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Hydrogen addition reactions of a three-membered ring in the solid-state: $c\text{-C}_3\text{H}_2\text{O}$

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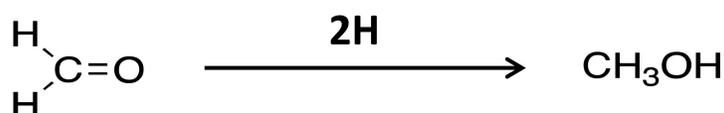
Abstract

Due to the relatively high abundance of hydrogen radicals in the interstellar medium, the H-addition reaction of unsaturated organic molecules in the solid phase and at very low temperatures is considered to play an important role in the chemical complexity of organic substances in the Universe. However, when interacting with hydrogen atoms, all unsaturated functional groups that may be present in several organic species exhibit different behaviors that can significantly alter the reaction pathways from one species to another. By coupling FTIR spectroscopy and TPD mass spectrometry, we have investigated the $\text{H} + c\text{-C}_3\text{H}_2\text{O}$ (cyclopropenone) solid state reaction using two different experimental methods. We show that cyclopropenone reacts with hydrogen atoms under interstellar medium conditions, leading to propynal (HCCCHO), propadienone (CH_2CCO), two thermodynamically most stable isomers of $c\text{-C}_3\text{H}_2\text{O}$. In excess of H atoms, the hydrogenation of cyclopropenone also leads to propenal (CH_2CHCHO), propanal ($\text{CH}_3\text{CH}_2\text{CHO}$), $c\text{-C}_3\text{H}_4\text{O}$ (cyclopropanone), in addition to two alcohols, namely cyclopropanol ($c\text{-C}_3\text{H}_6\text{O}$) and propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$).

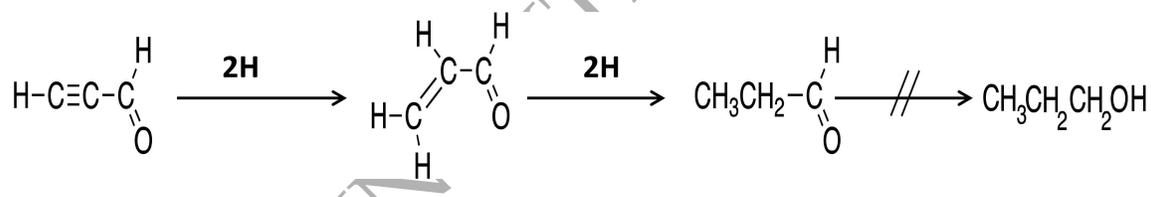
Keywords: astrochemistry, molecular processes, methods: laboratory: molecular, techniques: spectroscopic, ISM: molecules

1. Introduction :

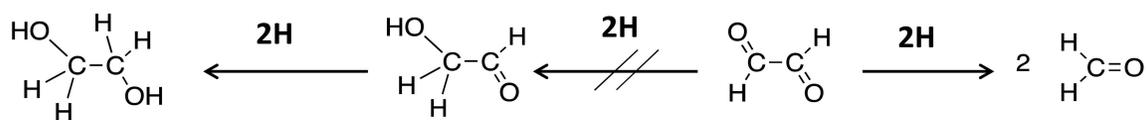
Pathways for the synthesis of complex organic molecules (COMs), carbon-containing molecules with at least six atoms (Herbst & Dishoeck 2009), continue to be of great interest to astrochemists, whether through laboratory experiments, astronomical observations or theoretical simulations. Due to the relatively high abundance of hydrogen radicals, the H-addition reaction on unsaturated organic molecules, in the physical conditions of dark interstellar clouds and in particular in solid phase and at very low temperature, is considered to play an important role in the chemical complexity of organics of the interstellar medium. However, when interacting with hydrogen atoms, all unsaturated functional groups that may be present in multiple COMs exhibit different behaviors that can significantly alter the reaction pathways from one species to another. Thus, formaldehyde reacts with hydrogen atoms to form methanol (Hidaka et al. 2004), showing that the HCO group may be easily reduced to CH₂OH or CH₃O through two successive H- addition reactions:



With propynal or propenal, only the CC triple or double bonds of these species, respectively, are reduced leading to propanal (Jonusas et al 2017). While the H-addition reactions on HCO groups of these three species seem to be less efficient:



Correspondingly, HCO groups in glyoxal, glycolaldehyde show different behavior. Upon interacting with hydrogen atoms (Leroux et al. 2019), the two HCO of glyoxal remain unreduced while its CC bond is cleaved to form two H₂CO. Unexpectedly, the HCO group of glycolaldehyde is reduced to CH₂OH or CH₃O, leading to ethylene glycol (Leroux et al.2021):



