A New “Non-energetic” Route to Complex Organic Molecules in Astrophysical Environments: The C + H₂O → H₂CO Solid-state Reaction

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Abstract

The solid-state reaction C + H₂O → H₂CO was studied experimentally following the co-deposition of C atoms and H₂O molecules at low temperatures. In spite of the reaction barrier and absence of energetic triggering, the reaction proceeds fast on the experimental timescale pointing to its quantum tunneling mechanism. This route to formaldehyde shows a new “non-energetic” pathway to complex organic and prebiotic molecules in astrophysical environments. Energetic processing by UV irradiation of the ice produced by co-deposition of C and H₂O reactants leads mainly to the destruction of H₂CO and the formation of CO₂, challenging the role of energetic processing in the synthesis of complex organic molecules under astrophysically relevant conditions.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Surface processes (2116)

1. Introduction

Understanding the reaction pathways to complex organic and prebiotic molecules at the conditions relevant to various astrophysical environments, such as prestellar cores, protostars, and planet-forming disks, will provide insight into the molecular diversity present during the planet formation process (Jørgensen et al. 2020). Modern astrochemical reaction networks contain thousands of reactions (see, e.g., astrochemical databases such as KIDA (http://kida.astrophy.u-bordeaux.fr/) and UDFA (http://udfa.ajmarkwick.net/)). However, these networks are very sensitive to inclusions of new reactions. Even the inclusion of one new reaction may lead to a considerable change of the predicted abundances of many molecules in the solid state as was recently demonstrated by the addition of the C + H₂ → CH₂ reaction into a well-developed network (Simončič et al. 2020). Thus, systematic studies of astrochemically relevant reactions, particularly, involving simple species (as these form at the beginning of reaction networks and may define their further evolution) are essential for the development of reliable astrochemical models.

Chemical reactions leading to the formation of molecules in cosmic environments can be divided into two groups: gas-phase and grain-surface reactions. Solid-state (or surface) reaction pathways at conditions relevant to interstellar and circumstellar environments lead to a greater complexity of molecular species up to prebiotic molecules, such as amino acids and nucleobases (Bernstein et al. 2002; Muñoz Caro et al. 2002; Holtom et al. 2005; Meinert et al. 2011; Nuevo et al. 2012; Krasnokutski et al. 2020; Ioppolo et al. 2021). In these reactions, the surface of grains may play an important role acting not only as a location for reactants but also as a catalyst. Concerning the catalytic role of dust grains, we refer the reader to a few relevant studies (Hill & Nuth 2003; Saladino et al. 2005; Potapov et al. 2019a, 2020a, 2020b) and a review (Potapov & McCoustra 2021).

H₂O ice is the main constituent of cosmic molecular ices covering the surface of dust grains in cold regions (Whittet 2003). Atomic carbon is one of the most abundant carbonaceous species in various astrophysical environments (Schilke et al. 1995; Gerin et al. 1998; Henning & Salama 1998; Tanaka et al. 2011). Thus, the reaction between H₂O and C is of fundamental interest and may considerably influence the evolution of astrochemical reaction networks. The high reactivity of C atoms is well known thanks to theoretical and experimental studies (Henning & Krasnokutski 2019; Krasnokutski et al. 2020; Qasim et al. 2020a, 2020b).

The low-temperature reaction C + H₂O was previously studied in the gas phase as well as in the solid state (Schreiner & Reisenauer 2006; Hickson et al. 2016). In the gas phase, a reactivity increase below 100 K was observed. As the rate of the C + D₂O reaction was much lower compared to that of the C + H₂O reaction, the increased reactivity was explained by the presence of a quantum tunneling mechanism (Hickson et al. 2016). In the solid state, the formation of formaldehyde (H₂CO) was detected, but assigned to the reactivity of excited C atoms in singlet states (Schreiner & Reisenauer 2006). It is well known from laboratory experimental studies that reactions referred to as “non-energetic” (typically, thermal atom addition reactions at low temperatures) may lead to high molecular complexity (Linnartz et al. 2015; Krasnokutski et al. 2017; Potapov et al. 2017; Ioppolo et al. 2021). As energetic processing, such as UV irradiation and particle (ions, electrons) bombardment, of molecular ices may play both constructive and destructive roles (Öberg 2016), “non-energetic” reactions may present an alternative route to the formation of complex organic molecules in astrophysical environments.

