CHAPTER 7

Competition between CO and O₂-ice hydrogenation channels and surface formation of CO₂ at low temperatures¹

In the past decade astrochemical laboratory studies have focused on the investigation of isolated surface reaction schemes, starting from the hydrogenation of simple and pure ices, like solid CO or O₂. The reaction products observed for CO hydrogenation are H₂CO and CH₃OH, while after O₂ hydrogenation H₂O₂ and H₂O are formed. We present here the first systematic laboratory study focusing on H-atom addition to a mixed CO:O₂ ice. Mixed ices are more relevant from an astrochemical point of view and can elucidate reactions with radicals that are not readily studied otherwise. The aim of this chapter is to investigate the competition between CO and O₂ hydrogenation, and the corresponding surface formation of CO₂ for astronomically relevant temperatures. Mixtures of CO:O₂ = 4:1, 1:1 and 1:4 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). The results show that the contemporary presence of CO and O₂ molecules in the ice influences the final product yields of the separate CO + H and O₂ + H channels, even though the formation rates are not significantly affected. CO₂ is efficiently formed through dissociation of the HO-CO intermediate complex in all studied CO:O₂ mixtures and within the experimental uncertainties no dependency on temperature or ice composition is observed. Moreover, the CO + O and HCO + O channels are not efficient at low temperature under our experimental conditions. The laboratory results demonstrate that CO₂ can be formed in interstellar ices at low temperatures in the absence of UV radiation and show a correlation between the formation of CO₂ and H₂O, which is consistent with the astronomical observation of solid CO₂ in water-rich environments.

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Figure 7.1 A schematic representation of the reaction network as discussed in the present study. The CO + H channel (Chapter 2) is shown on the left-side of the figure, while the O/O₂/O₃ + H channels are plotted as presented in Chapter 5 on the right-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 Chapter 8; 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).

7.1 Introduction

Infrared Space Observatory and Spitzer Space Telescope observations have shown that H₂O, CO, CO₂, and, in some cases, CH₃OH represent the bulk of solid-state species in dense molecular clouds and star-forming regions. Other ice components, such as CH₄, NH₃, OCN⁻, H₂CO, HCOOH, SO₂, and OCS have abundances <5% relative to H₂O (e.g., Gibb et al. 2004, Boogert et al. 2008, Pontoppidan et al. 2008, Öberg 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, first outlined by Tielens & Hagen (1982). Although these reactions have been postulated nearly 30 years ago, few have been measured in the laboratory at low temperatures and UHV conditions until recently. Over the past decade, detailed laboratory studies have started to investigate isolated surface reaction schemes, starting from the hydrogenation of simple and pure ices, like solid CO or O₂.

Several groups proved that the hydrogenation of CO ice at low temperatures (12–20 K)
leads to the subsequent formation of H$_2$CO and CH$_3$OH (e.g., Watanabe et al. 2004, 2006a, Fuchs et al. 2009). The experiments showed that this hydrogenation process involves only the upper monolayers (4 ML, where 1 ML corresponds to $10^{15}$ molecules cm$^{-2}$) 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$_3$OH proceeds in four steps,

$$\text{CO} \xrightarrow{H} \text{HCO} \xrightarrow{H} \text{H}_2\text{CO} \xrightarrow{H} \text{H}_3\text{CO} \xrightarrow{H} \text{CH}_3\text{OH},$$  \hspace{1cm} (7.1)

where the first step from CO to HCO and the third step from H$_2$CO to H$_3$CO have a barrier.

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., Miyauuchi et al. 2008, Ioppolo et al. 2008, 2010, Cuppen et al. 2010). This hydrogenation process

$$\text{O}_2 \xrightarrow{2H} \text{H}_2\text{O}_2 \xrightarrow{2H} 2\text{H}_2\text{O}$$  \hspace{1cm} (7.2)