Therefore, it is difficult to rationalize the behavior of the H-addition reaction on unsaturated organic molecules in the interstellar medium and laboratory simulations are needed to specify the behavior of each chemical species whatever its functional group. In this study, we will focus on the reduction of cyclopropenone under the extreme conditions of the interstellar medium. Organic species can be formed on the surface of grains and they can also form in the gas phase before accreting on the surface of grains. Due to the high mobility of hydrogen atoms at 10 K, successive hydrogenations of small organic molecules leading to large complex organic molecules are much more efficient in the solid phase than in the gas phase. Although interstellar ices are mainly composed of H₂O and CO and other molecules observed in the interstellar medium, we have studied the hydrogenation of pure *c*-C₃H₂O ices in order to obtain as many reaction products as possible, which will enable to describe all the possible mechanisms involved in the transformation of *c*-C₃H₂O in the solid phase. As mentioned above, we have already shown that the reduction of propynal, a carbonyl derivative with a CC triple bond, leads mainly to propanal, the HCO group being unaffected by H. Cyclopropenone, a compound detected in the interstellar medium, is a cyclic isomer of propynal with an HCO functional group and a CC double bond. The question that can be asked is whether the hydrogenation of these two isomers leads to the same final reaction product, namely propanal?

The three isomers cyclopropenone, propynal and propadienone C₃H₂O are considered to be of astrophysical interest and have been the subject of several experimental and theoretical studies (Yang et al. 2004, Zhou et al. 2008, Karton & Talbi 2014, Jonusas et al. 2017, Zaverkin et al. 2018, Etim et al. 2018, Shingledgecker et al. 2019, Hudson & Gerakines 2019, Abplanalp et al. 2019, Kleimeir et al. 2021, Zsimev et al. 2021, Muller et al. 2021, Song et al. 2022). While propadienone (CH₂CCO) is energetically the most stable isomer (Loomis et al. 2015), propynal (HCCCHO) and cyclopropenone (*c*-C₃H₂O) are less stable by 22.7 and 45.0 kJ mol⁻¹, respectively, but only propynal and cyclopropenone have been detected in the interstellar medium. Propynal was first detected by Irvine et al. (1988) on TMC-1. Later, the smallest aromatic organic molecule *c*-C₃H₂O was observed in Sagittarius B2, in the cold molecular cloud L1527 and in four dark clouds or prestellar cores TMC-1, B1-b, L483, and

Lupus-1A by Hollis et al. (2006), Tokudoume et al. (2013) and Loison et al. (2016), respectively. In the present paper, we report the solid phase H-addition reaction on cyclopropanone ($c\text{-C}_3\text{H}_2\text{O}$) under interstellar medium conditions. Cyclopropanone is an unsaturated ketone and an aromatic compound (Wang et al 2011). Laboratory investigations show that aromatic hydrocarbons such as benzene are well known to be much more difficult to reduce than alkenes. In the case where the reduction of $c\text{-C}_3\text{H}_2\text{O}$ occurs on the CC bond of cyclopropanone, the chemistry of the three-membered ring remains truly peculiar and the reaction of $c\text{-C}_3\text{H}_2\text{O} + 2 \text{H}$ in the solid phase would likely lead to cyclopropanone or ring opening. These assumptions make particularly rich the astrophysical laboratory study of the hydrogenation processes of small aromatic compounds such as cyclopropanone.

2. Experimental setup

The experimental setup used in this study has been described in detail previously (Jonusas and Krim 2017). The solid samples are formed under ultrahigh vacuum in a cryogenic chamber at 10^{-10} mbar through a condensation of the $c\text{-C}_3\text{H}_2\text{O}$ on a highly polished, rhodiated copper mirror maintained at 10 K using a closed-cycle helium cryogenerator (Sumitomo cryogenics F-70) and programmable temperature controller (Lakeshore 336). Cyclopropanone has been synthesized as previously reported (Breslow 1988) and kept for months at -80°C in a closed cell. Cyclopropanol was purchased from Fluorochem and used without purification. Unstable at room temperature, Cyclopropanone is stored in a tank bathed in liquid nitrogen (-196°C). It is then partially evaporated at 10°C in the injection ramp and introduced into the experimental chamber then condensed on the mirror maintained at 10 K. The pressure in the injection ramp is measured with a digital Pirani gauge, while the fractions of cyclopropanone gas injected into the experimental chamber are controlled using a leak valve. The hydrogenation of cyclopropanone in solid state has been carried out through two different experiments:

- Exp 1, $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ surface reaction: After solid sample deposition, the $c\text{-C}_3\text{H}_2\text{O}$ ices are bombarded during 45 min by H-atoms at 10 K.
- Exp 2, $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ bulk reaction: H-atoms and $c\text{-C}_3\text{H}_2\text{O}$ molecules are co-injected at 10 K during 30 min.

