Hydrogenation of Accreting C Atoms and CO Molecules—Simulating Ketene and Acetaldehyde Formation Under Dark and Translucent Cloud Conditions

Gleb Fedoseev1,2, Danna Qasim1,6, Ko-Ju Chuang1, Sergio Ioppolo3, Thanja Lamberts1,4, and Harold Linnartz1,2

1 Laboratory for Astrophysics, Leiden Observatory, Leiden University, PO Box 9513, 2300 RA Leiden, The Netherlands
2 Research Laboratory for Astrochemistry, Ural Federal University, Kuibysheva St. 48, 620026 Ekaterinburg, Russia
3 School of Electronic Engineering and Computer Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK
4 Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2333 CC Leiden, The Netherlands
5 Leiden Observatory, Leiden University, P.O. Box 9513, NL 2300 RA Leiden, The Netherlands

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Abstract

Simple and complex organic molecules (COMs) are observed along different phases of star and planet formation and have been successfully identified in prestellar environments such as dark and translucent clouds. Yet the picture of organic molecule formation at those earliest stages of star formation is not complete and an important reason is the lack of specific laboratory experiments that simulate carbon atom addition reactions on icy surfaces of interstellar grains. Here we present experiments in which CO molecules as well as C and H atoms are codeposited with H2O molecules on a 10 K surface mimicking the ongoing formation of an “H2O-rich” ice mantle. To simulate the effect of impacting C atoms and resulting surface reactions with ice components, a specialized C-atom beam source is used, implemented on SURFRESIDE3, an ultra-high vacuum cryogenic setup. Formation of ketene (CH2CO) in the solid state is observed in situ by means of reflection absorption IR spectroscopy. C18O and D isotope labeled experiments are performed to further validate the formation of ketene. Data analysis supports that CH2CO is formed through C-atom addition to a CO molecule, followed by successive hydrogenation transferring the formed :CCO into ketene. Efficient formation of ketene is in line with the absence of an activation barrier in C+CO reaction reported in the literature. We also discuss and provide experimental evidence for the formation of acetaldehyde (CH3CHO) and possible formation of ethanol (CH3CH2OH), two COM derivatives of CH2CO hydrogenation. The underlying reaction network is presented and the astrochemical implications of the derived pathways are discussed.

Key words: Interstellar medium – Dark interstellar clouds – Diffuse molecular clouds – Laboratory astrophysics – Surface ices – Surface processes – Interstellar molecules – Infrared astronomy – Interstellar dust

1. Introduction

Astronomical gas-phase observations show that a variety of simple and complex organic molecules (COMs) exist in translucent and dense clouds as well as dark cores (Matthews et al. 1985; Turner et al. 1999; Baumann et al. 2012; Soma et al. 2018). Astrochemical models show that gas-phase reactions generally lack the efficiency to explain the observed COM abundances (Millar et al. 1991; Charnley et al. 1992; Garrod et al. 2006). For this reason, it is assumed that many of the observed COMs are primarily formed on the icy surfaces of inter- (and circum-) stellar dust grains that act both as cryogenic molecule reservoirs and catalytic surfaces.

The onset of solid-state COM formation is usually associated with the beginning of the CO freeze-out stage in dense clouds, where gas-phase atomic carbon is largely locked up in CO (see van Dishoeck & Black 1988, Snow & McCall 2006). CO forms an ice coating layer on top of a previously formed H2O-rich ice (Pontoppidan 2006; Boogert et al. 2015) and is hydrogenated by accreting H atoms to form H2CO, CH3OH, and various ≥2-carbon bearing COMs, such as aldehydes, aldoses and (poly)
Following this specific scenario, the growth of the carbon skeleton takes place through direct C-atom addition to or insertion in the various C-carbon bearing radicals produced along with simpler species (Tielens & Charnley 1997; Charnley et al. 2001; Charnley & Rodgers 2005). The key reaction step responsible for the growth of the carbon skeleton and formation of 2-carbon bearing COMs suggested in these modeling works is the insertion of a C atom into the HCO radical, ultimately resulting in the formation of ketene (CH2CO):

\[
\begin{align*}
\text{CO} + \text{H} &\rightarrow \text{HCO}, \\
\text{HCO} + \text{C} &\rightarrow \text{HCCO}, \\
\text{HCCO} + \text{H} &\rightarrow \text{CH2CO}.
\end{align*}
\]

Strictly speaking, ketene is not a COM because of the astronomical definition that COMs comprise of at least six atoms. However, ketene is an important oxygen-bearing organic compound that acts as a COM precursor due to the presence of unsaturated CC and CO bonds. The produced CH2CO can be further hydrogenated to form the astronomically defined COM derivatives, acetaldehyde (CH3CO + 2H → CH3CHO) and ethanol (CH3CHO + 2H → CH3CH2OH), see Bisschop et al. (2007).

