Dissociative recombination branching ratios and their influence on interstellar clouds

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Abstract. Cross sections and branching ratios for the dissociative recombination (DR) reactions of the astrophysically important ions HN2+, HCO+, DOCO+, and SO2+ at reactant kinetic energies from 1 to 1000 meV have been measured using the CRYRING ion storage ring facility at the Manne Siegbahn Laboratory, Stockholm University. Whereas the break-up of the N-N bond leading to NH + N is the major pathway in the DR of HN2+, the analogous reaction in HCO+ almost exclusively leads to H and CO. In the DR of both DOCO+ and SO2+ three-body break-up was observed. Inclusion of the newly measured branching ratios into a standard model on dark interstellar clouds leads to an improvement of the predictions of such models, especially concerning the abundances of nitrogen compounds. The impact of these newly found branching ratios and reaction rates on the chemistry of different astronomical environments like dark clouds, circumstellar envelopes and planetary ionospheres, is discussed.

1. Introduction

Dissociative recombination (DR) is one of the most important destruction mechanisms of molecular ions, especially in environments with low densities such as interstellar clouds or the upper layers of planetary atmospheres. Therefore, considerable research efforts have been dedicated to gauge the reaction rates and branching ratios of such processes. Whereas there exist ample data on the rates of interstellar DR reactions, the branching ratios of their different pathways are, to a large extent, still unknown. Given the fact that, apart from the most simple ions, a multitude of different reaction channels are energetically available, this leads to a great uncertainty of astrophysical model calculations that use these branching ratios as input. Knowledge of the branching ratios of the different pathways is therefore crucial to accurately model large reaction networks in interstellar clouds [1]. In an earlier theoretical treatment of DR processes by Bates it was predicted that those pathways which involve the least rearrangement of orbitals should be favoured [2]. However, recent experiments showed that many DR reactions do not follow this pattern and processes requiring orbital rearrangement on a large scale like the fracture of multiple bonds and three-body break-up are quite common [3,4,5].

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Measurements have been performed on the DR reactions of the astrophysically and atmospherically relevant ions HCO⁺, N₂H⁺, HOCO⁺, N₂OD⁺, SO₂⁺, and N₂O⁺. HCO⁺, N₂H⁺ and HCO⁺ have been identified in different interstellar environments [6,7,8,9,10] and N₂H⁺ and HCO⁺ have also been detected in the upper layers of Martian atmosphere [11]. Furthermore, HOCO⁺ and N₂H⁺ can be used as tracers for N₂ and CO₂, both of which are particularly difficult to observe astronomically. The DR of some of the ions deserves special attention, since it might provide a clue about some fundamental questions in molecular astrophysics. The branching ratio and rate of the DR of N₂H⁺ has great influence on the abundance of many nitrogen compounds in dense clouds and the percentage of the total nitrogen that is stored in the form of N₂ therein. Protonation of CO₂ to HOCO⁺ with its subsequent DR could provide a suitably efficient destruction mechanism and explain the reduced abundance of this molecule observed in the vicinity of embedded massive young stars [12]. The DR of SO₂⁺ plays a crucial role in the destruction of this ion in Io’s ionosphere [13]. In this contribution we present a comprehensive study of the dissociative recombination rates and branching ratios of the above mentioned astrophysically important ions.