Atomic hydrogen are produced by a microwave driven atom source (SPECS PCR-ECS). This source uses a microwave discharge to generate gas plasma in a chamber fed with molecular hydrogen. H gas is injected in the reaction chamber at a pressure of 10^{-5} mbar with an H-atom

flux estimated around 1×10^{15} atoms $\text{cm}^{-2} \text{s}^{-1}$. The resulting solid samples are analyzed by recoding infrared spectra in the transmission-reflection mode between 5000 and 500 cm^{-1} , with a resolution of 0.5 cm^{-1} , using a Bruker 120 FTIR spectrometer with an incidence angle of 8° (Pirim & Krim 2011). Temperature programmed desorption (TPD) controlled by a quadrupole mass spectrometer (QMS - Hidden Analytical) was used in this study to characterize the $\text{c-C}_3\text{H}_2\text{O} + \text{H}$ reaction products formed in the solid phase and released into the gas phase during the thermal desorption of the solid sample between 10 and 300 K.

3. Results

3.1. Infrared spectroscopy analysis

Figure 1a shows the IR spectrum of pure cyclopropenone ice ($\text{c-C}_3\text{H}_2\text{O}$) formed at 10K. We note two main signals at 1849 and 1476 cm^{-1} due to C=O and C=C stretching modes, respectively, and two bands at 3052 and 1168 cm^{-1} attributed to C-H and C-C stretching modes, respectively. Three CH wagging modes are observed between 790 and 910 cm^{-1} , while CO_2 is detected as main impurity in our pure cyclopropenone ices. The assignments of the main vibrational modes of $\text{c-C}_3\text{H}_2\text{O}$, deduced from experimental and theoretical studies carried out by Yang et al. (2004) Brown et al. (1975), are reported in Table 1.

Table 1. Infrared absorption bands of pure $\text{c-C}_3\text{H}_2\text{O}$ ice formed at 10K.

Frequency	$\text{c-C}_3\text{H}_2\text{O}$ ice at 10 K (cm^{-1})	Theoretical	Vibrational modes ^b
ν_1	3090	3216	C-H str.
ν_9	3052	3182	C-H str.
ν_2	1849	1933	C=O str.
$2\nu_{11}$	1783	-	overtone
ν_3	1476	1524	C=C str.
ν_{10}	1168	1156	C-C antisym. str
ν_{11}	909	823	C-H wag (in-plane)
ν_5	864	855	C-H wag (in-plane)
ν_7	792	767	C-H wag (out-of-plane)

a-Yang et al. 2004, b-Brown et al. 1975

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After this IR spectral analysis, the pure cyclopropenone ($c\text{-C}_3\text{H}_2\text{O}$) ice has been bombarded during 45 min by hydrogen atoms. Figure 1b shows the IR spectrum of the $c\text{-C}_3\text{H}_2\text{O}$ ice after H-bombardment, and Figure 1.c represents the difference spectrum before and after ice hydrogenation. From the latter figure, we note that after hydrogenation processes, the band at 2242 cm^{-1} corresponding to CO_2 remains constant, while the negative and positive IR signals are due to the amounts of cyclopropenone consumed and the reaction products formed, respectively. After H-bombardment of $c\text{-C}_3\text{H}_2\text{O}$ ice, a wide absorption band appears at 3228 cm^{-1} in the OH stretching region and three IR signals at 2885.3 , 2945.3 , 2975.4 cm^{-1} in the CH stretching region. These first observations show that $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction lead both to C=C and CO reduction. Unexpectedly, the same experiments (Jonusas et al 2017) that were performed by our group for non-cyclic species with CHO functional groups such as propynal (HCCCHO), propenal (CH_2CHO), and propanal ($\text{CH}_3\text{CH}_2\text{CHO}$) never led to carbonyl reduction and alcohol formation but only to the transformation of multiple CC bonds into single bonds.

