Branching ratios in dissociative recombination of formyl and isoformyl cations

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Abstract. The energy dependence of the branching ratios in dissociative recombination of DCO+ with a known small admixture of DOC+ has been measured for collision energies from 0 to 25 eV using an energy- and position-sensitive surface barrier detector which is designed for the analysis of multi-fragment events occurring in a molecular fragmentation study. The measurements are compared with theoretical calculations on the direct mechanism of dissociative recombination of HCO+ including the contribution from HOC+ at the experimental abundance fraction. At low collision energies, dissociative recombination of HCO+ is dominated by dissociation into H + CO. For collision energies above 2 eV there is a transition into dissociation to HC + O, which can be explained by electron capture into resonant states. Signatures of DOC+ dissociative recombination are found experimentally and confirmed by the calculations for HOC+. Three-body breakup becomes important for collision energies above 6 eV.

1. Introduction

Low energy dissociative recombination (DR) of HCO+ is known to be a reaction crucial for the chemistry of interstellar space. The reaction has been studied extensively both experimentally and theoretically [1]. The measurements agree on a relatively large DR rate of about $2 \times 10^{-7}$ cm$^3$s$^{-1}$ at 300 K [1]. On the theory side there has been a debate on the mechanism for the low energy DR of HCO+. Recent calculations indicate that at low energies the reaction is driven by the electron capture into Rydberg states situated below the ion. The Renner-Teller effect couples
the electronic and nuclear motions. The calculated rate using the multichannel quantum defect theory is about a factor of 2–3 lower than measured rates [2]. At low energies measurements of the branching ratios showed that in this reaction the H-C bond will break [3, 4], in agreement with the prediction [5] that this is the only energetically accessible channel. Analysis of the CO band emission in flowing afterglows shows that with a yield of $0.23 \pm 0.12$ [5] the DR of HCO$^+$ also forms the long-lived excited $a^3\Pi$ state of CO.

Another ion formed in plasmas containing HCO$^+$ is the isonormyl cation HOC$^+$, whose ground state lies approximately 1.7 eV higher than that of the formyl ion. About the DR of HOC$^+$ much less is known, although it has been observed in both dense and diffuse molecular clouds [6, 7, 8] and it also was found in the plasmas used when studying HCO$^+$ [5]. To the best of our knowledge neither an experimental nor a theoretical determination of the DR rate coefficient of HOC$^+$ exists to date.

The present paper gives experimental results on the energy dependence of DR branching ratios for the deuterated species DCO$^+$ and DOC$^+$ in the energy range from 0 to 25 eV. The measurements were performed with fast merged ion and electron beams in the heavy-ion storage ring TSR using the energy-sensitive multi-strip detector EMU [9]. The EMU detector records the impact positions [10] of multi-fragment events with a simultaneous identification of the recombination products by their masses, which yields a determination of the fragmentation channel on an event-by-event basis.

In this fast-beam fragmentation experiment, the products undergo an angular deflection from the beam direction depending on the kinetic energy they gain in the rest frame of the reaction. At the large kinetic energy release (KER) of the DR reaction toward ground-state fragments in the channel H + CO from HCO$^+$ [5] (and similarly from HOC$^+$) the H fragments would reach the detector position with too large transverse offsets from the beam axis, outside the available detector size; hence, the deuterated species were chosen, yielding considerably smaller transverse velocities and, correspondingly, transverse positions falling within the detector size. The final product channels of the DR of DCO$^+$ and DOC$^+$ are listed in Table 1 together with their exothermicities at vanishing electron impact energy from the ground state of the cation to the ground states of the products.

The results for DCO$^+$ and DOC$^+$ are compared to theoretical results for HCO$^+$ and HOC$^+$. In a previous study [11] the electronic resonant states of HCO and HOC were computed by combining electron scattering calculations with structure calculations. We have here performed two-dimensional wave packet propagation on the resonant states to study the direct mechanism of DR. In the model autoionization is included, but no couplings between the neutral states. Also DR of the HOC$^+$ ion is theoretically investigated and by assuming a 9% contamination of HOC$^+$ ions in the TSR experiment, the measured branching ratios are compared with theoretical predictions.