2. Experimental

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 [14] and is only briefly summarised here. N₂H⁺ and HCO⁺ ions were produced in a hot filament discharge ion source (Nielsen m/57) from a mixture of hydrogen with N₂ and CO, respectively; DOCO⁺ and DON₂⁺ from a mixture of D₂ with CO₂ and N₂O, respectively. To obtain better resolution in the fragment energy spectra, DOCO⁺ was used as the parent ion instead of HOCO⁺ since it has been shown in a number of systems that branching ratios and cross sections change only slightly upon deuteration [14]. For SO₂⁺, S¹⁸O₂⁺ was used for experimental reasons, as was H¹³CO⁺ for HCO⁺. After extraction of the ions from the source at 40 keV, they were mass selected, injected into the ring and accelerated to the maximum energy possible (2-3.5 MeV dependent on the ion mass). The stored ion beam was merged with a monoenergetic electron beam in an electron cooler, the length of the interaction region being 0.85 m. During the first 3-4 s after acceleration, the electron and the ion beams were kept at the same average velocity, allowing heat transfer from the ion to the electron beam in order to reduce the translational energy spread of the ions, which results in an increase of their density in phase space. Furthermore, such long storage times enables radiative vibrational relaxation and superelastic cooling of the ions. 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 34 mm, mounted at a distance of 4.4 m from the centre of the ion-electron interaction region. A background signal due to neutral products emerging from collisions of the ions with residual gas molecules was also present, and this was measured with the relative translational energy of ions and electrons tuned to 1 eV, where the DR cross section is very low and neutral fragments are therefore almost exclusively produced by rest gas collisions. This background was subsequently subtracted from the total SBD spectrum collected at 0 eV collision energy.

3. Results

3.1. Branching ratios

The fragments produced by a DR event reach 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 of the DR channels a metal grid with a transmission \( T = 0.297 \pm 0.015 \) was inserted in front of the detector [14]. Particles stopped by the grid did not reach the detector. DR events where 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 (shown for the DR of N$_2$H$^+$ in figure 1) 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 ratios of the reaction. For example, in the DR of N$_2$H$^+$ the intensity of the peak corresponding to $m = 28$ amu (2N) is proportional to $T(1-T)\alpha$, with $\alpha$ being the branching ratio of the pathway leading to N$_2$ + H. Owing to the high kinetic energy release of this pathway, some of the hydrogen atoms produced might receive a large transversal velocity relative to the propagation direction, and therefore miss the detector. This reduces the contribution of the N$_2$ + H reaction channel to the $m = 29$ amu peak to $T^2(1-L)\alpha$, where $L$ is the H-atom loss factor. Conversely, the contribution to the 2N mass peak is augmented to $T(1-T)(1-L)\alpha + T\alpha L$. Using the transmission probabilities mentioned above, the following matrix equation is formulated for the relative intensities (which have been obtained by fitting the fragment energy spectrum shown in figure 1 to double-Gaussian peaks after subtraction of the background signal recorded at 1 eV relative kinetic energy of the reactant) of the different energy (mass) channels,

\[
\begin{pmatrix}
T^2(1-L) & T^2 \\
T(1-T)(1-L)+TL & 0 \\
0 & T(1-T) \\
T(1-T)(1-L) & 0
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
= \begin{pmatrix}
I_{2N+H} \\
I_{2N} \\
I_{N+H} \\
I_N
\end{pmatrix}
\begin{pmatrix}
0.151 \\
0.204 \\
0.263 \\
0.121
\end{pmatrix}
\]  

(1)

where $\beta$ is the branching ratio of the NH + N pathway. The loss $L$ can be assessed in the following way: If one records a spectrum with the grid removed ($T=1$), the intensity ratio of the $I_{2N+H}$ to the $I_{2N}$ channel is $L\alpha/(1-L\alpha)$. Comparing these two intensities with a given branching ratio from a calculation assuming no loss gives a first estimate of the loss factor which can then be used as an input for a new matrix evaluation. The new branching ratio $\alpha$ obtained is then used to get a new loss factor, which is in turn used to perform a new solution of the matrix. This is repeated until consistency is achieved, which then delivers the final branching ratios and the correct loss factor. In the case of the DR of N$_2$H$^+$ this leads to a branching ratio of 0.36 for the N$_2$ + H and 0.64 for the NH + N pathways with a loss factor of 0.33 for the N$_2$ + H channel.
Table 1. Branching ratios of the thermodynamically allowed channels of the DR reactions of the N$_2$H$^+$, HCO$^+$ and SO$_2^+$ ions [4,17].

|       | Branching Ratio |       | Branching Ratio |       | Branching Ratio |
|-------|----------------|-------|----------------|-------|----------------|
| N$_2$H$^+$ |                | HCO$^+$ |                | SO$_2^+$ |                |
| N$_2$ + H | 0.36 ± 0.05    | H + CO | 0.92 ± 0.03    | SO + O | 0.61 ± 0.08    |
| N + NH   | 0.64 ± 0.05    | HC + O | 0.01 ± 0.01    | S + O$_2$ | 0.00 ± 0.02 |
|         |                | C + OH | 0.07 ± 0.02    | 2S + O | 0.39 ± 0.08    |

