Surface formation of CO\textsubscript{2} ice at low temperatures

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ABSTRACT
The surface formation of CO\textsubscript{2} at low temperatures through the reaction CO + OH and direct dissociation of the resulting HO–CO complex is shown by hydrogenation of a CO:O\textsubscript{2} ice mixture. Such a binary ice is not fully representative for an interstellar ice, but the hydrogenation of O\textsubscript{2} ice produces OH radicals, which allows the investigation of the interstellar relevant CO + OH solid state reaction under fully controlled laboratory conditions. Similar recent astrophysical ice studies have focused on the investigation of isolated surface reaction schemes, starting from the hydrogenation of pure ices, like solid CO or O\textsubscript{2}. For such ices, no CO\textsubscript{2} formation is observed upon H-atom exposure. The hydrogenation of binary ice mixtures presented here allows to investigate for the first time the influence of the presence of other species in the ice on the pure ice reaction schemes. Mixtures of CO:O\textsubscript{2} are deposited on a substrate in an ultra high vacuum setup at low temperatures (15 and 20 K) and subsequently hydrogenated. The ice is monitored by means of Reflection Absorption InfraRed Spectroscopy (RAIRS). Results show that solid CO\textsubscript{2} is formed in all studied CO:O\textsubscript{2} mixtures under our laboratory conditions. Within the experimental uncertainties no dependency on ice temperature or composition is observed. The laboratory results show a correlation between the formation of CO\textsubscript{2} and H\textsubscript{2}O, which is consistent with the astronomical observation of solid CO\textsubscript{2} in water-rich environments. The results also show that the contemporary presence of CO and O\textsubscript{2} molecules in the ice influences the final product yields of the separate CO + H (H\textsubscript{2}CO, CH\textsubscript{3}OH) and O\textsubscript{2} + H (H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O) channels, even though the formation rates are not significantly affected.

Key words: astrochemistry – methods: laboratory – ISM: atoms – ISM: molecules – infrared: ISM.

1 INTRODUCTION

Infrared Space Observatory and Spitzer Space Telescope observations have shown that H\textsubscript{2}O, CO, CO\textsubscript{2} and, in some cases, CH\textsubscript{3}OH represent the bulk of solid-state species in dense molecular clouds and star-forming regions. Other ice components, such as CH\textsubscript{4}, NH\textsubscript{3}, OCN\textsuperscript{−}, H\textsubscript{2}CO, HCOOH, SO\textsubscript{2} and OCS have abundances <5 per cent relative to H\textsubscript{2}O (e.g. Gibb et al. 2004; Boogert et al. 2008; Pontoppidan et al. 2008; """"ber et al. 2008; Zasowski et al. 2009; Bottinelli et al. 2010). Several of these species are assumed to be formed in solid state reactions on the surfaces of icy dust grains, as outlined by Tielens & Hagen (1982). Although these reactions have been postulated nearly 30 yr ago, few have been measured in the laboratory at low temperatures and under ultra high vacuum (UHV) conditions until recently. Over the past decade, detailed laboratory experiments have started to investigate isolated surface reaction schemes, starting from the hydrogenation of simple and pure ices, like solid CO or O\textsubscript{2}.

Several groups proved that the hydrogenation of CO ice at low temperatures (12–20 K) leads to the subsequent formation of H\textsubscript{2}CO and CH\textsubscript{3}OH (e.g. Watanabe et al. 2004, 2006; Fuchs et al. 2009). The experiments showed that this hydrogenation process involves only the upper monolayers (~4 ML, where 1 ML corresponds to 10\textsuperscript{15} molecules cm\textsuperscript{−2}) of the CO ice and formation rates drop at temperatures higher than 15 K, since the desorption of H atoms becomes important at these temperatures. The hydrogenation of CO to CH\textsubscript{3}OH proceeds in four steps,

\begin{equation}
\text{CO} \xrightarrow{1} \text{HCO} \xrightarrow{2} \text{H}_{2}\text{CO} \xrightarrow{3} \text{H}_{3}\text{CO} \xrightarrow{4} \text{CH}_{3}\text{OH},
\end{equation}

where the first step from CO to HCO and the third step from H\textsubscript{2}CO to H\textsubscript{3}CO have a barrier.

