New quantum chemical computations of formamide deuteration support a gas-phase formation of this prebiotic molecule

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ABSTRACT

Based on recent work, formamide might be a potentially very important molecule in the emergence of terrestrial life. Although detected in the interstellar medium for decades, its formation route is still debated, whether in the gas phase or on the dust grain surfaces. Molecular deuteration has proven to be, in other cases, an efficient way to identify how a molecule is synthesised. For formamide, new published observations towards the IRAS16293-2422 B hot corino show that its three deuterated forms have all the same deuteration ratio, 2–5%, and that this is a factor 3–8 smaller than that measured for H$_2$CO towards the IRAS16293-2422 protostar. Following a previous work on the gas-phase formamide formation via the reaction NH$_2$ + H$_2$CO $\rightarrow$ HCONH$_2$ + H, we present here new calculations of the rate coefficients for the production of monodeuterated formamide through the same reaction, starting from monodeuterated NH$_2$ or H$_2$CO. Some misconceptions regarding our previous treatment of the reaction are also cleared up. The results of the new computations show that, at the 100 K temperature of the hot corino, the rate of deuteration of the three forms is the same, within 20%. On the contrary, the reaction between non-deuterated species proceeds three times faster than that with deuterated ones. These results confirm that a gas-phase route for the formation of formamide is perfectly in agreement with the available observations.

Key words: ISM: abundances — ISM: molecules

1 INTRODUCTION

Among the zoo of detected interstellar molecules formamide (HCONH$_2$) has a peculiar role in prebiotic chemistry because it can generate both genetic and metabolic molecules (e.g. Saladino et al. 2012). It has been speculated that formamide could have been brought in large quantities on Earth from the interstellar/planetary dust and comets that rained on primitive Earth (e.g. Ferus et al. 2014). Recent observations in star forming regions (e.g. Lopez-Sepulcre et al. 2015) and, in particular, in regions that will eventually form stars like the Sun and planetary systems like the Solar System (e.g. Kahane et al. 2013; Mendoza et al. 2014) are in favour of this scenario. Kahane et al. (2013) have also found that the relative abundances of formamide and water, [HCONH$_2$]/[H$_2$O], in the solar type protostar IRAS16293-2422 (hereinafter IRAS16293) and in the coma of the comet Hale-Bopp are very similar. Furthermore, Jaber et al. (2014) have found that formamide abundance shows an increase by more than two orders of magnitude in the interior of IRAS16293, in the so-called hot corino region. There, the formamide abundance is $\sim 6 \times 10^{-10}$, equivalent to a mass of more than ten Mediterranean seas.

One peculiar aspect of the solar type star forming regions is the largely enhanced deuterium fractionation observed in H-bearing molecules (e.g. Ceccarelli et al. 2014). Indeed, the deuteration of molecules formed in the first cold prestellar phase can be several orders of magnitude larger than the statistical value based on the elemental D/H ratio (1.5 $\times$ 10$^{-5}$; Linsky 2007). Emblematic examples are those...
of formaldehyde and methanol, where the doubly (and even triply, for methanol) deuterated forms have been detected with D-bearing/H-bearing ratios up to 30 (and 5) per cent (e.g. Ceccarelli et al. 1998; Parise et al. 2003, 2006). Interestingly, the deuteration ratio in different molecules might provide the temporal sequence of their formation and, possibly, information on their synthetic route (e.g. Caselli & Ceccarelli 2012; Ceccarelli et al. 2014).

Very recently, Coutens et al. (2016; hereinafter CJW2016) have reported the detection of deuterated formamide in the solar-type protostar IRAS16293 (see Jørgensen et al. 2016 and Jaber Al-Edhari et al. 2017, for a recent description of the source). In their work, CJW2016 detected the three forms of deuterated formamide: trans- and cis- HCONH and, DCONH2. They found that they have approximately the same deuteration ratio, 2-5 %. Note that the latter observations have been obtained with the ALMA interferometer and that they refer to the hot corino region only. CJW2016 noticed that the fact that the three forms have a similar deuteration ratio provides constraints on the synthesis of formamide. Different routes have been suggested in the literature: the gas-phase reaction NH2 + H2CO (Barone et al. 2015; Vazart et al. 2016), grain-surface radical recombination (e.g. Fedoseev et al. 2016), synthesis dominated by UV or ion irradiation of ices containing various species, like methanol (e.g. Jones et al. 2011, Kamoucha et al. 2016). CJW2016 noted that the relatively small percentage of deuterated formamide with respect to formaldehyde might suggest a preference for synthesis on ice, as gas phase routes should mostly retain the deuteration ratio of parent molecules.