2. Experiment

The DR of the isomeric systems DCO$^+$ and DOC$^+$ is probed in a molecular fragmentation study making use of the merged-beam facility provided by the electron target [12, 13] at the TSR at the Max-Planck Institute for Nuclear Physics in Heidelberg. The ion beam is produced by the same method as in a previous experiment at the TSR [14], which analyzed the isomeric composition of the stored ion beam as discussed below. A tandem Van-de-Graaff accelerator is applied, starting with D$_3$CO$^-$ from a Cs sputter ion source operated with deuterated methanol. These ions are stripped to DCO$^+$ or DOC$^+$ at an energy of ~1.6 MeV in the terminal of the tandem accelerator and further accelerated to reach an energy of 3.1 MeV at their injection into the TSR. In the storage ring, the beam velocity of the electron target is matched to the ion beam velocity for phase-space cooling during 7 s after the injection. In the time interval from 7 to 17 s after injection, the electron beam energy is set to detune its velocity from that of the
ions. For measuring intervals of 50 ms, switching with a duty cycle of 50\% between detuned and matched beam velocities, variable detuning energies $E_d$ in the ion beam rest-frame are applied. By using different values of $E_d$ during the measurement intervals of subsequent injections, the energy dependence of the reaction is investigated.

Upon electron capture the molecule breaks into neutral fragments which travel forward to the detector at the ion beam velocity, undeflected by the magnetic field of the downstream dipole magnet of the storage ring; behind this deflector they impinge on the EMU detector [9] in a dedicated beamline, creating pulses proportional to their kinetic energy. The 128 vertical and horizontal stripes, respectively, on the front and back sides of the $10 \times 10$ cm$^2$ detector are read out individually. Thus the recombination products can be identified by their masses on an event-by-event basis by coincidence imaging and the corresponding fragmentation channel can be assigned. Furthermore, each fragment impact position is known so that one can obtain the distribution of (mass-weighted) fragment separations, which in turn represents the distribution of the KER under the assumption of an isotropic breakup [9, 10].

The relative contributions of each final DR channel (Table 1) resulting from the detector data need small corrections to be applied since the slight deviations of the detection efficiencies from unity do not have the same values for the various fragment channels. They are caused by dead areas separating the strips, geometrical limitations and finite mass resolution. Thus, events of special geometry where the fragments CO and D (mass 30 amu) arrive on a single stripe cannot be resolved from those of a single CO (mass 28 amu) on the same stripe; this slightly reduces the efficiency for identifying the channel CO + D. These efficiency corrections are determined by Monte-Carlo simulations taking all details of the experimental geometry into account [9]. In addition, a background from dissociative electron capture of DCO$^+$ and DOC$^+$ ions in the residual gas was observed, composed of $\sim$91\% CO + D, $\sim$5.5\% of D + C + O, $\sim$2.5\% of DC + O, and $\sim$1\% of DO + C. It could be analyzed by fragment imaging with EMU and amounts to a few percent of the rate at $E_d = 0$; at higher energies, it causes a significant uncertainty of the DR rate to be assigned to CO + D, while it only little affects the DR rates of the other channels, which are also clearly found to be caused by DR through their variation with the electron energy. The final analysis regarding the efficiency correction and the subtraction of this background is ongoing and could slightly modify the branching ratios at higher energies, but not their overall energy dependences.

