioned that methanol cations tend to protonate neutral methanol quite efficiently, probably through the following reaction

$$\text{CH}_3\text{OH}^+ + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{O}$$ (6)

that is exoergic by 61.2 kJ/mol [8]. This led to much stronger CH$_3$OH$_2^+$ than CH$_3$OH$^+$ mass signals (often by a factor of 5 or more) obtained from our source. Reaction 6 probably proceeds over small
clusters of protonated methanol, which have been found to be preferentially formed in methanol/noble gas mixtures by electron impact ionization [9]. Due to the large intensity of the CH$_3$OH$_2^+$ signal relative to that of CH$_3$OH$^+$, contaminations from $^{13}$CH$_3$OH$^+$ or CH$_3$OD$^+$, which possess the same mass as CH$_3$OH$_2^+$ are very unlikely. The same applies for CD$_3$OD$_2^+$, which could be contaminated by CD$_3^{18}$OD$^+$. After extraction of the ions from the source at 40 keV, they were mass selected, injected into the ring and accelerated to 2.90 MeV (CH$_3$OH$_2^+$), 2.53 MeV (CD$_3$OD$_2^+$), 1.78 MeV (C$_2$H$_3$CNH$^+$ and DCCCND$^+$) and 2.09 MeV (CD$_3$CND$^+$) translational energies, respectively. The stored ion beam was merged with a mono-energetic electron beam in an electron cooler, the length of the interaction region being 0.85 m. During the first couple of seconds after acceleration, the electron and ion beams were kept at the same average velocity to allow heat transfer from the ion to the electron beam in order to reduce the translational temperature of the ions, which then results in an increase of their phase-space density. Furthermore, such storage time enables radiative vibrational cooling of those ions that might have been formed in a rovibrationally excited state. Neutral products generated by DR reactions in the electron cooler left the ring tangentially and were detected by an energy-sensitive silicon surface barrier detector (SBD) with a diameter of 17 mm mounted at a distance of 3.85 m from the centre of the interaction region. A background signal due to neutral products emerging from collisions of the ions with residual gas was also present: this was measured with the relative translational energy between the ions and electrons tuned to 1 or 2 eV, where the DR cross section is very low and the measured neutral fragments are therefore almost exclusively produced by rest gas collisions. This background was subsequently subtracted from the total SBD signal.

3. Results

3.1. Reactive cross sections and rate constants

For the cross section measurements, the relative translational energy between the ions and the electrons was steplessly varied between 1 and 0 eV. This was achieved by changing the cathode voltage of the electron cooler over a certain time interval (1-2 s) from a high value corresponding to a centre-of-mass energy of 1 eV, the electrons being faster than the ions, down to a low-value also corresponding to 1 eV where the electrons were slower than the ions. Thus, a voltage corresponding to a centre-of-mass energy of 0 eV is reached during the scan. Before the measurement was started, several seconds of cooling with the electrons tuned to 0 eV collision energy was carried out. The signal from the SBD was monitored by a single channel analyser, selecting signals only when all the fragments reach the detector simultaneously and thereafter recorded by a multichannel scaler, yielding the number of counts vs. storage time and, therefore, at a given relative translational collision energy. The experimental DR rate coefficient in the electron cooler is expressed by the formula:

$$\langle v_e \sigma \rangle = \left( \frac{dN}{dt} \right) \frac{v_e v_i r_e^2 \pi}{l I_e I_i}$$  \hspace{1cm} (7)$$