behaves differently compared to the hydrogenation of CO ice (reaction scheme 7.2 shows the simplified version of this route, as discussed by Tielen & 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 surface reactions in a more complex and realistic interstellar ice analogue by studying the competition between the two hydrogenation channels in a binary CO:O$_2$ ice mixture as well as the inherent formation of solid CO$_2$. The latter is not found as a reaction product for the separate channels. CO$_2$ is one of the most common and abundant ices, yet its formation routes are still very uncertain. Figure 7.1 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 Tielen & Hagen (1982) and Ruffle & Herbst (2001), that are not experimentally confirmed at low temperature in our studies. As discussed in § 7.4.4, 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 photodissociation of H$_2$O ice. Our experiments are designed to test the interaction of the aforementioned individual surface reaction channels rather than simulate a complete realistic interstellar ice evolution. Hence, our experiments show that OH radicals can get further hydrogenated, leading to H$_2$O formation, or, alternatively, can react with the CO present in the ice, forming solid CO$_2$. These results give the experimental evidence for the correlation of H$_2$O and CO$_2$ formation. Indeed, observations by the Infrared Space Observatory (e.g., Gerakines et al. 1999, Nummelin et al. 2001, Gibb et al. 2004) and the
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*Spitzer Space Telescope* (e.g., Boogert et al. 2004, Bergin et al. 2005, Pontoppidan et al. 2005, 2008, Whittet et al. 2007) show that roughly \( \frac{2}{3} \) of the solid CO₂ 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 CO₂ ice is predominantly found in a H₂O-poor, CO-rich environment (Pontoppidan et al. 2008). The origin of this common ice mantle component remains uncertain.

It is widely accepted that CO₂ is not formed efficiently in the gas phase, with subsequent accretion onto the grains (CO₂/CO₂⁺ ≪ 1; van Dishoeck et al. 1996, Boonman et al. 2003). Therefore, the observed CO₂ most likely has to be formed in the solid phase. Several reaction mechanisms have been proposed with a relevance depending on astronomical environment. Energetic processing, such as UV and ion irradiation of interstellar ice analogues, has been investigated in various laboratories and proposed as an efficient CO₂ formation mechanism (Chapter 9 and references therein). 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 CO₂ abundance observed in cold clouds (e.g., Tielens & Hagen 1982, Ruffle & Herbst 2001, Stantcheva & Herbst 2004, Fraser & van Dishoeck 2004, Goumans et al. 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 → CO₂ 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, because the CO(\(^3\Sigma\)) + O(\(^3\P\)) reactants do not correlate directly with the singlet ground state CO₂(\(^1\Sigma\)) (2970 K in the gas phase; Talbi et al. 2006). Ruffle & Herbst (2001) found in their astrochemical model that they were only able to reproduce the CO₂ 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 tunneling through the activation barrier increases the classical reaction rate for reaction CO + O at low temperatures (10–20 K), the onset of tunneling is at too low temperatures for the reaction to efficiently contribute to CO₂ formation in quiescent clouds.

Solid CO₂ is further suggested to be formed through the surface reaction HCO + O, which presents two exit channels (CO₂ + H and CO + OH; Ruffle & Herbst 2001). Alternatively, solid CO₂ can be formed through the surface reaction CO + OH, which yields a HO-CO intermediate. This complex can directly dissociate, forming solid CO₂ 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 CO₂ and H₂ (Goumans et al. 2008). Oba et al. (2010) investigated the reaction CO + OH depositing CO molecules on a cold substrate (10 and 20 K) together with H₂O fragments (OH, H, O and H₂) produced by dissociating H₂O molecules in a microwave source. They confirmed the formation of solid CO₂ at low temperature by using CO and OH beams to initiate surface reactions on a cold substrate. However, their experiments differ from ours. In the present work we hydrogenate CO₂ ice and OH radicals are produced in the ice through the O₂ + H channel. Therefore, our experiments give also hints on the interaction
7.2 Experimental details

between different surface reaction channels. In chapter 8 we investigated experimentally the hydrogenation of the HO-CO complex, which presents three exit channels (CO₂ + H₂, HCOOH, H₂O + CO) with a branching ratio purely statistical as suggested by density functional theory models and in agreement with our experimental results (Goumans et al. 2008, Ioppolo et al. 2010a). In the present study the HO-CO complex itself is not observed in the ices under our experimental conditions, since it is efficiently dissociated to form CO₂. More details are reported in § 7.4. First, in § 7.2 and 7.3 the experimental method and data analysis are discussed.

7.2 Experimental details

The experiments are performed using an ultra high vacuum setup (SURFRESIDE), which consists of a main chamber (10⁻¹⁰ mbar) and an atomic beam line. Details are available in Chapters 2 and 4. 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\(^{16}\)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. The interstellar solid CO₂ mixing ratio is observationally constrained to >1:1 (Pontoppidan et al. 2003). After deposition the ice mixture is exposed to a cold H-atom beam. H₂ molecules are dissociated into the capillary of a well-characterized thermal cracking source (Tschersich & von Bonin 1998, Tschersich 2000, Tschersich et al. 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; H₂) 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 Chapter 2. The final H-atom flux (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 A of Chapter 4. The absolute error in the II-atom flux determination is within 50%. 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. RAIR difference spectra (ΔA) relative to the initial unprocessed CO₂ ice are acquired every few minutes during H-atom exposure.