An alternative route to form CH2CO was recently found in experiments condensing atomic carbon together with H2, H2O, and CO molecules inside a superfluid helium nanodroplet (Krasnokutski et al. 2017). The key reaction step responsible for the growth of the carbon skeleton in this scenario is the association of CO molecules with methylene:

\[
\begin{align*}
\text{H} + \text{C} &\rightarrow \text{H}_{2}\text{C}, \\
\text{H}_{2}\text{C}:+\text{CO} &\rightarrow \text{CH}_{2}\text{CO}.
\end{align*}
\]

The second reaction step (2b) does, however, have a 1500–1700 K barrier that needs to be overcome (King et al. 1998; Ogihara et al. 2010). This may decrease the overall feasibility of this reaction route in view of the competing reactions with H atoms and molecular H2.

Recent quantum chemical calculations offer a third reaction path that can lead to ketene formation in the ice following a barrierless association reaction between CO molecules and C atoms, see Papakondylis & Mavridis (2019):

\[
\begin{align*}
\text{CO} + \text{C} &\rightarrow :\text{CCO}, \\
:\text{CCO} + \text{H} &\rightarrow \text{HCCO}, \\
\text{HCCO} + \text{H} &\rightarrow \text{CH}_{2}\text{CO},
\end{align*}
\]

where (3c) is identical to (1c).

To date, there are no reported experimental studies that have tested such carbon atom induced reaction pathways on the surface of H2O-rich interstellar ice analogs, i.e., using (more) representative astronomical conditions. The topic of the present study is to experimentally investigate the formation of ketene following the third suggested mechanism as well as the formation of two of its proposed derivatives, acetaldehyde and ethanol, under solid-state conditions resembling the early phases of dark clouds or translucent clouds in which atom addition reactions play a key role. In the following sections, we discuss experiments in which C atoms and H atoms are codeposited with CO molecules along with an overabundance of H2O molecules. The latter simulates the growth of an interstellar H2O-rich ice mantle before the CO accretion phase, i.e., the so-called CO freeze-out stage, when the solid-state chemistry is mainly driven by hydrogenation of CO molecules. The dominating reaction routes under these experimental conditions are proposed. In Section 2, the experimental procedure is described. Section 3 presents the results. The paper is completed with a discussion on the astronomical implications, which incorporates the newly verified reaction pathways into a larger astrochemically relevant reaction network.

2. Experimental

The experiments are performed using SURFRESIDE3, an ultra-high vacuum (UHV) setup extended from a two-atom beam line system as described by Ioppolo et al. (2013) to a system with an additional C-atom beam source (Qasim et al. 2020b). In both papers, the experimental procedures have been described in detail. Ices are grown on a gold-coated copper substrate that is mounted on the cold finger of a closed-cycle He cryostat and placed in the center of the main UHV chamber with a base pressure on the order of 10−10 mbar. Simultaneous codeposition of H2O molecules with C atoms, CO molecules, and H atoms is performed to grow a mixed ice analog on the 10 K cold substrate. Isotope labeling using C18O isotope or D atoms is used for further validation.

A beam of H atoms mixed with undissociated H2 molecules or D atoms mixed with undissociated D2 molecules is obtained by partial dissociation of molecular H2 or D2 in a microwave discharge beam line (Oxford Scientific; Schmidt et al. 1996; Antoon et al. 2000) mounted in a separate vacuum chamber with a base pressure of ∼1 × 10−9 mbar. Any charged particles are deflected by means of an applied electric field which prohibits them from reaching the ice surface. Then, the electronically or vibrationally excited neutral species in the obtained beam are de-excited through collisions with the walls of a U-shaped quartz pipe placed along the path of the beam, and directed to the substrate plane. The H-atom flux used is derived to be 2 × 1012 cm−2 s−1. This value is evaluated using a quadrupole mass spectrometer (QMS) with the ion head positioned on the place of the substrate along the path of the atom beam. See also Ioppolo et al. (2013). First, the D-atom beam flux values are estimated for a range of relevant plasma parameters. Then the H-atom beam flux values are obtained by multiplication of the D-atom beam flux values by a factor of 2 (rounded) accounting for the higher thermal velocity of the lighter H atoms.