where $dN/dt$ is the count rate, $v_e$ and $v_i$ are the electron and ion velocities, respectively, $r_e$ is the radius of the electron beam, $l$ the length of the interaction region, and $I_e$ and $I_i$ are the electron and ion current, respectively. The absolute ion beam current was measured using a Bergoz Beam Charge Monitor with continuous averaging (BCM-CA) and an integrating current transformer in combination with a neutral particle detector installed at the end of one of the straight sections of the ring. Simultaneously with the measurement of the dissociative recombination count rate, a signal of the ion current was monitored to normalise the DR measurement to it [10]. The following corrections to the measured data had to be performed: (a) The voltage of the electron cooler cathode (and therefore $v_e$) had to be corrected for space charge effects. (b) The measured rate coefficient $<\sigma v_{cm}>$ had to be
adjusted because of the toroidal effect [11]. The toroidal effect arises from the zones at both ends of the interaction region where the electron beam is bent into or out of the ion beam. In these regions, the transversal electron velocity is higher than in the merged interaction region leading to larger collision energies. (c) The electron beam has (in contrast to the ion beam) a non-negligible energy spread. If the collision energy of the reactants is much higher than the energy spread of the electron beam, the DR reaction can be computed by dividing the rate constant by the centre-of-mass velocity: 

\[\sigma = \sigma_{\text{cm}} \sigma_{\text{cm}}.\]

At lower collision energies the measured reaction rate constant \(\sigma_{\text{cm}}\) is given by:

\[
\sigma_{\text{cm}} = \int_{-\infty}^{\infty} f(v_e) \sigma(v_e) dv_e.
\]

(d) Drag force effects [13] were neglected due to the relatively large mass of the investigated ion. From the resulting cross section constants, the (comparatively) very small contribution to the data due to charge transfer processes with the rest gas had to be subtracted, as described in the previous section. The reaction rate can be calculated from the cross-section using the following equation:

\[
k(T) = \frac{8\pi m_e}{(2\pi m_e kT)^{3/2}} \int_{0}^{\infty} E \sigma(E) e^{-E/kT} dE.
\]

where \(m_e\) is the mass of the electron. The cross-sections and computed reaction rates of the DR reactions of the different ions are listed in Table 1. The errors from rate include errors from the current uncertainty of the ion current measurement (about 5%) as well as statistical errors from the data analysis: The total errors (statistical + systematic) can be estimated to be 10%.

| Ion \(\text{H}_2\text{O}^+\) | Cross section / \(\text{cm}^2\) (E in eV) | Rate constant / \(\text{cm}^2 \text{s}^{-1}\) (T in K) |
|--------------------------|----------------------------------------|-----------------------------------------|
| \(\text{CH}_3\text{OH}^+\) | \(1.2 \pm 0.1 \times 10^{-15} E^{1.15 \pm 0.02}\) | \(8.9 \pm 0.9 \times 10^{-7} (T/300)^{0.592 \pm 0.02}\) |
| \(\text{CD}_3\text{OD}^+\) | \(9.6 \pm 0.9 \times 10^{-16} E^{1.20 \pm 0.02}\) | \(9.1 \pm 0.9 \times 10^{-7} (T/300)^{0.632 \pm 0.02}\) |
| \(\text{CD}_3\text{CN}^+\) | \(7.4 \pm 1.5 \times 10^{-16} E^{1.23 \pm 0.02}\) | \(8.1 \pm 0.8 \times 10^{-7} (T/300)^{0.692 \pm 0.02}\) |
| \(\text{C}_2\text{H}_3\text{CN}^+\) | \(1.1 \pm 0.2 \times 10^{-15} E^{1.29 \pm 0.02}\) | \(1.8 \pm 0.2 \times 10^{-6} (T/300)^{0.802 \pm 0.02}\) |
| DCCCND^+ | \(2.3 \pm 0.4 \times 10^{-15} E^{1.10 \pm 0.02}\) | \(1.5 \pm 0.3 \times 10^{-6} (T/300)^{0.58 \pm 0.02}\) |