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The other surface reaction channel that has been well investigated is the hydrogenation of O$_2$ ice, which leads to the formation of H$_2$O$_2$ and H$_2$O (e.g. Ioppolo et al. 2008, 2010; Miyauchi et al. 2008; Cuppen et al. 2010). This hydrogenation process

$$\text{O}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}$$

behave differently compared to the hydrogenation of CO ice (reaction scheme 2 shows the simplified version of this route, as discussed by Tielens & Hagen 1982). In this case, the penetration depth of H atoms in the O$_2$ ice increases with temperature, even at values close to the desorption temperature of the O$_2$ layer, involving the bulk of the ice (tens of monolayers). Thus, H atoms trapped in the ice can diffuse and eventually react up to much higher temperatures. Moreover, at least the formation of H$_2$O$_2$ does not exhibit any noticeable barrier.

The present work is a further step towards a laboratory investigation of interstellar relevant surface reactions in more complex ices by studying for the first time the formation of solid CO$_2$ through hydrogenation of a binary CO:O$_2$ ice mixture as well as investigating the competition between the two separate hydrogenation channels (CO + H and O$_2$ + H).

CO$_2$ is one of the most common and abundant ices (d’Hendecourt & Jourdain de Muizon 1989), yet its formation routes are still uncertain. It is widely accepted that CO$_2$ is not formed efficiently in the gas phase, with subsequent accretion on to the grains (CO$_{2\text{gas}}$/CO$_{2\text{ice}}$ $\ll$ 1; van et al. 1996; Boonman et al. 2003). Therefore, the observed CO$_2$ most likely has to be formed in the solid phase. Several reaction mechanisms have been proposed with an efficiency depending on astronomical environment. Energetic processing, such as UV and ion irradiation of interstellar ices analogues, has been investigated in various laboratories and proposed as an efficient CO$_2$ formation mechanism (e.g. Hagen, Allamandola & Greenberg 1979; Mennella, Palumo & Baratta 2004; Loeffler et al. 2005; Mennella et al. 2006; Ioppolo et al. 2009). Furthermore, in the absence of UV irradiation, several cold solid-phase reaction channels have been reported in the past decades as an alternative formation mechanism to explain the CO$_2$ abundance observed in cold clouds (e.g. Tielens & Hagen 1982; d’Hendecourt et al. 1985; Grim & d’Hendecourt 1986; Ruffle & Herbst 2001; Fraser & van Dishoeck 2004; Stantcheva & Herbst 2004; Goumans, Uppal & Brown 2008; Goumans & Andersson 2010). The most straightforward surface reaction channel is the addition of an O atom to solid CO ice. The reaction CO + O → CO$_2$ has been experimentally investigated only by temperature programmed desorption experiments using thermal O atoms below 160 K (Roser et al. 2001) and by energetic O atoms (Madzunkov et al. 2006). This surface reaction channel has a high reaction barrier (Grim & d’Hendecourt 1986), because the CO($^3\Sigma$) + O($^3\Pi$) reactants do not correlate directly with the singlet ground state CO$_2$(1$^\Sigma^+$) (2970 K in the gas phase; Talbi, Chandler & Rohl 2006). Ruffle & Herbst (2001) found in their astrochemical model that they were only able to reproduce the CO$_2$ abundances observed towards the cold (10 K) cloud Elias 16, if they artificially lowered the barrier to 130 K. Recently, Goumans & Andersson (2010) used harmonic quantum transition state theory to conclude that whilst quantum mechanical tunnelling through the activation barrier increases the classical reaction rate for reaction CO + O at low temperatures (10–20 K), the onset of tunnelling is at too low temperatures for the reaction to efficiently contribute to CO$_2$ formation in quiescent clouds.

Solid CO$_2$ is further suggested to be formed through the surface reaction HCO + O, which presents two exit channels (CO$_2$ + H and CO + OH; Ruffle & Herbst 2001). Alternatively, solid CO$_2$ can be formed through the surface reaction CO + OH, which yields a HO-CO intermediate. This complex can directly dissociate, forming solid CO$_2$ and leaving a H atom, or can be stabilized by intramolecular energy transfer to the ice surface and eventually react with an incoming H atom in a barrierless manner to form CO$_2$ and H$_2$ (Goumans et al. 2008).

Fig. 1 shows a schematic representation of all the reaction networks investigated in this work (solid arrows) and links the previously studied CO + H and O$_2$ + H channels through the observed CO$_2$ formation. The dashed and dotted arrows represent suggested CO$_2$ formation routes in the networks of Tielens & Hagen (1982) and Ruffle & Herbst (2001), that are not experimentally confirmed at low temperature in our studies.