In a previous experiment at TSR, the isomeric composition of a stored ion beam produced under essentially the same conditions as in the present case was investigated by Coulomb explosion imaging [14]. After a relaxation time of $\sim$4 s following the injection into the TSR, the deuterated isomofyl cation DOC$^+$ was found at stable fractional abundance of 9\% up to 12 s

| Channel | Exothermicity |
|---------|---------------|
|         | DCO$^+$ | DOC$^+$ |
| (α)     | D + CO   | 7.25   | 8.97   |
| (β)     | DC + O   | −0.17  | 1.55*  |
| (γ)     | DO + C   | 0.57*  | 2.29   |
| (δ)     | D + C + O | −3.90 | −2.18  |

Table 1. List of channels available in the DR of DCO$^+$ and DOC$^+$ and their respective exothermicities (in eV). The corresponding energy gains for HCO$^+$ and HOC$^+$ [5] are reduced by 0.06 eV and 0.08 eV for DCO$^+$ and DOC$^+$, respectively, to account for the shift in the zero point energies in these parent species. For channels which would imply a reconfiguration and which therefore are highly unlikely to occur, the exothermicities are marked by an asterisk.
of storage time. The previous study also showed that both isomers internally cooled down from a strong initial vibrational excitation during the above relaxation time; however, the bending vibration was not completely relaxed in DCO\(^+\) with a remaining excitation energy of \(\sim 0.2\) eV, while a lower remaining excitation was found in DOC\(^+\).

At low collision energy, only the final channels (\(\alpha\)) and (\(\gamma\)) of Table 1 are energetically open for DR of DCO\(^+\); of these, channel (\(\gamma\)) would need the removal of the central C atom while creating a new DO bond, which can be considered unlikely. For DOC\(^+\) in low-energy DR these two channels are open as well, together with channel (\(\beta\)) which, however, reciprocally can be considered unlikely because of the strong re-arrangement required for its formation. Energetic thresholds at higher \(E_d\) are expected at only 0.17 eV for DCO\(^+\) towards channel (\(\beta\)) and starting at \(\sim 2-4\) eV for the three-body fragmentation channel.

3. Theory

3.1. Calculation of resonant states

The details of the calculations of the energies and autoionization widths of the electronically resonant states of HCO and HOC have been outlined in a previous study [11] and hence only a short summary is given here. The potential energy surfaces of the electronically bound states are computed using the Multi-Reference Configuration Interaction (MRCI) method with natural orbitals of the ground state of the ion. In the calculations the \((1\sigma)(2\sigma)\) core orbitals are kept doubly occupied and the reference configurations are obtained by excitations of 11 electrons (10 for the ion) among eight orbitals. The MRCI wave function is constructed by allowing all single excitations out of the reference configurations. By using the Complex-Kohn variational method [15] the energy positions and autoionization widths of the resonant states are determined. The same MRCI wave function for the target ion is used in both the structure and electron scattering calculations.

The Rydberg states converging to the ground state of the ion as well as the ionization continuum have the same configuration as the ion plus an outer electron in a diffuse orbital. The resonant states are Rydberg states converging to an excited ionic core. These resonant states all have vacancies in the \((5\sigma)\) or \((1\pi)\) molecular orbitals. By following the states with these configurations a quasidiabatization of the resonant states relative to the Rydberg manifold can be performed. In the present model no electronic couplings between the diabatic states are included.

For the HCO system no electronic states that cross the ion close to its minimum is obtained. At collision energies larger than 2 eV several resonant states can be reached. As a function of the H-C coordinate the resonant states of HCO show clear indications of avoided crossing among each other. The resonant states are repulsive as a function of the C-O coordinate.

The resonant states of HOC are lower in energy relative to the ion compared with HCO. Also the HOC resonant states show indications of avoided crossings and are repulsive as a function of the O-C coordinate.

As a function of the bending angle the resonant states of both HCO and HOC are relatively flat in the Franck-Condon region. In the present study the two radial coordinates are included while the bending angle is kept at the linear geometry. The resonant states are constructed on a product grid where the C-O distance (O-C for HOC) is ranging from 1.5 to 10.0 \(a_0\) and H-C (H-O for HOC) from 1.0 to 10.0 \(a_0\).