We performed a control experiment at 15 K in which a CO₂ 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 H₂O is detected in this experiment, which gives us an estimate for the background contamination, that is negligible. None of the other products are detected in this way. It should be noted that we use in the present experiments the same H-atom flux as used in Chapters 2 and 4. Therefore, the hydrogenation of our mixtures involves effectively a lower H-atom flux per (CO and O₂) channel.
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Figure 7.2 RAIR difference spectrum of the CO:O₂=1:4 ice, with respect to the spectrum before H-atom addition, at 15 K after a H-atom fluence of 1.3 × 10¹⁷ atoms cm⁻².

7.3 Data analysis

Figure 7.2 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. 7.2 is caused by the CO use-up in surface reaction processes. O₂ is infrared in-active, and therefore cannot be observed in the infrared spectrum. All the final reaction products obtained from the hydrogenation of a pure CO ice (H₂CO and CH₃OH; e.g., Watanabe et al. 2004, 2006a, Chapter 2) and a pure O₂ ice (H₂O and H₂O₂; e.g., Miyachi et al. 2008, Chapters 3 and 4) 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 H₂CO₂, are observed. However, a new feature appears at ~2344 cm⁻¹, which belongs to the asymmetrical stretching mode of CO₂ ice. This molecule is formed in all our performed experiments at 15 and 20 K, with different CO:O₂ mixing ratios, but was not found in the previous CO + H or O₂ + 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 H₂O bending mode (~1650 cm⁻¹) and the H₂CO ν(C=O) 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 H₂O₂ band overlaps with the 1500 cm⁻¹ H₂CO band, a spectrum of pure H₂O₂

¹Solid H₂CO₃ is observed only in control experiments presented in Chapter 8.
ice is fitted in addition to a Gaussian to our infrared spectrum. The spectrum of solid H$_2$O$_2$ is obtained as discussed in Chapter 5, 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: $N_X = \int A(\nu) d\nu / S_X$, where $A(\nu)$ 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 Chapters 2, 4 and 5. 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 are experimentally difficult to deposit, because of their chemical instability, the values for $S_{H_2CO}$ and $S_{H_2O}$ are obtained by assuming mass balance as reported in Chapters 2 and 5, respectively.

### 7.4 Results and discussion

#### 7.4.1 Hydrogenation of O$_2$ molecules

Figure 7.3 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 panels and 20 K right panels). For comparison, results from the hydrogenation of pure O$_2$ ice (Chapter 4) are also plotted (diamonds). Note that the top-right panel has a different scale for the column density 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 Chapter 2 we showed that H atoms can penetrate only a few layers of CO ice. 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, is 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 behavior as seen in pure O$_2$ ices: a constant formation rate is followed by a sharp transition toward saturation (Chapter 4). For high concentration of CO in the ice, the H$_2$O$_2$ column density increases with a much lower rate and does not
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Figure 7.3 H2O2 (top panels) and H2O (bottom panels) column densities as a function of the H-atom fluence and time of H-atom exposure at 15 K (left panels) and 20 K (right panels) for the three mixtures studied: CO:O2 = 4:1 (circle), 1:1 (square), and 1:4 (triangle). For comparison, results from the hydrogenation of pure O2 ice are plotted (diamond). Note different vertical scale for upper right panel.

appear to reach a steady state, even at the highest fluence. The H2O2 final yield increases with temperature, like for hydrogenation experiments of pure O2 ice. The amount of H2O2 formed in the ice is inversely proportional to the amount of CO in the mixture, as expected.

In the case of CO-rich ice (4:1), a more efficient conversion of H2O2 ice into H2O ice can explain the high H2O final yield with respect to the O2-rich ice experiment. In chapter 4 we showed that H2O2 is more effectively formed in the bulk of the ice (Chapter 4). However, the presence of CO in the ice limits the hydrogenation reactions to the surface of the ice. This means that a larger percentage of H2O2 formed at the surface of the ice is easily converted into H2O. This may also explain the lower effective synthesis of H2O2 with the increase of the number of CO molecules in the ice. In addition, H2O can be formed from OH radicals (see Fig. 7.1 and Chapter 5), which can also react to form CO2 in our ices. The H2O column density is constant through almost all our experiments. This is also the case for CO2 as we will show in § 7.4.4 and indicative for a correlation between the formation channels of these two species.