3.2. Branching ratios

The fragments produced by a DR event reached the detector within a very short time interval compared with the integration time of the detection system. The pulse height of the SBD signal was therefore proportional to the kinetic energy carried by all the products of the reaction and therefore the total mass. To measure the branching ratios a metal grid with a transmission \(T = 0.297 \pm 0.015\) was inserted in front of the detector [7]. Particles stopped by the grid did not reach the detector. DR events where one of the fragments hit the grid resulted in a signal whose amplitude was proportional to the sum of the kinetic energies of the fragments passing through the grid. The registered DR spectrum
therefore splits into a series of peaks with different energies, the intensities of which can be expressed in terms of the probability of the particles passing the grid and the branching ratio. In the case of CH$_3$OH$_2^+$ and CD$_3$OD$_2^+$ the peaks separated by a mass/charge ratio of m/z=1 and m/z=2, respectively were sufficiently separated. However, in the fragment energy spectra of the investigated nitriles the resolution was insufficient to distinguish between peaks separated by only one hydrogen (deuterium) mass and therefore only the channels leading to product molecules containing different numbers of heavy atoms could be distinguished. For CH$_3$OH$_2^+$ and CD$_3$OD$_2^+$, possible losses of signals due to light (mainly D or H) fragments picking up enough transversal energy to pass the detector had to be taken into account. A detailed description of the procedure to calculate the branching ratios of the DR of these ions including these losses is described elsewhere [14]. Furthermore, some of their reaction channels delivered products with identical masses and therefore were indistinguishable (see Table 2). However, since the formation of CD$_4$ would involve a considerable rearrangement of the neutral intermediate, it can be argued that channels (j) and (k) are unlikely to play a major role. DR branching ratios of the investigated ions are listed in Tables 2 and 3.

### Table 2. DR branching ratios of the CH$_3$OH$_2^+$ and CD$_3$OD$_2^+$ ions. (See Ref.14 for details)

| Reaction Channel | CD$_3$OD$_2^+$ Products | Branching ratio | Reaction Channel | CH$_3$OH$_2^+$ Products | Branching ratio |
|------------------|-------------------------|----------------|------------------|-------------------------|----------------|
| a (k)            | CD$_3$ + D$_2$O         | 0.11 ± 0.02    | a                | CH$_3$ + H$_2$O       | 0.09 ± 0.02    |
|                  | (CD$_3$ + OD)           |                |                  |                         |                |
| B                | CD$_3$ + DO + D         | 0.59 ± 0.04    | b                | CH$_3$ + OH + H        | 0.51 ± 0.04    |
| c (j)            | CD$_2$ + D + D$_2$O     | 0.17 ± 0.02    | c                | CH$_3$ + H + H$_2$O   | 0.21 ± 0.02    |
|                  | (CD$_2$ + O + D)        |                |                  |                         |                |
| D                | CD + D$_2$ + D$_2$O     | 0.01 ± 0.01    | d                | CH+ + H + H$_2$O       | 0.00 ± 0.01    |
| E                | CD$_3$OD + D            | 0.06 ± 0.02    | e                | CH$_3$OH + H           | 0.03 ± 0.02    |
| F                | CD$_2$O + D$_2$         | 0.05 ± 0.02    | f                | CH$_3$O + H$_2$        | 0.06 ± 0.02    |
| G                | CD$_2$O + 2D            | 0.00 ± 0.01    | g                | CH$_3$O + 2H           | 0.00 ± 0.01    |
| H                | CD$_2$O + D$_2$ + D     | 0.02 ± 0.01    | h                | CH$_2$O + H + H$_2$    | 0.10 ± 0.01    |

### Table 3. DR branching ratios of the DCCCND$^+$, CD$_3$CND$^+$ and C$_2$H$_3$CNH$^+$ ions. (See Refs. 14, 15, 16 and 17 for details)

| Product channel | DCCCND$^+$ Branching ratio | CD$_3$CND$^+$ Branching ratio | C$_2$H$_3$CNH$^+$ Branching ratio |
|-----------------|---------------------------|-----------------------------|-----------------------------------|
| Retention of carbon chain | 0.52 ± 0.05 | 0.65 ± 0.02 | 0.50 ± 0.02 |
| Fissure of central C-C bond | 0.48 ± 0.05 | 0.35 ± 0.05 | 0.50 ± 0.02 |