In Section 4.1 we discuss that CO$_2$ is formed under our experimental conditions through the reaction CO + OH. Here OH radicals are formed through the hydrogenation of O$_2$ ice, while in space they can also result from the O + H reaction or from the photodissociation of H$_2$O ice. Recently, Oba et al. (2010) also investigated the reaction CO + OH depositing CO molecules on a cold substrate (10 and 20 K) together with H$_2$O fragments (OH, H, O and H$_2$) produced by dissociating H$_2$O molecules in a microwave source. They observed the formation of solid CO$_2$ at low temperature by using CO and OH beams to initiate surface reactions on a cold substrate. Their experiments differ from ours. In the present work, we hydrogenate CO:O$_2$ ices and OH radicals are produced in the ice through the O$_2$ + H channel, providing additional information on the interaction between different surface reaction schemes. In a previous paper (Ioppolo et al. 2011), we investigated experimentally the hydrogenation of the HO–CO complex, which has three exit channels (CO$_2$ + H$_2$, HCOOH, H$_2$O + CO) with a purely statistical branching ratio as suggested by density functional theory models and in agreement with our experimental results (Goumans et al. 2008; Ioppolo et al. 2011). In the present study, the HO–CO complex itself is not observed since it is efficiently dissociated under our experimental conditions to form CO$_2$. More details are reported in Section 4. In Sections 2 and 3, the experimental method and data analysis are discussed.

2 EXPERIMENTAL DETAILS

The experiments are performed using an UHV setup, which consists of a main chamber (10$^{-10}$ mbar) and an atomic beam line. Details are available from Fuchs et al. (2009) and Ioppolo et al. (2010). The ice is grown on a gold coated copper substrate (12–300 K) that is mounted on the cold head of a close-cycle He cryostat. Deposition of selected $^{12}$C$^{16}$O:$^{18}$O$_2$ mixtures (4:1, 1:1 and 1:4) proceeds under an angle of 45° and with a rate of 0.7 ML min$^{-1}$. After deposition the ice mixture is exposed to a cold H-atom beam. H$_2$ molecules are dissociated into the capillary of a well-characterized thermal cracking source (Tschersich & von Bonin 1998; Tschersich 2000; Tschersich, Fleischhauer & Schuler 2008), which is used to hydrogenate the sample. A quartz pipe with a nose-shaped form is placed along the path of the dissociated beam to efficiently thermalize all H atoms to room temperature through surface collisions before they reach the ice sample. In this way, hot species (H, H$_2$) cannot reach the ice directly. Furthermore, the relatively high temperature of 300 K of the incident H atoms in our experiments does not affect the experimental results, since H atoms are thermally adjusted to the surface temperature as has been shown in Fuchs et al. (2009). The final H-atom flux

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Figure 1. A schematic representation of the reaction network as discussed in the present study. The CO + H channel is shown on the left-hand side of the figure, while the O/O₂/O₃ + H channels are plotted as presented in Cuppen et al. (2010) on the right-hand side. The possible CO₂ formation routes are shown in between the CO + H and O/O₂/O₃ + H channels: the dissociation of the HO–CO intermediate (solid arrow) is one of the topics of this work; the hydrogenation of the HO–CO complex (solid arrow) is presented in Ioppolo et al. (2011); the suggested CO + O (dashed arrow) and HCO + O (dotted arrow) routes are not experimentally confirmed at low temperature (Tielens & Hagen 1982; Ruffle & Herbst 2001).

(2.5 × 10¹³ atoms cm⁻² s⁻¹) is measured at the substrate position in the main chamber using a quadrupole mass spectrometer, following the procedure as described in the appendix of Ioppolo et al. (2011). The error in the absolute H-atom flux determination is within 50 per cent. Ices are monitored by means of Reflection Absorption InfraRed Spectroscopy (RAIRS) using a Fourier Transform InfraRed spectrometer (FTIR), which covers the range between 4000 and 700 cm⁻¹ (2.5–14 μm). A spectral resolution of 1 cm⁻¹ is used and 128 scans are co-added for one spectrum. RAIR difference spectra (ΔA) relative to the initial unprocessed CO:O₂ ice are acquired every few minutes during H-atom exposure.