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Figure 7.4 H$_2$CO (top panels) and CH$_3$OH (bottom panels) column densities as a function of the H-atom fluence and time of H-atom exposure at 15 K (left panels) and 20 K (right panels) for the three mixtures studied: CO:O$_2$ = 4:1 (circle), 1:1 (square), and 1:4 (triangle). For comparison, results from the hydrogenation of pure CO ice are plotted (diamond).

### 7.4.2 Hydrogenation of CO molecules

Figure 7.4 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 panels and 20 K right panels). For comparison, results from the hydrogenation of pure CO ice (Chapter 2) are also plotted (diamonds). For the hydrogenation of pure CO ice, the H-atom fluence is corrected according to recent H-atom flux measurements (Chapter 4), which improve the original H-atom flux estimation derived in Chapter 2. The hydrogenation of CO molecules in our mixtures shows the same behavior seen for pure CO ice in terms of temperature dependence (Chapter 2). An optimum in the final yield for H$_2$CO and CH$_3$OH is found at 15 K, while at 20 K no CH$_3$OH is formed and H$_2$CO has a low formation rate. The H$_2$CO and CH$_3$OH formation rates are hardly affected by the presence of O$_2$ in the ice (within the experimental uncertainties). The higher final yield for H$_2$CO and CH$_3$OH in the CO:O$_2$ = 4:1 experiment at 15 K compared to the pure CO ice
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cannot be explained by only a difference in the effective H-atom flux. In this case, the presence of O2 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 O2 concentration is increased in the 15 K ice, the final yield decreases for both H2CO and CH3OH molecules. Clearly, the formation of H2CO is more sensitive to the O2 concentration in the ice than CH3OH. As we saw for the hydrogenation of O2 ice, the intermediate products (H2O2 and H2CO respectively) are more efficiently converted in the final products (H2O and CH3OH, respectively), when the ices are mixed.

7.4.3 Competition between the CO and O2 channel

The results presented in the former sections reflect the competition between the two channels CO vs. O2, as shown in the left and right part of Fig. 7.1. 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 O2 than the O2 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 CO2 as an additional product, since OH radicals, formed through the O2 channel, are used to yield CO2 instead of H2O and H2O2.

In a CO-rich environment at 15 K, the presence of O2 molecules enhances the production of H2CO and CH3OH, 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 O2 molecules in the ice. Moreover, in a CO-rich ice the formation of H2O2 is limited by the small amount of O2 molecules in the ice, by the amount of OH radicals used to form CO2 and by the lower penetration depth of H atoms in the ice, caused by the presence of CO molecules. H2O2 ice is also more efficiently converted to H2O on the surface of the ice. This explains the high final yield for H2O in a CO-rich environment at 15 K.

In a O2-rich environment at 15 K, the formation of H2CO and CH3OH is limited by the small amount of CO molecules, which limits the formation of H2O2 and H2O, since the penetration depth of H-atoms is lower than in the pure O2 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 O2 molecules. Also in this case the final yields for H2O2 and H2O are lower than those in the pure O2 ice experiment.

7.4.4 Formation of solid CO2

Figure 7.5 shows the CO2 column density as a function of the H-atom fluence, confirming the CO2 formation for the three different mixing ratios and two temperatures investigated. Neither the CO2 formation rate nor its final yield depend significantly on either temperature or mixing ratio for the values studied here. Such a behavior is unexpected, since the
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Figure 7.5 CO$_2$ column density as a function of the H-atom fluence and time of H-atom exposure at 15 K (left) and 20 K (right) for the three mixtures studied: CO:O$_2$ = 4:1 (circle), 1:1 (square), and 1:4 (triangle).

separate reaction routes CO + H and O$_2$ + H clearly depend on temperature, as shown in Chapters 2 and 4. The limiting factor for the CO$_2$ synthesis in our experiments is, therefore, the amount of ice that can be penetrated by 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 (Chapter 2). 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. (2007b) showed experimentally that CO$_2$ does not react with H atoms and is a stable molecule under interstellar ice analogue conditions.