A C-atom beam with a Cn/C (n > 1) ratio of less than 0.01 is produced by a state-of-the-art customized C-atom source based on a commercial design (Dr. Eberl, MBE, Krasnokutski & Huisken 2014; Albar et al. 2017) located in another separate vacuum chamber with a base pressure of (3–5) × 10−9 mbar. A series of apertures are used to collimate the C-atom beam on the substrate avoiding deposition of carbon on the walls of the main UHV chamber. The C-atom flux used in this study is ∼5 × 1011 cm−2 s−1, and only ground state C(3P) atoms are expected to be present in the beam. The C-atom flux is measured by performing a set of C+/18O2 codeposition experiments and quantifying the yield of this barrierless reaction, see Qasim et al. (2020b) for more details. The produced C-atom beam contains minor fractions of CO and CO2 as main contaminants. A third separate vacuum chamber with a base pressure of ∼1 × 10−9 mbar is used for H2O molecular beam deposition with a rate equal to 8 × 1012 cm−2 s−1. C18O gas is prepared in a regular all-metal dosing line prepumped to <1 × 10−4 mbar and guided...
toward the substrate through an all-metal leak valve and a capillary. The CO and C\textsuperscript{18}O deposition rates are determined to be \(8 \times 10^{11}\) cm\(^{-2}\) s\(^{-1}\) and \(1.4 \times 10^{12}\) cm\(^{-2}\) s\(^{-1}\) at the substrate surface, respectively.

The ice growth is monitored in situ by means of reflection absorption infrared spectroscopy (RAIRS; Greenler 1966). In the present study, the band strength ratio between transmission and reflection modes is assumed to be constant for all studied species. The setup specific conversion factor between the band strength values of two modes equals \(5.5 \pm 0.8\) and is obtained by comparing the values for the pure solid CO, H\textsubscript{2}CO, and CH\textsubscript{3}OH reported for our setup geometry in Chuang et al. (2018) to the values reported for transmission in Bouilloud et al. (2015). Both measurements utilize a laser interference technique (at 632.8 nm laser wavelength) allowing to evaluate the absolute thickness of an ice with known refractive index by measuring the interference curve of the reflected light. Subsequently, the absolute thickness of the ice can be converted into an absorption band strength by using the ice density available from the literature.

Additional diagnostic information is extracted through temperature programmed desorption (TPD) and continuous monitoring of the gas-phase composition by means of a QMS. A 5 K min\(^{-1}\) heating rate with a data acquisition rate of one point per 0.5 K is used in the experiments. The combination of RAIRS and TPD-QMS, particularly when using isotopes, has been shown to provide an effective tool to realize unambiguous identifications of newly formed species and even to discriminate between structural isomers (Maity et al. 2015; Fedoseev et al. 2017; Chuang et al. 2020).