Table 2. Branching ratios of the thermodynamically allowed channels of the DR reactions of the N$_2$OD$^+$, DOCO$^+$ and N$_2$O$^+$ ions [15,16].

|       | Branching Ratio |       | Branching Ratio |       | Branching Ratio |
|-------|----------------|-------|----------------|-------|----------------|
| N$_2$OD$^+$ |                | DOCO$^+$ |                | N$_2$O$^+$ |                |
| N$_2$O + D | 0.00 ± 0.02    | D + CO$_2$ | 0.05 ± 0.02    | NO + N | 0.36 ± 0.03    |
| N$_2$ + OD | 0.46 ± 0.05    | DO + CO | 0.27 ± 0.04    | O + N$_2$ | 0.48 ± 0.04 |
| NO + DN  | 0.09 ± 0.03    | OD + O  | 0.00 ± 0.02    | 2N+O | 0.16 ± 0.03    |
| D + O + N$_2$ | 0.40 ± 0.08   | D + CO + O | 0.68 ± 0.02    |       |                |
| NO + N + D | 0.00 ± 0.02    | CD + O$_2$ | 0.00 ± 0.02    |       |                |

The loss factor can also be computed from the intensity ratio of the H vs. 2N peak in the measurement with the grid in, which yields 0.32. The branching ratios for the other ions have been obtained in an analogous manner [15,16,17] and are listed in table 1 and 2.

3.2. Absolute cross sections and thermal reaction rates

Absolute cross sections have been determined by changing the relative translational energies of the reactants between 0 and 1 eV. Before the measurement was started, 3-4 s of cooling, with the electrons tuned to 0 eV collision energy, was carried out. The signal from the SBD was discriminated by a single channel analyser, selecting only the signals arising from all fragments reaching the detector simultaneously, and recorded on a multichannel scaler, yielding the number of counts vs. relative translational collision energy. The experimental DR rate coefficient in the electron cooler is expressed by the formula

$$\langle v_{cm} \sigma \rangle = \frac{dN}{dt} \frac{v_e r_e^2 \pi}{l I_e I_i}$$

(2)

where $dN/dt$ is the number of counts per unit time, $v_e$ 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. Simultaneously with the measurement of the dissociative recombination count rate, the ion current was monitored using an AC integrating current transformer in combination with a neutral particle detector installed at the end of one of the straight sections of the ring. After corrections for space charge and toroidal effects [18] the measured reaction rate coefficient $<\sigma_{cm}>$ was obtained according to the following convolution formula:

$$\langle v_{cm} \sigma \rangle = \int_{-\infty}^{\infty} v_e f(v_e) \sigma(v_e) d^3v_e$$

(3)
where $\tilde{f}(v)$ is the velocity distribution. Drag force effects were neglected due to the relatively large masses of the investigated ions [19]. The thermal reaction rate $k$ as a function of temperature $T$ can then be deduced as follows:

$$k(T) = \frac{8\pi m_e}{(2\pi m_e k_B T)^{3/2}} \int_{-\infty}^{\infty} E \sigma(E) \exp\left(-\frac{E}{k_B T}\right) dE$$

(4)

where $m_e$ is the mass of the electron. From the resulting rate constants, the (comparatively) very small contribution to the data due to charge transfer processes with the rest gas (measured at 1 eV collision energy where the cross section of the DR is very low) had to be subtracted. The dependences of the DR rates on the temperature for the different ions are listed in table 3 [4,15,16,17].