The aim of the present study was to investigate the low-temperature solid-state reaction C + H₂O → H₂CO involving ground-state C(³P) atoms. The temperatures of the experiments, 10–80 K, correspond to a wide range of astrophysical environments from interstellar clouds through hot cores and protostars to planet-forming disks and debris disks. In addition, the effect of UV irradiation on the ice produced by co-deposition of C and H₂O reactants was studied.

2. Experimental Part

The experiments were performed in the INterStellar Ice Dust Experiment (INSIDE) setup presented in detail elsewhere (Potapov et al. 2019b). H₂O ice and C atoms were deposited...
onto a KBr substrate at 10, 20, 50, and 80 K and a base pressure of a few \(10^{-10}\) mbar through two independent gas lines placed at a 45° angle to the substrate. C atoms were produced by an atomic source via thermal evaporation. The source is described in detail elsewhere (Krasnokutski & Huiskes 2014). Briefly, it operates as follows. Carbon powder is placed inside a tantalum tube, which is resistively heated. Carbon powder dissolves into tantalum and diffuses to the outer surface of the tube walls, from which it evaporates in the form of single carbon atoms only. The source was connected to one of the flanges of the main chamber of INSIDE through a valve, which, when open, lets the C atoms enter the chamber and reach the substrate. As the binding energy C \(\cdot\) H\(_2\)O is about 3500 K, we expect that all C atoms adsorb on the surface at the given experimental conditions.

The H\(_2\)O deposition time in all experiments was 40 minutes with a constant deposition rate for H\(_2\)O of about \(3 \times 10^{15}\) molecules minute\(^{-1}\). The number of deposited H\(_2\)O molecules was calculated from the vibrational stretching band at 3250 cm\(^{-1}\) using a band strength of 2 \(\times 10^{-16}\) cm molecule\(^{-1}\) (Hudgins et al. 1993). C atoms were deposited during 35 minutes (between the 4th and the 38th minutes of the H\(_2\)O deposition). The flux of C atoms from the source was estimated elsewhere by means of scanning tunneling microscopy on an Ag(111) substrate (Krasnokutski et al. 2019). The H\(_2\)O/C ratio of the deposited species in our experiments was estimated to be more than 10 (up to a few tens considering the high uncertainty of the estimated flux of C atoms).

In an additional experiment, D\(_2\)O ice and C atoms were deposited at 10 K. In addition, in order to study the direct contribution of cold C atoms in the C + H\(_2\)O reaction, a layered H\(_2\)O/Ar/C sample was produced at 10 K. We deposited about 10 monolayers of H\(_2\)O, then 10 monolayers of Ar, and then C atoms for 3 minutes. The procedure was repeated 10 times. Efficient diffusion of C atoms in Ar ice is well known (Thompson et al. 1971), thus, after the C deposition, C atoms were expected to diffuse through Ar layers and interact with the pre-deposited top layers of H\(_2\)O ice.

Two series of experiments have been performed: (i) C + H\(_2\)O deposition and subsequent heating of the samples and (ii) C + H\(_2\)O deposition, UV irradiation at the deposition temperature, and subsequent heating of the samples. In the second series of experiments, after deposition, the ice was heated by co-deposition of C and H\(_2\)O reactants and irradiated for 2 hours at 45° incidence by a broadband deuterium lamp (L11798, Hamamatsu) with a flux of \(10^{15}\) photons s\(^{-1}\) cm\(^{-2}\) and a final fluence of \(7 \times 10^{18}\) photons cm\(^{-2}\). The lamp has a broad spectrum from 400 to 118 nm with the main peak at 160 nm (7.7 eV) and an additional peak at 122 nm (10.2 eV) corresponding to the emission of molecular and atomic (Ly\(_\alpha\) line) hydrogen, respectively.

Temperature-programmed desorption (TPD) experiments were performed by heating the samples to 300 K using a linear temperature ramp of 2 K minute\(^{-1}\). Infrared spectra were measured in the spectral range from 6000 to 600 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\) using an FTIR spectrometer (Vertex 80v, Bruker) in transmission mode. Mass spectra during the TPD experiments were taken in the mass range from 0 to 90 amu with a scanning time of one minute for one spectrum using a quadrupole mass spectrometer (HXT300M, Hositrad).