A significant overabundance of H\textsubscript{2}O molecules is used in the performed experiments. On the one hand, this aims to represent the surface coverage during the H\textsubscript{2}O-rich ice formation stage of molecular clouds. On the other hand H\textsubscript{2}O also acts as a diluting agent between structural isomers and even to discriminate between isomers (Maity et al. 2015; Fedoseev et al. 2017; Chuang et al. 2020). Figure 1 presents the RAIR spectra obtained for three selected experiments involving C-atom deposition with H\textsubscript{2}O molecules along with CO and H (spectrum a), CO and D (spectrum b) and CO/C\textsuperscript{18}O and H (spectrum c). The experiments are performed for identical settings. The amount of deposited H\textsubscript{2}O is the same in all of the presented experiments, which is confirmed by comparing the absorbance of the broad water absorption band peaking around 1660 cm\(^{-1}\) (\(\nu_2\)), (Gerakines et al. 1995). In the same way similar amounts of newly formed formaldehyde are found, based on the comparison of the absorbances of its characteristic features at 1718 cm\(^{-1}\) (\(\nu_2\)), 1499 cm\(^{-1}\) (\(\nu_3\)) and 1252 cm\(^{-1}\) (\(\nu_2\)) (Hidaka et al. 2004, 2009). No efficient formation of D\textsubscript{2}CO or H\textsubscript{2}C\textsuperscript{18}O is observed in our experiments, as no clear absorption signals are found at 1676 cm\(^{-1}\) for D\textsubscript{2}CO (\(\nu_2\)) and/or 1694 cm\(^{-1}\) (\(\nu_2\)) and 1488 cm\(^{-1}\) (\(\nu_3\)) for H\textsubscript{2}C\textsuperscript{18}O. This indicates that H\textsubscript{2}CO in our experiments is primarily formed through reactions of C atoms with H\textsubscript{2}O molecules, while the direct hydrogenation of CO molecules by H atoms is a minor channel under our selected experimental conditions. This is in line with the lower total H-atom fluence used in the present work in comparison with the values used in the previous CO+H experiments (Fuchs et al. 2009; Fedoseev et al. 2015; Chuang et al. 2016).

Absorption features of CD\textsubscript{4} (\(\nu_1\), 2251 cm\(^{-1}\)) and CH\textsubscript{4} (\(\nu_3\), 1303 cm\(^{-1}\)) are, however, clearly observed in spectrum (b) and (c) of Figure 1, respectively. This is consistent with the lack of an activation barrier for the hydrogenation of C atoms into methane as reported very recently (Qasim et al. 2020a), whereas CO hydrogenation involves an activation barrier (Watanabe & Kouchi 2012).

It should be noted, that the amount of H\textsubscript{2}CO formed through interaction of C atoms with H\textsubscript{2}O molecules in our experiments scales directly with the C-atom flux and H\textsubscript{2}O surface coverage, and is the same for the experiments performed at 10 and 25 K. The formation of H\textsubscript{2}CO from C and H\textsubscript{2}O is an important finding, and is the subject of a very recently published work (Molpeceres et al. 2021). For the present work it is important to note that the fraction of C atoms that does not react with H\textsubscript{2}O is assumed to be thermalized and available for the reaction with CO molecules and H atoms.

The multicomponent absorption feature centered at 2137 cm\(^{-1}\) with a high wavenumber component around 2150 cm\(^{-1}\) in spectrum (a) of Figure 1 is assigned to CO molecules with an unknown fraction of CH\textsubscript{2}CO. The use of D atoms, see spectrum (b) of Figure 1, results in only a tentative detection of CD\textsubscript{3}CO because of the weak intensity decrease of the peak centered at 2137 cm\(^{-1}\) contributed by unlabeled CH\textsubscript{3}CO and observation of the poorly resolved absorption features of CD\textsubscript{2}CO at 2152 cm\(^{-1}\) (\(\nu_1\)) and 2116 cm\(^{-1}\) (\(\nu_2\)), see comparison between spectra (a) and (b) in the right panel of Figure 1 (Arendale & Fletcher 1957; Kogure et al. 1993).

Only in the experiment with C\textsuperscript{18}O addition, see spectrum (c) of Figure 1, the CH\textsubscript{2}C\textsuperscript{18}O absorption feature centered at 2107 cm\(^{-1}\) (\(\nu_2\), Hudson & Loefller 2013) can be clearly resolved from the C\textsuperscript{18}O feature centered at 2087 cm\(^{-1}\). The appearance of the CH\textsubscript{2}C\textsuperscript{18}O absorption feature correlates with the visual decrease in the intensity of the CH\textsubscript{2} production feature centered at 1303 cm\(^{-1}\) (\(\nu_3\)) in spectrum (c) of Figure 1. This is in line with the appearance of a new C-atom consumption channel, which competes with the production of CH\textsubscript{2} and yields CH\textsubscript{2}C\textsuperscript{18}O in addition to the regular CH\textsubscript{2}CO isotope.
To further validate this CH$_2$C$^{18}$O assignment, spectra are recorded after heating the ice to 55 and 165 K. These spectra are shown in spectra (d) and (e) of Figure 1, respectively. At 55 K, i.e., well above the CO desorption temperature, only a small fraction of CO and C$^{18}$O entrapped in H$_2$O ice remains, making the distinct CH$_2$C$^{18}$O absorption feature even more evident. The spectrum at 165 K is obtained after desorption of H$_2$O ice together with all the entrapped highly volatile compounds. The characteristic bands around 2100 cm$^{-1}$ are all gone, confirming that the absorption at 2107 cm$^{-1}$ is not caused by unidentified low volatile species.