Table 3. Thermal rates of the DR reactions

| Reaction          | Thermal rate / cm$^3$s$^{-1}$ |
|-------------------|-------------------------------|
| N$_2$H$^+$ + e$^-$ | $1.0 \pm 0.1 \times 10^{-7}$ (T/300)$^{-0.51\pm0.02}$ |
| HCO$^+$ + e$^-$   | $3.0 \pm 0.9 \times 10^{-7}$ (T/300)$^{-0.64\pm0.02}$ |
| N$_2$OD$^+$ + e$^-$ | $1.4 \pm 0.1 \times 10^{-6}$ (T/300)$^{-0.74\pm0.02}$ |
| DOCO$^+$ + e$^-$  | $1.2 \pm 0.1 \times 10^{-6}$ (T/300)$^{-0.64\pm0.02}$ |
| SO$_2^+$ + e$^-$  | $4.6 \pm 0.2 \times 10^{-7}$ (T/300)$^{-0.52\pm0.02}$ |
| N$_2$O$^+$ + e$^-$ | $3.3 \pm 0.8 \times 10^{-7}$ (T/300)$^{-0.57\pm0.03}$ |

4. Discussion

The predominant channel in the HCO$^+$ recombination leads to H and CO. The small importance of the exoergic HO + C channel is consistent with earlier flowing afterglow measurements [20], which have not observed OH in the DR reaction of HCO$^+$. The possible minute presence of the slightly endoergic HC + O pathway is probably due to the presence of HCO$^+$ in excited vibrational states. This assumption is strengthened by the fact that the branching ratio of the analogous pathway in DCO$^+$, where the excited vibrational modes of the bending vibration have a much longer lifetime, is considerably higher. The HO + C channel can originate from the presence of HCO$^+$ in excited vibrational states. But, assuming the formation of HCO$^+$ (and HOC$^+$) proceeds by reaction of H$_3^+$ with CO (which is reasonable given the present experimental conditions), the abundance of HOC$^+$ can be calculated from the rates of the H$_3^+$ + CO → HCO$^+$ and H$_3^+$ + CO → HOC$^+$ reactions obtained in a hollow cathode discharge experiment$^{11}$. This yields an abundance of only 2% of that of HCO$^+$. In the DR of the isoelectronic N$_2$H$^+$ the high branching ratio of the N-N break-up channel is surprising. Unlike the analogous pathway in HCO$^+$, this channel is exoergic, which can partly explain the different behaviour of these two isoelectronic ions. Notwithstanding the great importance of N$_2$H$^+$ in the interstellar medium, no detailed investigation of the DR branching ratio of this molecule has been previously reported, although it was briefly mentioned that the DR branching ratio of the N$_2$ + H channel was close to 1.0 [22]. The short lifetime of vibrationally excited states [23] of N$_2$H$^+$ rules out the responsibility of such states to the unexpected branching ratio. Rotationally excited states would probably favour the N$_2$ + H pathway. Furthermore, it was observed in an infrared spectroscopy study [24] that N$_2$H$^+$ ions created in a discharge of a mixture of helium, nitrogen and hydrogen at low pressures are much colder rotationally than vibrationally.

In the DR of DOCO$^+$ and DON$_2^+$ three-body fragmentation is very prominent. Such processes, which have been esteemed improbable by Bates [2], have also been detected in other systems [3]. On the other hand, the breaking off of a deuterium atom producing CO$_2$ and N$_2$O is marginal, and non-existent, respectively. It is interesting to compare the current findings with earlier flowing afterglow
Langmuir probe measurements. For the DR of HOCO⁺, Herd et al. [25] report a branching ratio of 0.34 for the production of CO + OH, which is in good agreement with our results. Furthermore, Adams et al. [20] observed that the branching ratio of OH and the branching ratio of H production in the DR of HOCO⁺ sum up to 1. Since all detected channels in the DR of DOCO⁺ reaction lead either to D or to OD, these findings are in perfect agreement with our experiments. In the case of DON₂⁺, our branching ratios of OD production are somewhat higher than in flowing afterglow measurements [20,26]. Three-body fragmentation is also detected to a minor extent in the DR of N₂O⁺ and SO₂⁺. Regarding thermal reaction rates, good agreement of our results with previous flowing afterglow measurements has been obtained for the DR of HCO⁺, N₂H⁺ and N₂O⁺, whereas in the case of DOCO⁺ and DON₂⁺ our rates are considerably higher [25,27,28,29,30].

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