For the presented experimental results, it is important to stress that the used atomic carbon source is characterized by a very low production of carbon clusters (<1% C\(_2\) and C\(_3\) molecules with respect to carbon atoms) and by the production of only ground-state C(P\(_2\)) atoms due to the formation process via thermal evaporation. This is in contrast to typically used energetic production methods such as laser ablation of a solid target or electric discharge of a gas mixture or a liquid. In our carbon source, C atoms are assumed to be in thermal equilibrium with the tantalum tube (about 2100 K). This high temperature is required to overcome the binding energy of C atoms to tantalum and evaporate them. The amount of energy required to reach the excited singlet state C(\(^3\)D) is 14665 K (Kramida et al. 2018). Thus, the presence of C atoms in singlet states can be completely excluded.

3. Results

First, the reaction C + H\(_2\)O \(\rightarrow\) H\(_2\)CO was studied following co-deposition of C atoms and H\(_2\)O molecules at low temperatures. In Figure 1, we present the IR spectra taken after the C + H\(_2\)O depositions at 10, 20, 50, and 80 K; and C + D\(_2\)O deposition at 10 K. The formation of H\(_2\)CO is clearly observable via its strongest vibrational bands at 1720 and 1500 cm\(^{-1}\) (Watanabe & Kouchi 2002; Pirim & Krim 2014). Other, less intense bands at 2890, 2828, and 1247 cm\(^{-1}\) are also observed (not shown in the figure). The main peak of doubly deuterated formaldehyde (D\(_2\)CO) is observable at 1670 cm\(^{-1}\). Reference spectra taken after the deposition of only either carbon atoms or H\(_2\)O ice show no evidence for H\(_2\)CO. The broad bands, in the H\(_2\)O spectra around 1650 cm\(^{-1}\) and in the D\(_2\)O spectrum around 1500 cm\(^{-1}\), are the HOH and DOD bending modes.

Experiments with heavy water were performed to check if there is a difference in the measured reaction rates between the C + H\(_2\)O and C + D\(_2\)O reactions at the lowest temperature. As the reactions were expected to proceed via proton tunneling, a lower tunneling rate of deuterium was anticipated as it was observed for the gas phase at 50 K (Hickson et al. 2016). However, the reaction in the gas phase was found to be pretty fast, occurring on a millisecond timescale. Our experiments showed that even at the lowest temperature of 10 K, the reaction occurs within less than one minute, the shortest time between our measurements. Thus, we could not detect any possible difference in the reaction rates of the C + H\(_2\)O and C + D\(_2\)O reactions.
Figure 2. Evolution of the column density of H$_2$CO at 10, 20, 50, and 80 K with the deposition time. Carbon atoms were deposited during 35 minutes between the 4th and 38th minutes of the H$_2$O deposition (marked in the figure by dashed lines).

Figure 3. TPD curves for masses 29 and 30 corresponding to formaldehyde measured after the depositions of H$_2$O + C at 10 K.

Figure 4. TPD curves for masses 29 and 30 corresponding to formaldehyde measured after the depositions of H$_2$O/Ar/C layers at 10 K.

H$_2$O molecules are initially separated by a layer of Ar, is direct evidence of the participation of cold C atoms in the C + H$_2$O → H$_2$CO solid-state reaction. The smaller amount of H$_2$CO points to the presence of the competitive reaction channel, probably, C + C$_n$. No other carbon molecules were detected by IR spectroscopy even after evaporation of all argon at about 33 K. Therefore, our results are explained by (i) efficient diffusion of C atoms in Ar ice (Thompson et al. 1971) and (ii) the formation of amorphous carbon in addition to H$_2$CO. The latter shows that the reaction rate of C + H$_2$O is much lower compared to the rates of barrierless C + C$_n$ reactions (Thompson et al. 1971).