Figure 7.1 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. Analyzing 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 center of Fig. 7.1) 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 (Chapter 8), 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 as well 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$_2$, which would indirectly prove the presence of abundant O atoms in the ice, is not observed. O$_2$ ice has been detected in pure O$_2$ hydrogenation experiments only for temperatures higher than 25 K, when the penetration depth of the H
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atoms is higher than a few monolayers and the O₂ molecules are most likely more mobile (Chapter 4). The hydrogenation of O₃ ice (Chapter 6) is therefore not considered here. Furthermore, Roser et al. (2001) tentatively observed CO₂ 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 H₂O 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. Reaction HCO + O (dotted arrow) should also be ruled out, since HCO radicals prefer to react in a barrierless manner with H atoms forming H₂CO rather than with O atoms, as shown in Chapter 2 and 8. Furthermore, O atoms are not abundant in our ices.

At low temperatures CO₂ is therefore 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 chapter 4 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 environment than in an apolar one. Our ice is mainly composed of CO and O₂, 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 hydrogenation of the HO-CO complex is in favor of the dissociation. H₂O is also formed through hydrogenation of the OH radicals. Hence, the formation of CO₂ is linked to the formation of H₂O in the ice. This is consistent with the presence of CO₂ in polar interstellar ice mantles.

7.5 Astrophyiscal implications

Recently, results from Spitzer Space Telescope observations (Whittet et al. 2007, Pontoppidan 2006, Pontoppidan et al. 2008) have shown that the formation of CO₂ in dark quiescent clouds occurs in two distinct phases. In the early stages, CO₂ forms together with H₂O on the surface of the interstellar dust grains, creating a polar ice mantle. A second phase in the CO₂ formation occurs during the heavy freeze-out of CO. During this second phase, a H₂O-poor ice is formed.

Our experimental results indeed make it likely that CO₂ and H₂O 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. H₂O 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 CO₂ ice through the direct dissociation of the HO-CO intermediate. CO₂ can be also formed at low temperatures through the hydrogenation of the HO-CO complex, which can lead to the formation of HCOOH and H₂O + CO as well as CO₂ + H₂. 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 >10⁵ 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. OH radicals will
therefore more likely react with a nearby CO molecule than with H atoms. 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 formed.

Energetic processing (UV irradiation and cosmic ray-induced photons) of polar and apolar ices is also an efficient mechanism for CO$_2$ formation for specific environments (Hagen et al. 1979, Mennella et al. 2004, Mennella et al. 2006, Loeffler et al. 2005, Ioppolo et al. 2009). All these channels could contribute to the total CO$_2$ column density component observed in quiescent clouds.

The experiments presented here are designed to test a possible CO$_2$ formation route (thermal CO + OH) under interstellar ice analogue conditions rather than simulate a complete realistic interstellar ice evolution. Although our experiments do not exclude other possible CO$_2$ formation mechanisms, they show that the dissociation of the HO-CO complex is efficient and can contribute to explain the presence of CO$_2$ in polar and apolar interstellar ices at low temperatures in absence of UV irradiation.

### 7.6 Conclusions

The present laboratory study shows that the CO and O$_2$ channels influence each other’s final product yields, when CO and O$_2$ molecules are mixed and hydrogenated at low temperature (15 and 20 K). The formation rate for all the final products is found to be less sensitive on 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 the experimental uncertainties to those found studying the isolated CO and O$_2$ hydrogenation channels corrected for the reduced effective H-atom fluxes. Therefore, the formation rates found in the isolated studies of the CO + H and O$_2$ + H channels are still valid for use in astrochemical models.

The formation of CO$_2$ from the reaction CO + OH is found here. CO$_2$ is efficiently formed under our laboratory conditions and no dependence on temperature or ice composition is found. 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 these 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 our results and the hydrogenation of pure O$_2$ ice.

Figure 7.1 shows how the H$_2$O formation through the O/O$_2$/O$_3$ + H channels is linked to the CO$_2$ formation. Here we investigated only the O$_2$ + H channel, even though OH radicals can be efficiently formed on dust grains through all H$_2$O formation channels as well as through the photodissociation of H$_2$O and CH$_3$OH ice. Thus, our experimental result on the efficiency of the CO + OH channel at low temperature has important astrophysical implications on the formation of solid CO$_2$ in cold dense molecular clouds shielded from strong UV fields and are consistent with the observation of solid CO$_2$ in H$_2$O-rich environments.