We performed a control experiment at 15 K in which a CO:O₂ ice is exposed to an H₂ molecular beam (i.e. without H atoms) to show that the products detected in the hydrogenation experiments are formed on the surface and do not originate from background deposition. Only small amounts of H₂O are detected in this experiment, which gives us an estimate for the background contamination, which is negligible. None of the other products is detected in this way. The present experiments use the same H-atom flux as adopted in Fuchs et al. (2009) and Ioppolo et al. (2011). Therefore, the hydrogenation of our mixtures involves effectively a lower H-atom flux per (CO + H and O₂ + H) reaction channel.

The interstellar solid CO:O₂ mixing ratio is observationally constrained to >1:1 (e.g. Vandenbussche et al. 1999; Pontoppidan et al. 2003). This conclusion was deduced earlier by d’Hendecourt et al. (1985) on the basis of a simple interacting gas-phase/solid-phase time-dependent model. In our experiments, the binary mixture ratios (CO:O₂ = 4:1, 1:1 and 1:4) are selected to efficiently produce thermal OH radicals in the ice in order to investigate the formation of CO₂. These experiments are also aimed to test the interaction of the aforementioned individual surface reaction channels, rather than simulating a complete realistic interstellar ice evolution.

Figure 2. RAIR difference spectrum of the CO:O₂ = 1:4 mixture acquired after a H-atom fluence of 1.3 × 10¹⁷ atoms cm⁻².

3 DATA ANALYSIS

Fig. 2 shows a RAIR difference spectrum of a CO:O₂ = 1:4 mixture acquired after a H-atom fluence (flux × time) of 1.3 × 10¹⁷ atoms cm⁻². The negative peak shown in Fig. 2 is caused by the CO use-up in surface reaction processes. O₂ is infrared inactive and therefore cannot be observed in this spectrum. All the final reaction products obtained from the hydrogenation of a pure CO ice (H₂CO and CH₃OH; e.g. Watanabe et al. 2004, 2006; Fuchs et al. 2009) and a pure O₂ ice (H₂O and H₂O₂; e.g. Ioppolo et al. 2008; Miyachi et al. 2008) are present. Neither the intermediate species from the separate CO and O₂ channels, like HCO, H₂CO, HO₂, OH and O₃,
nor more complex species, like the stabilized HO–CO intermediate, HCOOH and H$_2$CO$_3$, are observed as was the case in experiments by Ioppolo et al. (2011) in which the CO:O$_2$ mixtures and H atoms were deposited simultaneously. However, a new feature appears at ∼2344 cm$^{-1}$, which belongs to the asymmetrical stretching mode of CO$_2$ ice. This molecule is formed in all our performed experiments at 15 and 20 K, with different CO:O$_2$ mixing ratios, but was not found in the previous CO + H or O$_2$ + H experiments.

The infrared spectra are reduced to obtain the column densities of the newly formed species. As a first step in the infrared data analysis, a straight baseline is subtracted from all spectra. Some absorption features, like the H$_2$O bending mode (∼1650 cm$^{-1}$) and the H$_2$CO ν(CO) stretching mode (∼1720 cm$^{-1}$) suffer from spectral overlap. Here a multi-Gaussian fit is used to determine the area of the selected bands. Since the asymmetric 1440 cm$^{-1}$ H$_2$O$_2$ band overlaps with the 1500 cm$^{-1}$ H$_2$CO band, a spectrum of pure H$_2$O$_2$ ice is fitted in addition to a Gaussian. The spectrum of solid H$_2$O$_2$ is obtained as discussed by Cuppen et al. (2010), by co-depositing H atoms and O$_2$ molecules with a ratio of H/O$_2$ = 20 and subsequently heating the ice to a temperature higher than 30 K, which is just above the O$_2$ desorption temperature (Acharyya et al. 2007).

The column density $N_X$ (molecules cm$^{-2}$) of species X in the ice is calculated using: $N_X = \int A(ν) dν/S_X$, where $A(ν)$ is the wavelength-dependent absorbance. Since literature values of transmission band strengths cannot be used in reflection measurements, an apparent absorption band strength, $S_X$ of species X, is determined by individual calibration experiments. These have been described in detail in Fuchs et al. (2009), Ioppolo et al. (2010) and Cuppen et al. (2010). Like for CO, CH$_3$OH and H$_2$O, an isothermal desorption experiment has been performed to determine the apparent absorption band strength of CO$_2$ by determining the transition from zeroth-order to first-order desorption. This is assumed to occur at the onset to the submonolayer regime and appears in the desorption curve as a sudden change in slope. Since pure H$_2$CO and H$_2$O$_2$ are experimentally difficult to deposit, because of their chemical instability, the values for $S_{H_2CO}$ and $S_{H_2O_2}$ are obtained by assuming mass balance as reported in Fuchs et al. (2009) and Cuppen et al. (2010), respectively.