However, this is not necessarily true. First of all, even though all the isotopologues are characterized by the same electronic energies, the reaction rate coefficients for the isotopic variants can be influenced by factors such as zero point energies (ZPE) and densities of states. In addition, the reaction mechanism controls whether D or H displacement is favored in gas phase reactions involving partially deuterated species. In particular, the release of D over H can be favored in direct abstraction processes, while the release of H over D is favored in indirect reactions involving partially deuterated species. Also, the details of the reactive potential energy surface can change these common-sense rules (Skouteris et al. 1999).

In this letter, we present new computations on the gas-phase reaction between partially deuterated amidogen (NH2) or partially deuterated formaldehyde (H2CO) and discuss the implications for the above mentioned astronomical observations.

2 GAS-PHASE FORMATION OF FORMAMIDE

The occurrence of the NH2 + H2CO reaction as a source of formamide was first suggested by Kahane et al. (2013) but no measurements or computations were available at the time. Later, Barone et al. (2015) carried out accurate electronic structure calculations coupled with capture theory and RRKM kinetic calculations to estimate the rate coefficient. They found that the reaction can be very fast also in the cold interstellar conditions. This result was later confirmed by even more accurate computations by Vazart et al. (2016). According to these first studies, the reaction proceeds with the formation of a bound intermediate and, therefore, emission of H over D should be favored. Interestingly, before the formation of the addition intermediate, a van der Waals complex is formed and a transition state has to be surmounted to form the addition intermediate (see Fig. 1). A second transition state connects the bound intermediate to the final products. It should be noted that, for this particular case, the vicinity of the energy levels of the transition states and the reactant asymptotes is a real computational challenge because the status of the transition states as “emerged” or “submerged” can fall within the uncertainty of the calculations (see Fig. 1). In Barone et al. (2015) and Vazart et al. (2016) the presence of the van der Waals complex has been deliberately neglected (see below). In a recently published theoretical paper on the formation of formamide on ice, a much smaller estimate of the rate coefficient was reported for the NH2 + H2CO reaction (Song & Kastner 2016) because the energy level of the transition state connecting the van der Waals complex to the addition intermediate with the inclusion of its ZPE was found to be significantly above the reactant asymptote. In this paper, we clarify further the choice of neglecting the formation of the van der Waals complex. In addition, since the substitution of an H atom by a D one affects the density of states of all intermediates and transition states, as well as the tunnelling efficiency, a thorough investigation of the NH2 + H2CO and NH2 + HDCO reactions is presented here to derive the specific rate coefficients and to assess whether they are compatible or not with a formamide formation in the gas-phase through the above reactions.

In particular, we consider the following isotopologues:

1. NH2 + H2O → DCONH2 + H, ΔH0 = −47.29 kJ mol⁻¹
2. NH2 + HCO → HCONH2 + D, ΔH0 = −39.07 kJ mol⁻¹
3. NHD + H2O → t-HCONH + H, ΔH0 = −48.49 kJ mol⁻¹
4. NHD + H2O → c-HCONH + H, ΔH0 = −48.50 kJ mol⁻¹

The exothermicities given above have been computed as described in Sec. 3. For each of the two monodeuterated versions of the reactants, there are two possible products to consider. In the case of HDCO, both normal and C-deuterated formamide is formed. In the case of NHD, HCONH2 can be formed in the cis or trans isomers (hindered rotation around the C-N bond).