3.2. Wave packet dynamics

The nuclear dynamics is studied using wave packet propagation with the Multi Configuration Time Dependent Hartree (MCTDH) method [16]. The direct mechanism of DR is investigated by numerically solving the time-dependent Schrödinger equation for the resonant states where
autoionization is included as a local complex term added to the potential.

\[ i \frac{\partial}{\partial t} \Psi = \left( T + V - i \frac{\Gamma}{2} \right) \Psi. \]  

(1)

The initial condition for the wave packets is given by

\[ \Psi(t = 0) = \sqrt{\frac{\Gamma}{2\pi}} \chi_{\text{ion}}, \]  

(2)

where \( \chi_{\text{ion}} \) is the ground vibrational wavefunction of the ion.

The wave packets are propagated for 140 fs until they have reached the asymptotic regions of the resonant states. At large internuclear coordinates (8.0 \( a_0 \)) complex absorbing potentials are used to determine the dissociating flux [17]. By applying projection operators of the one-dimensional eigenstates of the asymptotic Hamiltonian, the state-specific transition probabilities can be computed. Summarizing over the vibrational bound states, a separation between the two- and three-body breakup channels can then be performed.

For the HCO system, two resonant states of each of the symmetries \( ^2\Sigma, ^2\Pi \) and \( ^2\Delta \) are included. For HOC, there are two states of \( ^2\Sigma \) and \( ^2\Delta \) symmetries and three states of \( ^2\Pi \) considered.

### 4. Results and Discussion

#### 4.1. Measured branching ratios

The observed ratios of occurrence for the different final channels represent the detector data with small corrections as discussed in Sec. 2. They are shown in Fig. 1 as a function of the collision energy \( E_d \) and correspond to a known mixture of DCO\(^+\) and DOC\(^+\) in the parent ion beam. At near-zero collision energy the fragmentation channel CO + D (\( \alpha \)) is dominant by more than 96%. Considering the low isomeric fraction of DOC\(^+\) present, this shows that this channel dominates the low-energy DR of DCO\(^+\), as expected (see Sec. 2). The small contribution of channel (\( \gamma \)) is likely due to DOC\(^+\) ions that recombine into this channel already at low energy.

As the collision energy increases the branching into the originally dominating channel D + CO decreases, while both other two-body channels (\( \beta \) and (\( \gamma \)) take a larger relative fraction of events. It is likely that the breakup into DO + C (\( \gamma \)) can be completely assigned to the DR of DOC\(^+\), while DC + O (\( \beta \)) should be caused by DCO\(^+\), considering the strong reconfiguration.

![Figure 1](image-url)
necessary to form either of these channels from the respective other isomer. Although the three-body channel ($\delta$) is accessible for energies above $\sim$2–4 eV, it is only observed from $\sim$7 eV onward. It first seems to increase on the expense of the dominant channel ($\alpha$), while above $\sim$12 eV it rather seems to be fed from channel ($\beta$). Above $\sim$18 eV only CO + D and D + C + O are significantly observed.

4.2. Calculations on HCO

The electronic resonant states of HCO do not contribute to the DR cross section at low energies (see Fig. 2 of Ref. [11]). An energy of about 1 eV is needed to capture into the resonant states. Above this energy the resonant states will produce a high-energy peak in the cross section. The largest contribution to this peak comes from the lowest $^2\Pi$ resonant states. The lower resonant states are dominated by a complete breakup into HC + O. For some of the higher resonant states ($^1\Sigma^+$ and $^2\Delta$) there are contributions of dissociation into H + CO. In Fig. 2 the calculated branching ratios for DR of HCO$^+$ are displayed. For low energy collisions we use the DR cross section calculated by Douguet et al. [2] and assume a 100% breakup into H + CO. As can be seen in the figure there is a complete transition from H + CO dissociation into HC + O dissociation around 1 eV when the energy is high enough to capture into the electronically resonant states. Above 6 eV the branching ratio for breaking both bonds is increasing.

In the present study the two radial coordinates are included while the angle is fixed at linear geometry. This is motivated by the fact that in the Franck-Condon region the energies of the resonant states are relatively independent with respect to changes in the angle. We have begun calculations on the dynamics where all three internal coordinates are included and preliminary results indicate that this will not significantly change the results presented here.