3.2. Mass Spectrometry

In order to provide further evidence for the formation of ketene in the performed experiments, an example of a typical TPD-QMS measurement is presented in Figure 2. This measurement is obtained for a codeposition of CO molecules with C and H atoms and overabundance of H$_2$O molecules. The four panels show the desorption curves for selected m/z values assigned to H$_2$O (a), CH$_2$CO (b), CH$_3$CHO (c), and CH$_3$CH$_2$OH (d). Ketene can be identified through its m/z signals at 14 (CH$_2$), 41 (HCCO$^+$), and 42 (CH$_2$CO$^+$) and reveals two desorption features (Figure 2(b)). The weaker peak can be identified in the range of 88–107 K, and corresponds to the desorption temperature reported previously in the literature, see Maity et al. (2015) and Chuang et al. (2020). The second feature in the range of 125–165 K corresponds to the fraction of entrapped ketene desorbing with H$_2$O ice (see also Figure 2(a)). Whereas in the IR spectra no resolved acetaldehyde and ethanol features could be unambiguously assigned, the TPD-QMS data reveals that, along with the CH$_2$CO itself, these two possible CH$_2$CO hydrogenation products (CH$_3$CHO and CH$_3$CH$_2$OH) can be identified as well. Figure 2(c) shows CH$_3$CHO signatures with characteristic m/z signals at 43 (CH$_3$CHO$^+$), 44 (CH$_3$CHOH$^+$), and 15 (CH$_3^+$). Similarly to ketene, TPD data in Figure 2(c) reveal two desorption features, i.e., the feature around a characteristic desorption temperature of CH$_3$CHO at 120–140 K (Abplanalp et al. 2016) and a feature at 140–160 K coinciding with the desorption of the bulk of H$_2$O ice. Figure 2(d) shows possible features of CH$_3$CH$_2$OH through (less prominent) mass peaks at m/z = 45 (C$_2$H$_3$O$^+$) and m/z = 46 (C$_2$H$_2$OH$^+$) between 150 and 163 K. The thermal desorption of CH$_3$CH$_2$OH has been reported to appear at temperatures several Kelvin higher than that of water ice, see Bergantini et al. (2017) and Chuang et al. (2020). This finding is confirmed in Figure 2.

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** In the left panel the IR spectra are shown obtained after the simultaneous codeposition of H$_2$O molecules with C atoms and (a) CO molecules and H atoms; (b) CO molecules and D atoms; (c) a mixture of CO with C$^{18}$O molecules with H atoms at a substrate temperature 10 K. All codepositions are performed for a period of 1920 s. Spectra (d) and (e) are obtained after warm up of the ice presented in spectrum (c) to 55 and 165 K, respectively. The H$_2$O:C:CO/(C$^{18}$O):H(D) ratio is estimated to be 16:1:1.5:1. The characteristic bands around 2100 cm$^{-1}$ are shown in spectra recorded after heating the ice to 55 and 165 K. These spectra are offset for clarity. Blue and red colors are used to indicate D and $^{18}$O labeled experiments and assignments, respectively. Tentative assignments are presented in brackets.