4 RESULTS AND DISCUSSION

4.1 Formation of solid CO$_2$

Fig. 3 shows the CO$_2$ column density as a function of the H-atom fluence, confirming the CO$_2$ formation for the three different mixing ratios and two temperatures investigated. Here neither the CO$_2$ formation rate nor its final yield depends significantly on either temperature or mixing ratio for the studied values. Such a behaviour is unexpected, since the separate reaction routes CO + H and O$_2$ + H clearly depend on temperature, as shown by Fuchs et al. (2009) and Ioppolo et al. (2010). The limiting factor for the CO$_2$ synthesis in our experiments is, therefore likely, the amount of ice that can be penetrated by the H atoms, which is only a few monolayers. This is caused by the presence of CO molecules affecting the penetration depth of the H atoms in the ice (Fuchs et al. 2009). Thus, the amount of CO$_2$ formed in all our experiments is always less than a monolayer. CO$_2$ subsequently does not contribute to further molecular synthesis in the ice upon ongoing hydrogenation. Bisschop et al. (2007) showed experimentally that CO$_2$ does not react with H atoms and is a stable molecule under interstellar ice analogue conditions.

Fig. 1 summarizes schematically the reaction network which leads to the formation of solid CO$_2$ starting from the combination of the CO + H and O$_2$ + H channels. Analysing the species present in our ice after H-atom addition, we can identify which reaction channel is most likely responsible for the formation of solid CO$_2$ ice. The hydrogenation of the HO–CO intermediate (black arrow in the centre of Fig. 1) should not occur in our experiments, since HCOOH is not detected in the infrared spectra. Density functional calculations (Goumans et al. 2008), confirmed by our previous experimental results (Ioppolo et al. 2011), suggest that the final products from the hydrogenation of the HO–CO complex have a purely statistical branching ratio. Therefore, HCOOH should be detected in the ice if CO$_2$ would be produced through this route, and this is not the case.

The oxidation of solid CO (dashed arrow) is also not likely to be the main formation reaction channel, since O$_3$, which would indirectly prove the presence of abundant O atoms in the ice, is not observed. O$_3$ ice has been detected in pure O$_2$ hydrogenation experiments only for temperatures higher than 25 K, when the penetration depth of the H atoms is higher than a few monolayers and the O$_2$ molecules are most likely more mobile (Ioppolo et al. 2010). The hydrogenation of O$_3$ ice (studied in Romanzin et al. 2011) is therefore not considered here. Furthermore, Roser et al. (2001) tentatively observed CO$_2$ formation through this channel only during the warm up of the ice and when CO molecules and O atoms were covered by a thick layer of H$_2$O ice, which allows the reactants to remain trapped in the ice for $T > 100$ K. The CO + O reaction contributes at best at high temperatures. The reaction HCO + O (dotted arrow) should also be ruled out, since HCO radicals prefer to react in a barrierless manner with H atoms forming H$_2$CO rather than with O atoms, as shown by Fuchs et al. (2009) and Ioppolo et al. (2011). Furthermore, as stated before, O atoms are not abundant in our ices.

At low temperatures, CO$_2$ is likely formed through the direct dissociation of the HO–CO complex in the ice (black arrow). The HO–CO complex is efficiently dissociated and, therefore, is not detected in our infrared spectra as a stable species. In a previous paper (Ioppolo et al. 2011), we observed this complex only in a water-rich environment. H-bonding should, indeed, improve coupling and heat dissipation through the ice, which stabilizes the HO–CO complex more easily in a polar than in an apolar environment. Our ice is mainly composed of CO and O$_2$, with a polar component on the surface of the ice. The amount of the HO–CO intermediate stabilized in the polar ice is also under the detection limit. Therefore, in a water-poor ice, the competition between dissociation and further

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1 Solid H$_2$CO$_3$ was observed only in control experiments by Ioppolo et al. (2011).
hydrogenation of the HO–CO complex is in favour of the dissociation.