4.3. Calculations on HOC

The resonant states of HOC (see Fig. 4 of Ref. [11]) are lower in energy relative to the ion compared to HCO. However, the nuclear dynamics reveal that the resonant states of HOC do not significantly contribute to the low energy DR cross section. The resonant states of HOC will produce a peak in the DR cross section centered around 0.6 eV. The largest contribution to this peak comes from the lowest resonant state of $^2\Delta$ symmetry. As can be seen in Fig. 3 at low energies, the HOC branching ratios are dominated by HO + C dissociation. In the present model the capture into the Rydberg states are not included and by including this indirect mechanism
of DR the low energy branching ratios could indeed change. At larger energies the branching ratios oscillate around 50% dissociation into H + OC and 50% breakup into HO + C. For energies above 6 eV the breaking of both bonds can occur.

4.4. Comparison between experiment and theory

In Fig. 4 the measured branching ratios are compared with the computed branching ratios. In the theoretical model a 9% fraction for the HOC\(^+\) component in the experiment is assumed. It should be noted that the experiments are carried out for the DCO\(^+\) ion while in the theoretical modeling HCO\(^+\) is studied. In the comparison, both the experimental and the calculated branching ratios show a transition into the dissociation channel equivalent to HC + O when the energy amounts to a few eV and electron capture into the resonant states of HCO can proceed. The calculated branching ratio for HC + O dissociation is larger than the measured one in the range up to about 7 eV on the expense of a strongly diminished observation of CO + H. Furthermore both experiment and theory show an opening of the three-body breakup for collision energies above 6 eV. There is some contribution of HO + C (DO + C) dissociation in both theory and experiment, which can be explained by the HOC\(^+\) (DOC\(^+\)) contamination.

The remaining differences between the computed and measured branching ratios might be explained by several different factors. First, in the theoretical modeling only the direct dissociative recombination mechanism is considered. No electronic couplings between the neutral states are incorporated. By including these couplings, flux may be redistributed among the electronic states and this can change the branching ratios. Furthermore, in the theoretical study electron capture with ro-vibrationally relaxed ions is investigated. Experimentally the ions are known to be rotationally excited and for DCO\(^+\) also vibrationally excited. Finally, for

![Figure 4. Measured branching ratios (a) are compared with the theoretical branching ratios (b) for a composite isomeric beam dominated by DCO\(^+\) (HCO\(^+\) in the theoretical model) with a 9% fraction of DOC\(^+\) (HOC\(^+\)).](image-url)
low energy collisions with HCO⁺, we use the cross section computed by Doughet et al. [2] and assume a 100% breakup into H + CO. This branching ratio has not been theoretically calculated.

5. Summary
We present results on the energy dependence of the branching ratios in the DR of DCO⁺ measured with a 9% contamination by DOC⁺ ions known from a previous measurement. The experimental branching ratios are compared with computations on the direct mechanism of DR for the undeuterated corresponding ions HCO⁺ and HOC⁺. Applying a 9% admixture of HOC⁺ ions in the calculations, a qualitative agreement between theory and experiment is found. In the present study the two radial coordinates are included in the study of dynamics; the angular dependence of the resonant states will be addressed in a future study.

Acknowledgments
We are grateful to V. Kokoouline for sharing unpublished data with us. Travel support for CN was provided from NSF and NASA. AL acknowledges support from the Swedish research council. AEO acknowledges support from the National Science Foundation under grant PHY-08-55092. ON was supported in part by the NSF Astronomy and Astrophysics Grant Program. ML was supported in part by the NASA Astronomy and Astrophysics Research and Analysis Program. HB and OH acknowledge partial support by the German Israeli Foundation for Scientific Research and Development (G.I.F.) under Grant I-900-231.7/2005 and by the European Project ITS LEIF (HRPI-CT-2005-026015). DS acknowledges support by the Weizmann Institute through the Joseph Meyerhoff program. Support by the Max-Planck Society is gratefully acknowledged.

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