**Figure 2.** This TPD-QMS measurement is presented in Figure 2. This measurement is obtained for a codeposition of CO molecules with C and H atoms and overabundance of H$_2$O molecules. The four panels show the desorption curves for selected m/z values assigned to H$_2$O (a), CH$_2$CO (b), CH$_3$CHO (c), and CH$_3$CH$_2$OH (d). Ketene can be identified through its m/z signals at 14 (CH$_2$), 41 (HCCO$^+$), and 42 (CH$_2$CO$^+$) and reveals two desorption features (Figure 2(b)). The weaker peak can be identified in the range of 88–107 K, and corresponds to the desorption temperature reported previously in the literature, see Maity et al. (2015) and Chuang et al. (2020). The second feature in the range of 125–165 K corresponds to the fraction of entrapped ketene desorbing with H$_2$O ice (see also Figure 2(a)). Whereas in the IR spectra no resolved acetaldehyde and ethanol features could be unambiguously assigned, the TPD-QMS data reveals that, along with the CH$_2$CO itself, these two possible CH$_2$CO hydrogenation products (CH$_3$CHO and CH$_3$CH$_2$OH) can be identified as well. Figure 2(c) shows CH$_3$CHO signatures with characteristic m/z signals at 43 (CH$_3$CHO$^+$), 44 (CH$_3$CHOH$^+$), and 15 (CH$_3^+$). Similarly to ketene, TPD data in Figure 2(c) reveal two desorption features, i.e., the feature around a characteristic desorption temperature of CH$_3$CHO at 120–140 K (Abplanalp et al. 2016) and a feature at 140–160 K coinciding with the desorption of the bulk of H$_2$O ice. Figure 2(d) shows possible features of CH$_3$CH$_2$OH through (less prominent) mass peaks at m/z = 45 (C$_2$H$_3$O$^+$) and m/z = 46 (C$_2$H$_2$OH$^+$) between 150 and 163 K. The thermal desorption of CH$_3$CH$_2$OH has been reported to appear at temperatures several Kelvin higher than that of water ice, see Bergantini et al. (2017) and Chuang et al. (2020). This finding is confirmed in Figure 2.
isolates the formed CH$_3$O species from each other preventing their efficient interactions.

### 3.3. C+H$_2$CO and C+CH$_3$OH Reactivity

Along with the sequential hydrogenation of CH$_2$CO yielding CH$_3$CHO and CH$_3$CH$_2$OH (Bisschop et al. 2007), a parallel reaction path may be involved. Insertion of C atoms into the C–H bond of H$_2$CO or CH$_3$OH followed by hydrogenation of the formed species can also result in the formation of CH$_3$CHO and CH$_3$CH$_2$OH. In line with the C-addition channel investigated here for ketene, such a process could also be relevant in the period just before the CO freeze-out stage. For this reason, a series of additional experiments is performed to confirm or exclude this reaction mechanism. The experiment presented in spectrum (c) of Figure 1 is repeated under the very same experimental conditions by using H$_2^{13}$CO and CH$_3$OH molecules instead of the admixture of C$^{18}$O. None of these experiments resulted in a clear identification of CH$_3$CHO or CH$_3$CH$_2$OH isotopes within the RAIRS sensitivity limits. This hints for the presence of activation barriers in C+H$_2$CO and C+CH$_3$OH reactions.

### 4. Astrochemical Implications and Conclusions

The experiments performed here aim at simulating chemical processes during the earliest stages of the star formation process. Upon transition from diffuse to translucent clouds, a fraction of elemental carbon previously locked in C$^+$ can be partially converted into neutral C atoms before ultimately getting locked in molecular CO in dense molecular clouds. At this stage, the abundance of C atoms with respect to elemental hydrogen can be as high as 10$^{-4}$, see van Dishoeck & Black (1988) and Snow & McCall (2006). This means that there is a period in the evolution of interstellar clouds when CO molecules and C atoms can both simultaneously accrete on grain surfaces. As this stage occurs early in or directly prior to the formation of the cold dark cloud core, it should coincide with the formation of the bulk of H$_2$O ice produced by hydrogenation of accreting O atoms (van Dishoeck et al. 2021). A few other main constituents of interstellar ices formed during this phase are simple hydrides NH$_3$ and CH$_4$, produced at least partially by hydrogenation of accreting N and C atoms, as well as CO$_2$ (Boogert et al. 2015; Linnartz et al. 2015). The latter one is produced from accreting CO molecules through interaction with OH radicals or direct addition of O atoms, see Chang & Herbst (2012) and Ioppolo et al. (2013). This stage directly precedes the so-called CO freeze-out stage, which implies higher densities and CO accretion rates.

In this study, the first experimental evidence for the formation of ketene on the surface of H$_2$O ice at 10 K through interaction of CO molecules with C and H atoms is presented. Moreover, it is shown that the possible products of CH$_2$CO hydrogenation, CH$_3$CHO, and traces of CH$_3$CH$_2$OH, form as well. Formation of CH$_2$CO is expected to be initiated by C+CO$^-$, as reported by Papakondylis & Mavridis (2019). The formed :CCO biradical, then, can be quickly hydrogenated into CH$_3$CO by H atoms by two consecutive barrierless radical–radical interactions, i.e., according to the reactions of the third scenario (Equations (3a)–(3c)) presented in the introduction.