3 COMPUTATIONAL DETAILS AND RESULTS

The main body of the calculations has been performed with a development version of the Gaussian suite of programs (Frisch et al. 2015). The computations have been carried out using the double-hybrid B2PLYP functional (Grimme 2006), in conjunction with the m-aug-cc-pVTZ basis set (Papajak et al. 2009, Dunning 1989), where d functions on hydrogens have been removed. Semiempirical dispersion contributions have also been included into DFT computations by means of the D3 model of Grimme, leading to the B2PLYP-D3 functional (Goerigk et al. 2011, Grimme et al. 2011). Full geometry optimizations, and calculations of frequencies and rotational constants, have been performed for all minima and transition states of all isotopomers, also checking the
nature of the obtained structures by diagonalizing their Hessians that have been used also to evaluate ZPEs at the harmonic level. Additional calculations based on coupled cluster methods have been performed in order to reevaluate the energies of all species. The coupled-cluster singles and doubles approximation augmented by a perturbative treatment of triple excitations (CCSD(T), Raghavachari et al. 1989) has been employed in conjunction with extrapolation to the complete basis set limit and inclusion of core-correlation effects (CCSD(T)/CBS+CV). At this level of calculations, the energy level of the van der Waals transition state is slightly above the energy of the reactants’ asymptote (see Table 1). However, when a full treatment of triple (fT) and quadruple excitations (fQ) has also been included, thus leading to the CCSD(T)/CBS+CV+fT and CCSD(T)/CBS+CV+fT+fQ approaches, the barrier issuing from this transition state significantly decreases (3.6 kJ/mol drops to 2.05 kJ/mol with full-T and to 1.67 kJ/mol with full-T and full-Q).

As in previous work (Barone et al. 2015), we have used the results of the electronic structure calculations to derive the capture theory rate constant for the formation of the initial bound intermediate (slightly dependent on the reduced mass). Subsequently, using the RRKM scheme as in previous work (Balucani et al. 2012, Leonori et al. 2013, Vazart et al. 2015a), we have calculated rate constants (as a function of energy) for the elimination of an H or D atom to form formamide or back-dissociate to the reactants. When using detailed balance the energy-dependent rate constant for back-dissociation of the intermediate to the reactants as done in Vazart et al. (2015b) and Skouteris et al. (2015). The master equation has been solved as a function of energy to determine the bimolecular rate constant for formamide formation and its isotopologues. Finally, Boltzmann averaging has been carried out to determine rate constants as a function of temperature. Each rate constant has been fitted to the rate law:

\[ k(T) = A \times (T/300K)^{2/3} \times e^{-\gamma/T} \] (1)

The results are listed in Table 2 together with those of the undeuterated case (from Vazart et al. 2016) for comparison.

4 RESULTS AND DISCUSSION

The interaction between the reactants starts with the formation of a shallow van der Waals complex and the subsequent formation of a bound intermediate. This can then eliminate an H atom to form formamide or back-dissociate to the reactants. The electronic potential energy surface is the same for all isotopomers, but the energy levels, vibrational frequencies, rotational constants and zero point energies depend on the masses involved. This can change the relative densities of states and the resulting reaction rate constants. As already mentioned, Song & Kastner (2016) disputed the gas-phase formation of formamide through the NH₂ + H₂CO reaction, arguing that the transition state connecting the van der Waals complex to the intermediate is too high when including the ZPE (from +2.7 kJ mol⁻¹ to 17.8 kJ mol⁻¹ with ZPE at the UCCSD(T)- F12/cc-pVTZ-F12 level of calculations) and the reaction rate coefficient very small (of the order of 10⁻₂² cm³ s⁻¹). Against this claim, it must be stressed that: i) Even though the calculated energy of the transition state leading from the van der Waals complex to the bound intermediate, as results from the coupled cluster calculations, is higher than the reactant asymptote, its energy substantially drops by including higher excitation orders in the cluster operator (see values in the previous section). Extrapolating to the full configuration interaction limit, the electronic energy of this transition state drops slightly below the reactant level (Vazart et al. 2016) in line with the variational principle of approximating from above. ii) The use of the ZPE correction for the van der Waals complex and its transition state is not warranted. In an electronic calculation the ZPE is derived from local considerations on the potential minimum (harmonic or anharmonic). However, the three new vibrational modes in the van der Waals complex consist of a very loose stretching mode (where even a perturbative approach including anharmonicity would tend to grossly overestimate the frequency) and two loose bending modes that constitute almost free rotations. Under these conditions, in order to derive the exact ground state level one would have to exactly solve the Schrödinger equation on the overall potential. We believe that it is a much more realistic approach to neglect what emerges as "the ZPE". Taking into
account the two points above, it is much more reasonable to omit the van der Waals complex from the reaction scheme rather than largely overestimate its role as done by Song & Kastner (2016). Kinetics experiments should be performed at very low temperatures in a CRESU apparatus to verify the main focus of these new calculations concerns the rate coefficients and product branching ratios of the partially deuterated species. The most relevant results can so be summarized: i) the reactions involving the exit of an H atom have essentially equal rates, which are lower by a factor of 2–4 than the rate of the undeuterated reaction. For the NH2 + HDCO reaction, the constant capture incoming flux is split between two distinct product channels accounting for a factor of 2 (that is the observed difference at 10 K). The larger factor observed at higher temperatures and the reduced k(T) for the NH2 + HDCO → DCONH2 + H rate are, instead, direct consequences of the prevailing back-dissociation; ii) the reaction NH2 + HDCO mainly produces DCONH2, with only 1–2% going into HCONH2. The reason for this is twofold: the lighter H atom tunnels more easily through the barrier towards the products by a factor of around 50 and the vibrational ZPE of the transition state is lower when an H rather than a D atom has started dissociating.