### 4. Discussion

4.1. General

In the case of CH$_3$OH$_2^+$ and CD$_3$OD$_2^+$ the predominance of the three-body break-up channels is striking. However, also in storage ring measurements investigating for the DR of the related H$_3$O$^+$ ion,
similar branching ratios of the analogue OH + 2H channels were detected [18,14]. Furthermore, if one compares the total branching ratio of all three-body channels in CH$_3$OH$_2$$^+$ and H$_2$O$^+$ the former is just slightly higher, which might be due to the higher number of three-body producing channels available in the DR of CH$_3$OH$_2$$^+$. Another interesting feature are the small branching ratios for pathways producing the comparatively stable CH$_3$O (CD$_2$O) radical, but no simple explanation for this fact springs to mind. In both ions no strong isotope effects upon deuteration are observed. A difference, however, is encountered regarding the DR rate coefficients of CD$_3$OD$^+$ and CH$_3$OH$_2$$^+$, which are about a factor of two higher than the ones measured for H$_2$O$^+$ (D$_2$O$^+$). Nevertheless, they agree very well with the value of $8.8 \times 10^{-7}$ cm$^3$ s$^{-1}$ obtained for CH$_3$OH$_2$$^+$ in an earlier afterglow experiment [19].

For protonated nitriles, the general pattern is that there are only two kinds of DR pathways observed: (a) the ones preserving the carbon-chain and (b) those breaking one bond between heavy atoms. For the ions containing three carbon atoms (C$_2$H$_3$CN$^+$ and DCCCND$^+$) only channels retaining the C$_3$N structure and such breaking the central C-C bond were found. The total rate coefficients observed were in the high range for DR reactions, for CH$_3$CN$^+$ they were measured to be a factor of 2.5 higher than those observed by Geoghegan et al. in an afterglow experiment [20].

4.2. Astrophysical implications

The new branching ratio and rate coefficient of the DR of CD$_3$OD$^+$ were used as input for a model calculation of a dark cloud resembling TMC-1 using the UMIST code [21]. Using the old data, the model predicted a methanol peak abundance relative to H$_2$ of $1 \times 10^{-9}$, which is in good agreement with the observations of Friberg et al. [22] which had yielded a methanol abundance in the low digits of $10^{-10}$ for TMC-1. With the present rate coefficient and branching ratios of the dissociative recombination of protonated methanol, the peak abundance is lowered to a value of $1 \times 10^{-10}$ while the one for steady-state sinks to $7 \times 10^{-11}$. If the recently measured rate coefficient for the radiative association of CH$_3$+$^+$ and H$_2$O [23] is also included, the steady-state abundance is further diminished to $8 \times 10^{-12}$, which is definitely below the observed values in dark clouds and probably below the detection limits for existing telescopes (see Fig. 1). It is therefore likely that interstellar methanol is produced on grain surfaces. This assumption is strengthened by the fact that formation of methanol by hydrogenation of CO with H on pure CO and mixed CO/H$_2$O ices proceeds efficiently at 10 K and the methanol product is not degraded by irradiation [24]. However, that assumption requires a mechanism to release methanol formed on grains into the gas phase at dark cloud temperatures, which is also not easy to accomplish under these conditions, since the desorption energy of methanol is comparatively high [25]. Desorption by vibrational excitation could be a possibility. Hydrogenation of the precursor methoxy or hydroxymethyl radicals is highly exoergic ($\Delta H = -4.51$ and - 4.07 eV, respectively) [8] and might lead to methanol in a highly excited vibrational states. The resulting methanol molecule might use a part of this energy to recoil from the surface and thus end up in the gas phase.