In a second series of experiments, the C + H$_2$O ice layers were irradiated by UV photons at the corresponding deposition temperatures. Our expectation was that dissociation of H$_2$O molecules into H and OH radicals in the presence of formaldehyde will lead to the formation of more complex species, first of all, methanol (CH$_3$OH) via barrierless hydrogenation of H$_2$CO. This possibility is well known from the experiments on hydrogenation of CO leading to the consequent formation of HCO, H$_2$CO, H$_2$CO, and CH$_3$OH (Hiraoka et al. 1994; Pirim & Krim 2014). However, UV irradiation of the ice produced by co-deposition of C and H$_2$O led to the destruction of formaldehyde with the formation of mainly CO$_2$, as illustrated in Figure 5.
amount of CO₂ synthesized during the irradiation at 10, 20, and 50 K (∼3 × 10^{15} molecule cm\(^{-2}\)) corresponds to the loss of H₂CO and CO (∼0.3 × 10^{15} molecule cm\(^{-2}\), a contamination from the carbon source, the CO band at 2140 cm\(^{-1}\) is visible in Figure 5). Only a very small amount of CH₃OH (∼1 × 10^{14} molecule cm\(^{-2}\), about 3% of H₂CO) was formed as a result of the UV irradiation. The CO₂, CO, and CH₃OH ice thicknesses were calculated from their vibrational bands at 2342, 2140, and 1020 cm\(^{-1}\) using the band strengths of 7.6 × 10^{-17} (Gerakines et al. 1995), 1.1 × 10^{-17} (Gerakines et al. 1995) and 1.8 × 10^{-17} cm molecule\(^{-1}\) (Hudgins et al. 1993), respectively.

We cannot exclude the possibility that CO participated in the UV-triggered chemistry leading to the formation of methanol, however, the amount of CO compared to H₂CO was about 10 times lower, thus, the effect of the CO contamination should not be important. It is known that more complex molecules than CH₃OH can be formed in CO, H₂O, and H₂CO containing ices (Butscher et al. 2017; Fedoseev et al. 2017). In our experiments, with and without UV, TPD curves show very weak signals, indicating desorption of different species; however, the intensity ratios at different masses do not allow us to consider unambiguous identification of other COMs by mass spectrometry. Due to the very low amounts of these species, we were also not able to detect them by IR spectroscopy.

**4. Discussion**

The C + H₂O reaction at \(T = 10\) K is found to be fast on the experimental timescale. The barrier of ∼8.3 kcal mol\(^{-1}\) (∼4180 K, Li et al. 2017) calculated for the entrance channel is at least two times higher than the average kinetic energies of C atoms provided by our source. Moreover, the experiment with argon provided direct evidence for spontaneous reaction C + H₂O → H₂CO at 10 K. The previous experimental and computational studies of this reaction in the gas phase showed an efficient tunneling of protons at low temperatures (Hickson et al. 2016; Keshavarz 2019). All this indicates that in our experiments the reaction likely proceeds through tunneling when hydrogen atoms move from oxygen to carbon after the formation of the C-OH₂ pre-reactive complex (Hickson et al. 2016). This is in contrast to the conclusion about the non-reactivity of ground-state C atoms with water molecules at low temperatures (Schreiner & Reisenauer 2006), where the C + H₂O → H₂CO reaction was observed in Ar matrices, but was assigned to the presence of singlet C atoms. We note that Schreiner & Reisenauer worked with “hot” C atoms and our experiments show that a low-temperature reaction channel also exists.

In contrast to the gas-phase study (Hickson et al. 2016), formaldehyde molecules forming in the solid state are not dissociated and are stabilized by transferring the excess reaction energy to a third body (the ice surface). The need to tunnel through the barrier implies a rather low reaction rate compared to rates of barrierless reactions. Therefore, if competitive barrierless reaction channels are available, the reaction would likely follow this barrierless route as it was observed in our experiment with Ar, where a smaller amount of H₂CO was detected. It would mean that in astrophysical environments when C atoms accrete on the surface of dust grains, the formation of H₂CO is efficient if the accretion site contains water molecules only. In the presence of CO or NH₃ molecules on the accretion sites, the barrierless formation of C₂O or H₂CNH molecules could be more efficient (Krasnokutski et al. 2020).