H$_2$O is also formed through hydrogenation of the OH radicals (Fig. 2). Hence, the formation of CO$_2$ is linked to the formation of H$_2$O in the ice. This is consistent with the presence of CO$_2$ in polar (water-rich) interstellar ice mantles (see discussion in Section 5).

4.2 Hydrogenation of O$_2$ molecules

In this section, we investigate to what extent the hydrogenation of O$_2$, previously studied also for a pure ice, is affected by the presence of other molecules. Fig. 4 shows the H$_2$O$_2$ (top panels) and H$_2$O (bottom panels) column densities as a function of the H-atom fluence for the three different mixing ratios [CO:O$_2$ = 4:1 (circles), 1:1 (squares) and 1:4 (triangles)] and two temperatures investigated [15 K (left-hand panels) and 20 K (right-hand panels)]. For comparison, results from the hydrogenation of pure O$_2$ ice (Ioppolo et al. 2010) are also plotted (diamonds). Note that the top-right panel has a different scale for the column density axis than the other three diagrams. Formation rate and final yield of H$_2$O$_2$ and H$_2$O for all the investigated mixtures are lower than those from the pure O$_2$ ice hydrogenation. The differences in the final yield are more evident at higher temperature, where the yield for the mixed ices only moderately increases, whereas it increases with several monolayers for the pure O$_2$ experiments. This cannot be explained only by a low effective H-atom flux for the O$_2$ channel. Hence, the presence of CO in the mixture influences the final results. In a previous paper on CO + H we showed that H atoms can penetrate only a few layers of CO ice (Fuchs et al. 2009). Therefore, the presence of CO in the mixture most likely diminishes the penetration depth of H atoms into the ice compared to O$_2$ + H, and, therefore, desorption of H atoms from the ice can become important at higher temperatures. This explains the difference in the H$_2$O$_2$ and H$_2$O final yields compared to those from the pure O$_2$ ice, which increases with temperature.

The formation rates of H$_2$O and H$_2$O$_2$, which are reflected by the initial slopes of the curves, are also altered by the presence of CO in the ice. In the O$_2$-rich ice (1:4), the H$_2$O$_2$ column density shows the same behaviour as seen in pure O$_2$ ices: a constant formation rate is followed by a sharp transition towards saturation (Ioppolo et al. 2010). For high concentration of CO in the ice, the H$_2$O$_2$ column density increases with a much lower rate and does not appear to reach a steady state, even at the highest fluence. The H$_2$O$_2$ final yield increases with temperature, like for hydrogenation experiments of pure O$_2$ ice.

In the case of CO-rich ice (4:1), a more efficient conversion of H$_2$O$_2$ ice into H$_2$O ice can explain the high H$_2$O final yield with respect to the O$_2$-rich ice experiment. In a previous paper, we showed that H$_2$O$_2$ is more effectively formed in the bulk of the ice (Ioppolo et al. 2010). However, the presence of CO in the ice restricts the hydrogenation reactions to the surface of the ice. This means that a larger percentage of H$_2$O$_2$ formed at the surface of the ice is easily converted into H$_2$O. This may also explain the lower effective synthesis of H$_2$O$_2$ with the increase of the number of CO molecules in the ice. In addition, H$_2$O can be formed from OH radicals (see Fig. 1 and Cuppen et al. 2010), which can also react to form CO$_2$ in our ices. The H$_2$O column density is constant through almost all our experiments. This is also the case for CO$_2$ as shown in Section 4.1 and indicative for a correlation between the formation channels of these two species.