To our knowledge, the hydrogenation of CH$_2$CO forming CH$_3$CHO at the specific conditions used in the present study was not demonstrated experimentally in the literature due to the difficulties associated with deposition of pure CH$_2$CO ice. Gas-phase experiments reported a rather low barrier for this reaction, e.g., 975 K (Umemoto et al. 1984). This barrier is considerably lower than the effective activation barrier reported for CO hydrogenation for similar temperatures, meaning that it may efficiently proceed at 10 K (Andersson et al. 2011). Hydrogenation of pure CH$_3$CHO into CH$_3$CH$_2$OH under similar experimental conditions was studied in detail by Bisschop et al. (2007) and Chuang et al. (2020), and was shown to proceed at 10 K. However, an activation barrier for H-atom addition to a CH$_3$CHO molecule was reported to be higher than that for CO hydrogenation, see Sivaramakrishnan et al. (2010). This means that formation of CH$_3$CH$_2$OH from CH$_3$CHO can be a rate limiting step, and therefore solid-state abundances of CH$_2$CO and CH$_3$CHO higher than that of CH$_3$CH$_2$OH are expected early in the dark clouds.

Our suggested mechanism does not explicitly exclude other reaction routes, such as association of CH$_3$ with CO.
Figure 3. Proposed COM formation network initiated by C-atom addition to CO molecules. The reaction routes investigated in the present study are marked in red. Filled arrows indicate experimentally verified formation routes. Empty arrows indicate reaction routes predicted theoretically. Gray dotted arrows and boxes account for the speculative routes resulting in the formation of 3 carbon bearing derivatives. These routes are suggested in view of the efficient reactivity of C atoms with the unsaturated carbon–carbon bonds (Kaiser & Mebel 2002; Henning & Krasnokutski 2019). (CH$_3$)CO and (CH$_3$)$_2$CO stand for cyclopropenone and cyclopropanone, respectively. (see footnote The activation barriers for the rate-determining reactions obtained in this work or from the literature: (a) 0 K (Papakondylis & Mavridis 2019); (b) 975 K, as the latter case only C atoms can readily be consumed by surrounding species in the ice. Indeed, as HCO radicals react with H atoms without the presence of an activation barrier, they have a significantly lower surface density than CO molecules, which are still required to bypass an activation barrier to be consumed in reaction with H atoms (see, for example, Figure 3 of Aikawa et al. 2020, and Figure 5 of Simons et al. 2020).

Following the successful identification of CH$_2$CO here and evidence for the formation of CH$_3$CHO and possibly CH$_3$CH$_2$OH starting from ketene molecules, the previously suggested theoretical networks utilizing solid-state C-atom addition reactions as the source of COM formation (see Charnley et al. 2001) can get their first experimental confirmation. The updated formation routes, with inclusion of the results obtained in the work presented here, are shown in Figure 3. The reactions concluded from our work are marked with red and comprise the core of the C-atom addition/insertion network. The key step responsible for the growth of carbon skeleton and formation of 2-carbon bearing COMs is suggested to be the addition of a carbon atom to a CO molecule. The solid boxes connected with solid arrows sum up other related and well-known reaction routes investigated previously both theoretically and in the laboratory, see Linnartz et al. (2015) and references therein. The gray dotted boxes and arrows suggest some of the speculative routes, which may result in a further increase of the chemical complexity and formation of 3 carbon bearing derivatives. These routes imply C-atom addition to the unsaturated carbon–carbon bonds followed by consequent hydrogenation of the formed reactive intermediates (Kaiser & Mebel 2002; Henning & Krasnokutski 2019) and are in line with the ideas initially presented by Charnley et al. (2001). Dedicated future work, combining experimental and theoretical approaches, will be required to fully pinpoint the relative impact for such C-atom induced solid state reaction routes, i.e., when comparing with pathways involving recombination of CH$_3$O radicals or addition of OH radicals to the unsaturated CC bonds of hydrocarbons (Chuang et al. 2016, 2020; Qasim et al. 2019).