In conclusion, even though the partially deuterated formamide products retain the degree of deuteration of the parent molecules, the three isotopic variants of the NH2 + H2CO reactions are not characterized by the same rate coefficient. In particular, since the fastest reaction is the one with undeuterated reactants, the expected value of the degree of formamide deuteration at 100 K is a factor of 3 lower than that of the parent molecules H2CO or NH2.

### 5 COMPARISON WITH ASTRONOMICAL OBSERVATIONS AND CONCLUSIONS

So far, deuterated formamide has only been detected towards the hot corino of IRAS16293-2422 B by CJW2016. They found that the DCONH2/HCONH2 and HCONHD/HCONH2 abundance ratios are similar and
around 0.02-0.05. Based on this and on the fact that these ratios are smaller than the measured HDCO/H$_2$CO abundance ratio, CJW2016 favoured a grain-surface formation of NH$_2$CHO. With the new computations reported in Table 2, we can now quantitatively discuss this issue. For that, we will consider the rates computed for a gas temperature of 100 K, namely the temperature in the IRAS16293-2422 B hot corino (e.g. Jaber et al. 2014).

(i) DCONH$_2$/HCONH$_2$ and HCONHD/HCONH$_2$ abundance ratios smaller than HDCO/H$_2$CO: The values in Table 2 show that there is a factor three difference in the rates of formation of H- against D- formamide. Therefore, the deuteration of formamide synthesised in the gas-phase will be three times smaller than that of the mother molecules NH$_2$ and H$_2$CO. No observations of NH/DH exist so far, so no constraints can be obtained from amilogen. Similarly, no observations exist of the HDCO/H$_2$CO abundance ratio in the hot corino of IRAS16293-2422 B. However, single-dish observations of deuterated formaldehyde towards IRAS16293 measured HDCO/H$_2$CO$\approx$ 0.15 (e.g. Ceccarelli et al. 1998; Loinard et al. 2000), namely a factor 3-8 larger than DCONH$_2$/HCONH$_2$. Therefore, within the uncertainty of the available observations, the hypothesis of formamide gas formation is fully consistent with them. In addition, as correctly pointed out by CJW2016, single-dish observations encompass both the hot corino and the extended envelope. Ceccarelli et al. (2001) mapped the D$_2$CO line emission towards IRAS16293 and showed that the D$_2$CO/H$_2$CO abundance ratio is about 0.03. Likewise, HDCO/H$_2$CO is also high in the extended envelope and, thus, the single-dish measurements are likely largely contaminated by the extended envelope.

(ii) Similar DCONH$_2$/HCONH$_2$ and HCONHD/HCONH$_2$ abundance ratios: The values in Table 2 show that indeed the two abundance ratios are similar (0.8-0.9) if the gaseous NH/DH and HDCO/H$_2$CO are similar. In this respect, then, the gas-phase formation of formamide is perfectly consistent with the observed values.

We conclude that the available observations do not allow to rule out a gas-phase formation route for formamide but, on the contrary, they support it. New high-spatial resolution observations of both NH and HDCO towards IRAS16293 will be necessary to challenge this conclusion.

Finally, we would like to note that the same approach could be used to address the deuteration of other complex organic molecules, such as methyl formate, for which a debate on gas-phase versus ice-assisted formation routes is currently ongoing (see, for instance, Balucani et al. 2015).

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