Formaldehyde is among the more abundant molecules in the solid state in cold astrophysical environments (Boogert et al. 2015). The formation of formaldehyde is one of the important steps toward molecular complexity. First, barrierless hydrogcnation of formaldehyde leads to the formation of methanol, which, in turn, is well known as a starting point for the formation of more complex organic molecules (Oberg et al. 2009; Vasyunin & Herbst 2013; Balucani et al. 2015). Second, the thermal formation of methyleneglycol (HOCH₂OH), a product of the thermal reaction between H₂CO and H₂O, and formaldehyde polymers (polyoxymethylene (POM), HO-(CH₂-O)ₙ-H) in H₂O:NH₃:H₂CO ice mixtures, where NH₃ played the role of a catalyst, was clearly demonstrated (Duvernay et al. 2014). However, the formation of methyleneglycol and POM occurs without NH₃ as well, just on a longer timescale (P. Theulé, 2021, private communication). In cold astrophysical environments, such as molecular clouds, protostars, and planet-forming disks beyond the snowline, both time and NH₃ are clearly available. Third, the studied reaction also opens a straightforward way to sugar formation. It was shown that H₂CO reacts with its isomer HCOH to give glycolaldehyde (HOCH₂-CHO) in a nearly barrierless reaction (Eckhardt et al. 2018). With the further addition of HCOH molecules, the formation of glyceraldehyde is possible. The HCOH radical is an intermediate in the studied C + H₂O reaction. The transformation of HCOH to formaldehyde was also found to take place due to the tunneling of hydrogen atoms (Schreiner et al. 2008). Therefore, if the reaction C + H₂O would take place close to another H₂CO molecule, the reaction HCOH + H₂CO → HOCH₂-CHO should be expected.

The typically considered mechanism of the H₂CO formation, hydrogenation of CO ice, is relevant to the regions beyond the CO snowline (around 30 K). The C + H₂O reaction shows an alternative pathway to H₂CO. In warmer environments, particularly, in the inner regions of planet-forming disks, CO is mainly in the gas phase, however, H₂O ice is present at much higher temperatures (until 140–170 K depending on the disk model). As mobility and reactivity of surface species increase with the temperature, there is no reason to assume that surface formation of H₂CO at higher temperatures proceeds less efficiently compared to lower temperatures. Thus, considering the presence of C atoms, the C + H₂O reaction might be an
important source of formaldehyde in planet-forming disks. The reaction should be included into existing models to evaluate its importance for astrochemical networks in different astrophysical environments.

To date, most of the work on the formation of complex organic and prebiotic molecules under astrophysically relevant conditions was done through the energetic processing of molecular ices (UV irradiation or ion/electron/proton bombardment). Here, we refer the reader to a couple of review papers (Öberg 2016; Arumainayagam et al. 2019). However, in the early evolutionary stages of interstellar clouds, the main state of matter is an atomic gas. The most important atoms for prebiotic astrochemistry (such as C, H, O, N, S, P, and etc.) are radicals. These radicals may react and build large organic molecules without an additional energy input as was shown in recent papers on the “non-energetic” formation of glycine (Krasnokutski et al. 2020; Ioppolo et al. 2021). During the formation of dense and cold regions (molecular clouds) in the ISM, the condensation of atoms on the surface of dust grains should lead to the synthesis of complex organic species.

In our experiments, UV irradiation of the ices produced by co-deposition of C and H2O reactants played mainly a destructive role (with respect to the formation of more or less complex species as compared to H2CO). The conversion of H2CO into CO2 rather than into CH2OH was observed. However, using the qualitative approach typical for many previous works on the formation of astrophysically relevant organic molecules in ices by UV irradiation (neglecting the amounts of the formed and destroyed molecules), we could conclude that UV light plays a constructive role leading to the formation of more complex species (methanol). On the other hand, if quantities are considered, our experiments show that the UV radiation plays mainly a destructive role. Only about a few percent of H2CO was converted into a more complex species (methanol) and the rest was converted into a simpler species (CO2). This result challenges the role of energetic processing in the synthesis of complex organic molecules under astrophysically relevant conditions and might be particularly important for the case of the formation of prebiotic molecules, which are commonly rather fragile. Therefore, the formation of organics and prebiotic molecules could be most efficient in areas where there are less energetic triggers of reactions, such as UV photons or cosmic rays. However, more studies are required for a better understanding of the role of energetic and “non-energetic” processes in the formation of complex organic and prebiotic molecules.

To conclude, the solid-state formation of H2CO at temperatures relevant to the ISM and colder regions of circumstellar environments of young stars proceeds through the C+H2O reaction involving quantum tunneling mechanism. This alternative, “non-energetic” route to formaldehyde has to complement astrochemical models and may lead to better understanding of the processes leading to the formation of organics in space.

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