Efficient solid-state formation of CH$_3$CO, CH$_3$CHO, and CH$_3$CH$_2$OH initiated by accretion of C atoms, H atoms, and CO molecules means that these COMs are likely already present in icy grains early in the lifetime of interstellar clouds, i.e., well before the occurrence of CO freeze-out stage commonly associated with formation of a large fraction of COMs described with formula (CO)$_n$H$_m$. The occurrence of C-atom induced solid-state COM formation routes makes CH$_3$CHO and CH$_3$CH$_2$OH promising candidates for upcoming James Webb Space Telescope observations, as they can be formed both during the early dark cloud evolution and later upon the processing of CO-rich ice containing CH$_3$OH by...
various chemical triggers; thus, higher total column densities of CH$_3$CHO and CH$_3$CH$_2$OH should be available for the observations (Öberg et al. 2009; Modica & Palumbo 2010; Vasyunin & Herbst 2013; Maity et al. 2015; Fedoseev et al. 2017). The abundance of CH$_3$CHO and CH$_3$CH$_2$OH prior to the CO freeze-out can be further enhanced by the C$_2$/C$_3$H$_6$-induced formation route presented in Bergner et al. (2019) and Chuang et al. (2020, 2021). Indeed, CH$_3$CHO and CH$_3$CH$_2$OH are a few of the COMs tentatively assigned in the solid state as the possible carriers of the 7.41 and 7.24 μm ice bands, respectively (Schutte et al. 1999; Öberg et al. 2011; Terwisscha van Scheltinga et al. 2018). The distinct profiles of CH$_3$CHO and CH$_3$CH$_2$OH absorption features in H$_2$O-rich and CO:CH$_3$OH-rich ices, see Terwisscha van Scheltinga et al. (2018), may also provide insights on the typical environment in which CH$_3$CHO and CH$_3$CH$_2$OH molecules are embedded, linking the formation of these molecules to specific star formation stages.

The formed CH$_2$CO and CH$_3$CHO, in turn, can be partially transferred from the solid state into the gas phase by various thermal and nonthermal mechanisms contributing to the gas-phase abundances of these species in dark and translucent clouds (Dulieu et al. 2013; Rawlings et al. 2013; Chuang et al. 2018; Dartois et al. 2019; Hoang & Tram 2020). Enrichment of the gas phase by CH$_2$CO and CH$_3$CHO or by intermediate products obtained along their solid-state formation routes may provide the initial reagents for otherwise inefficient gas-phase reactions. This can further enhance the gas-phase composition during the earliest stages of star formation (Vasyunin & Herbst, 2013). In the near future, detailed astrochemical simulations utilizing gas-grain models will be required to estimate the exact impact of the verified formation routes on the gas-phase and solid-state abundances of CH$_2$CO, CH$_3$CHO, and CH$_3$CH$_2$OH, providing more information on the relative amounts of these species during the earlier and later stages of star formation.

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Appendix

The RAIR spectra presented in Figure 1 from 2250–1200 cm$^{-1}$ are shown in Figure A1 for the full recorded range from 4000–700 cm$^{-1}$. Several additional assignments can be made: CH$_4$ ($\nu_1$, 3009 cm$^{-1}$) and CD$_4$ ($\nu_3$, 994 cm$^{-1}$), see Chapados & Cabana (1972), and the broad H$_2$O absorption bands peaking around 3390 and 820 cm$^{-1}$, see Gerakines et al. (1995). The absorption feature of solid-state CO$_2$ ($\nu_3$, 2343 cm$^{-1}$) is in part concealed by the absorption feature of gas-phase CO$_2$ present in the purging gas along the path of the IR beam outside of the setup. The weaker absorption feature in the range from 3700–3600 cm$^{-1}$, in the shoulder of the strong 3390 cm$^{-1}$ H$_2$O band, is assigned to the dangling OH vibrations of H$_2$O molecules, see Sadlej et al. (1995). The increase in the absorption of dangling OH mode of H$_2$O molecules in the spectrum (c) is consistent with the addition of C$^{18}$O molecules to the codeposition experiment and increased separation between H$_2$O molecules in the bulk of the mixed ice.

![Figure A1](image-url)  
**Figure A1.** The full range IR spectra (4000–700 cm$^{-1}$) of the RAIRS signals shown in Figure 1. Spectra are offset for clarity.