4.3 Hydrogenation of CO molecules

Fig. 5 shows the H$_2$CO (top panels) and CH$_3$OH (bottom panels) column densities as a function of the H-atom fluence for the three different mixing ratios [CO:O$_2$ = 4:1 (circles), 1:1 (squares) and 1:4 (triangles)] and two temperatures investigated [15 K (left-hand panels) and 20 K (right-hand panels)]. For comparison, results from the hydrogenation of pure CO ice (Fuchs et al. 2009) are also plotted (diamonds). For the hydrogenation of pure CO ice, the H-atom fluence is corrected according to recent H-atom flux measurements (Ioppolo et al. 2010), which improve the original H-atom flux.
estimation derived in Fuchs et al. (2009). The hydrogenation of CO molecules in our mixtures shows the same behaviour seen for pure CO ice in terms of temperature dependence (Fuchs et al. 2009). An optimum in the final yield for $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$ is found at 15 K, while at 20 K no $\text{CH}_3\text{OH}$ is formed and $\text{H}_2\text{CO}$ has a low formation rate. The $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$ formation rates are hardly affected by the presence of $\text{O}_2$ in the ice (within the experimental uncertainties). The higher final yield for $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$ in the $\text{CO}:\text{O}_2 = 4:1$ experiment at 15 K compared to the pure CO ice cannot be explained by only a difference in the effective H-atom flux. In this case, the presence of $\text{O}_2$ in the ice, as a minor component, increases the penetration depth of H atoms in the ice compared to pure CO and, therefore, the probability that the H atoms get trapped and react in the ice. However, if the $\text{O}_2$ concentration is increased in the 15 K ice, the final yield decreases for both $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$ molecules. Clearly, the formation of $\text{H}_2\text{CO}$ is more sensitive to the $\text{O}_2$ concentration in the ice than the formation of $\text{CH}_3\text{OH}$. As we saw for the hydrogenation of $\text{O}_2$ ice, the intermediate products ($\text{H}_2\text{O}_2$ and $\text{H}_2\text{CO}$, respectively) are more efficiently converted in the final products ($\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}$, respectively), when the ices are mixed.

4.4 Competition between the CO and $\text{O}_2$ channel

The results presented in the former sections reflect the competition between the two channels CO versus $\text{O}_2$, as shown in the left and right part of Fig. 1. It is clear from the experimental results that the presence of one component in the ice influences the reactivity of the other component. The formation rate of the CO hydrogenation reaction products is less affected by the presence of $\text{O}_2$ than the $\text{O}_2$ hydrogenation reaction products are affected by the presence of CO. This can be explained by the lower penetration depth of H atoms in CO ice and by the formation of $\text{O}_2$ as an additional product, since OH radicals, formed through the $\text{O}_2$ channel, are used to form $\text{CO}_2$ instead of $\text{H}_2\text{O}$ and $\text{H}_2\text{O}_2$.

In a CO-rich environment at 15 K, the presence of $\text{O}_2$ molecules enhances the production of $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$, since H atoms can penetrate deeper in the ice than in the pure CO ice experiment. However, the formation rate of the final products seems not to be affected by the presence of the $\text{O}_2$ molecules in the ice. Moreover in a CO-rich ice, the formation of $\text{H}_2\text{O}_2$ is limited by the small amount of $\text{O}_2$ molecules in the ice, by the amount of OH radicals used to form $\text{CO}_2$ and by the lower penetration depth of H atoms in the ice, caused by the presence of CO molecules. $\text{H}_2\text{O}_2$ ice is also more efficiently converted to $\text{H}_2\text{O}$ on the surface of the ice. This explains the high final yield for $\text{H}_2\text{O}$ in a CO-rich environment at 15 K.

In a $\text{O}_2$-rich environment at 15 K, the formation of $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$ is limited by the small amount of CO molecules, which limits the formation of $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}$, since the penetration depth of H-atoms is lower than in the pure $\text{O}_2$ ice experiment.

At 20 K, the CO channel is not efficient, although the H atoms penetrate deep in the ice; at this temperature H atoms prefer to react with $\text{O}_2$ molecules. Also in this case, the final yields for $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}$ are lower than those in the pure $\text{O}_2$ ice experiment.

5 ASTROPHYSICAL IMPLICATIONS

Observations by the Infrared Space Observatory (e.g. Gerakines et al. 1999; Nummelin et al. 2001; Gibb et al. 2004) and the Spitzer Space Telescope (e.g. Boogert et al. 2004; Bergin et al. 2005; Pontoppidan et al. 2005; Pontoppidan et al. 2006; Whittet et al. 2007; Pontoppidan et al. 2008) have shown that roughly two-third of the solid CO$_2$ observed in quiescent molecular clouds and star-forming regions is found in water-rich environments, suggesting that the formation routes of these two molecules are linked. The remaining CO$_2$ ice is predominantly found in a H$_2$O-poor, CO-rich environment (Pontoppidan et al. 2008). These observations suggest that the formation of CO$_2$ in dark quiescent clouds occurs in two distinct phases. In the early stages, CO$_2$ forms together with H$_2$O on the surface of the interstellar dust grains, creating a polar ice mantle. A second phase in the CO$_2$ formation occurs during the heavy freeze-out of CO. During this second phase, a H$_2$O-poor ice is formed.