The CH$_3$OH$_2$$^+/H_2$O$^+$ ratio was used to calculate the electron temperature in the inner coma of comet Halley. The rate coefficient used in that model [26] for the DR of CH$_3$OH$_2$$^+$ was a rounded down value compared to the one determined by Adams and Smith [19], namely $8 \times 10^{-7}$ $(T/300)^{0.50}$ cm$^3$ s$^{-1}$. Although DR is predicted to be the by far dominant process of CH$_3$OH$_2$$^+$ in the inner coma (2000 – 18000 km from the core) and the DR rate coefficient is included as the square into the formula for the electron temperature, a dramatic change of this temperature resulting from the slightly higher DR rate coefficient found in our experiment is unlikely.

Due to the importance of nitriles as biomolecule precursors, DR of these reactions is included in models of dark clouds and planetary ionospheres. The UMIST [27] model applies a total rate of $k(T) = 3.2 \times 10^{-7}$ $(T/300)^{0.50}$ cm$^3$ s$^{-1}$ for the DR processes of HCCCN$^+$ (DCCCND$^+$) leaving the carbon-nitrogen chain intact, whereas we find a rate of $k(T) = 7.5 \times 10^{-7}$ $(T/300)^{0.58}$ cm$^3$ s$^{-1}$, which is
somewhat higher. The rate constants used by the Ohio model [28] are slightly lower ($1.44 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$). Both models – rightly, as we know now – do not include channels leading to fragments with three heavy atoms for this ion. In analogy to methanol, the DR of protonated nitriles has also been invoked as intermediate step for synthesis of the unprotonated compounds according to Reactions (3) and (4). However, it has been shown by Anicich et al. [29] that the product of Reaction (3) with $R=\text{CH}_3$ is actually a highly excited state of protonated methylisonitrile:

$$\text{CH}_3^+ + \text{HCN} \rightarrow (\text{CH}_3\text{NCH}^+)^{**}$$ \hspace{1cm} (11)

which can isomerise to $\text{CH}_3\text{CNH}^+$ by collisions with inert molecules:

$$(\text{CH}_3\text{NCH}^+)^{**} + \text{M} \rightarrow \text{CH}_3\text{CNH}^+ + \text{M}$$ \hspace{1cm} (12)

Unfortunately, under the pressure conditions prevailing in interstellar molecular clouds and high layers of planetary ionospheres there is in practice no chance for $(\text{CH}_3\text{NCH}^+)^{**}$ to undergo a scattering process prior to radiative deexcitation. This and the fact that only a fraction in the DR of $\text{CH}_3\text{CNH}^+$ preserves the CCN chain makes the reaction sequence (3-4) an unlikely production pathway of interstellar acetonitrile.

**Fig. 1** Model calculations using the unchanged reaction rate constants from the new UMIST database from 2004 (solid line), with the DR branching rate constants and the rate constant from the present paper but with the previously used radiative association rate constant (dotted line), and with both new rate constants and new branching ratios (dashed line).

5. Conclusions

The DR of the investigated protonated biomolecule precursors only partly lead to the unprotonated species. In the case of protonated methanol $\text{CH}_3\text{OH}^+$ the low yield of methanol in DR in addition to the low rate coefficient of the radiative association of $\text{CH}_3^+$ and $\text{H}_2\text{O}$ make a gas-phase production of interstellar methanol quite unlikely. Therefore, hydrogenation of CO on ice surface process, as successfully demonstrated experimentally, is a much more promising candidate [24], but several problems related to this mechanism are still unsolved. The DR of the studied protonated nitriles only
partially proceeds under retention of the carbon chain and the overall reaction rate constants observed are comparatively high. For nitriles containing three carbon atoms, only channels either preserving the carbon-nitrogen chain or leading to rupture of the central C-C bond have been observed. Future model calculations on planetary and satellite ionospheres and interstellar clouds including the new data on nitrogen-containing ions will gauge the impact of the new data on model predictions.

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