Our experimental results indeed make it likely that CO$_2$ and H$_2$O are formed together in the early stages of the clouds through surface reactions assuming that both CO and OH are present in sufficiently high abundances. H$_2$O ice forms from continued hydrogenation of OH radicals formed on the surface of the dust grains. Alternatively, OH radicals can react with nearby CO molecules, which are present in small amounts in the ice before the strong CO freeze-out phase, forming CO$_2$ ice through the direct dissociation of the HO–CO intermediate. CO$_2$ can be also formed at low temperatures through the hydrogenation of the HO–CO complex, which can lead to the formation of HCOOH and H$_2$O + CO as well as CO$_2$ + H$_2$. The concentration of CO in the ice with respect to H atoms determines the probability of OH to react with a CO molecule or with another H atom.

In the second stage, during the heavy CO freeze-out, the gas density is $>10^5$ cm$^{-3}$ and the CO accretion rate could be as high as, or even higher than, the H-atom accretion rate, which makes CO more abundant on the surface than H atoms. Any OH radicals will therefore more likely react with a nearby CO molecule than with H atoms. As long as some OH is present, CO$_2$ can thus be efficiently formed through the dissociation or further hydrogenation of the HO–CO complex, while just little H$_2$O ice is formed.

Energetic processing (UV irradiation and cosmic ray-induced photons) of polar and apolar ices is another efficient mechanism for CO$_2$ formation for specific (water-rich) environments (e.g. Hagen et al. 1979; Mennella et al. 2004, 2006; Loeffer et al. 2005; Ioppolo et al. 2009). All these channels, including the scheme discussed here, can contribute to the total CO$_2$ column density component observed in quiescent clouds.

In addition, in our experiments only a small amount of H$_2$O$_2$ ice is formed. This work shows that the competition between different channels (CO + H and O$_2$ + H), together with the penetration depth of the incoming H atoms into the ice, which decreases when the amount of CO in the ice increases, explains the differences in the H$_2$O$_2$ and H$_2$O final yield between a mixed and pure O$_2$ ice. Our results are consistent with the observed lack of H$_2$O$_2$ in the interstellar ices.

6 CONCLUSIONS

The experiments presented here show that CO$_2$ can be formed in the solid state for astronomically relevant temperatures via a thermal CO + OH reaction path. An efficient dissociation of the HO–CO complex is observed and this may explain the presence of CO$_2$ in polar and apolar interstellar ices in absence of UV irradiation. For the investigated laboratory conditions, CO$_2$ is formed efficiently and no strong dependency on temperature or ice composition is found. It is explicitly stated here that this conclusion does not rule out other CO$_2$ formation routes in space. Fig. 1, for example, shows how the H$_2$O$_2$ formation through the O$_2$/O$_3$ + H channels is linked to the CO$_2$ formation. Here we investigated only the O$_2$ + H channel, and it should be noted that OH radicals can be also efficiently formed.
on dust grains through the other H$_2$O formation channels as well as through the photodissociation of H$_2$O and CH$_3$OH ice.

The formation of CO$_2$ is linked to the formation of H$_2$O and, therefore, competes with the O$_2$ hydrogenation channel in our experiments. The competition of the two channels, together with the composition of the ice and the penetration depth of H atoms into the ice, explains the differences in the H$_2$O$_2$ and H$_2$O formation rate between a mixed and pure O$_2$ ice. Also the CO + H and O$_2$ + H channels are in competition and clearly affect each other’s final product yields. This is consistent with the lack of observed H$_2$O$_2$ in the interstellar ices. The formation rate for all the final products is found to be less sensitive to the mixture composition than the final yield. The penetration depth of the incoming H atoms is the main limiting factor. It depends on the composition of the ice and decreases when the amount of CO in the ice increases. Our results show that the formation rates found for H$_2$CO, CH$_3$OH, H$_2$O$_2$ and H$_2$O are similar within their experimental uncertainties to those found for the isolated CO and O$_2$ hydrogenation channels (corrected for the reduced effective H-atom fluxes). Those values, therefore, are still valid for use in astrochemical models. Finally, the experiments presented here chemically link CO$_2$ and H$_2$O, consistent with the observation of CO$_2$ in H$_2$O-rich environments in space.

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