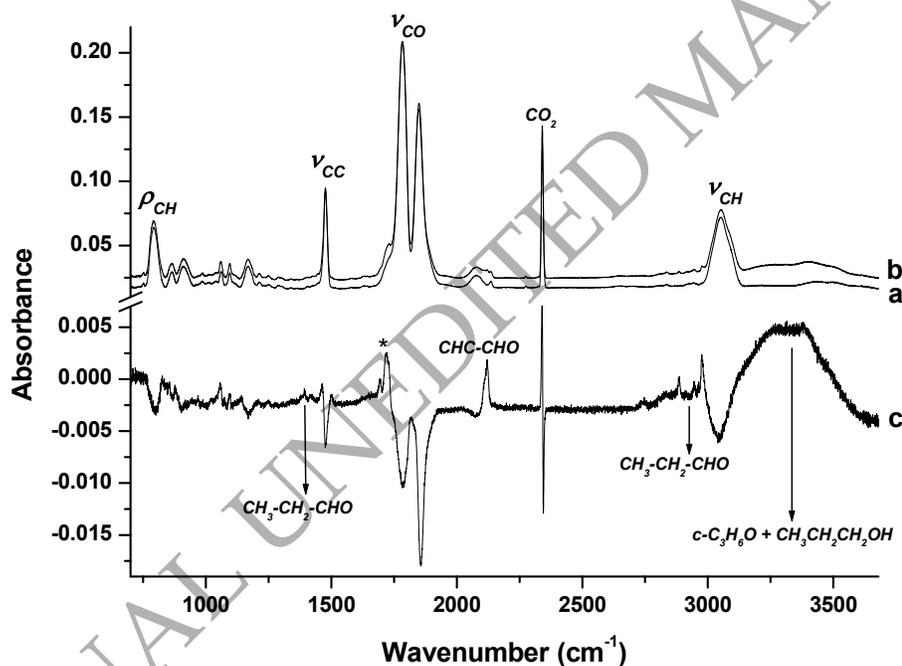


Figure 1. IR spectrum of cyclopropenone ($c\text{-C}_3\text{H}_2\text{O}$) ice formed at 10 K (a) before H-bombardment. (b) IR spectrum of cyclopropenone ice after H-bombardment (c) Difference spectrum before and after H-bombardment of $c\text{-C}_3\text{H}_2\text{O}$ ice.

Additionally, from figures 1b and 1c new IR signals are detected in the C=O stretching region at 1694.7, 1712.1, 1730.5 cm^{-1} and may be assigned to the formation of new organic carbonyls from $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ solid state reaction. Two IR signals are observed in the C=C spectral region at 2107.4 and 2121 cm^{-1} and can be attributed to propynal ($\text{HC}\equiv\text{C-CHO}$) and propadienone (CH_2CCO), respectively, the two most thermodynamically stable isomers of cyclopropanone, and which can be formed during ring opening by competitive H- addition and H- abstraction processes. In the CH_3 bending region the detection of an IR signal at 1393.4 cm^{-1} would indicate the transformation of C=C bond of cyclopropanone into single bond with or without a ring opening. Table 2 summarizes the new infrared signals observed after $c\text{-C}_3\text{H}_2\text{O}$ ice hydrogenation and their tentative assignments. We will discuss these assignments later.

Table 2. Spectral positions (cm^{-1}) of the main reaction products resulting from H-bombardments of $c\text{-C}_3\text{H}_2\text{O}$ ice.

Present work	Literature ^{a,b}	Reaction products
1393.7	1391.3	$\text{CH}_3\text{-CH}_2\text{-CHO}$
1694.7	1659.6	CHC-CHO
1712.1	1704.2	$\text{CH}_2\text{-CH-CHO}$
1730.5	1729.6	$\text{CH}_3\text{-CH}_2\text{-CHO}$
2107.4	2096.8	CHC-CHO
2121.0	2125.0	CH_2CCO
2885.3	2883.3	$\text{CH}_3\text{-CH}_2\text{-CHO}$
2945.3	2942.2	$\text{CH}_3\text{-CH}_2\text{-CHO}$
2975.4	2975.4	$\text{CH}_3\text{-CH}_2\text{-CHO}$
3328.0	3330.0	Cyclopropanol ^c or propanol

^a (Jonusas et al 2017, Hudson and Gerakines 2019, Yarnall et al. 2020), ^b (Zasimov et al. 2021), ^c (measured in our laboratory).

The negative IR signals in the difference spectrum of figure 1c show that only 6% of $c\text{-C}_3\text{H}_2\text{O}$ is consumed during the hydrogenation process. However, the H-bombardments are efficient only on the first layers of $c\text{-C}_3\text{H}_2\text{O}$ ice which may limit the yield of the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction. In order to increase the yield of such a reaction, we investigated the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ bulk reaction. H-atoms and $c\text{-C}_3\text{H}_2\text{O}$ molecules are then co-injected at 10 K during 30 min and the resulting IR spectrum is shown in figure 2b. As a reference spectrum of figure 2a shows the IR spectrum corresponding to the co-injection under the same experimental conditions of $c\text{-C}_3\text{H}_2\text{O}$ and H_2 molecules. Without any surprises, the resulting reference spectrum of figure 2a is similar to the IR spectrum of $c\text{-C}_3\text{H}_2\text{O}$ ice formed at 10 K (figure 1a). Comparison of figures 2.a and 2.b shows that the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ co-injection experiment leads

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to the same reaction products as those obtained for the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ surface reaction performed through H bombardment of the $c\text{-C}_3\text{H}_2\text{O}$ ice, but with an efficiency 7 times higher.

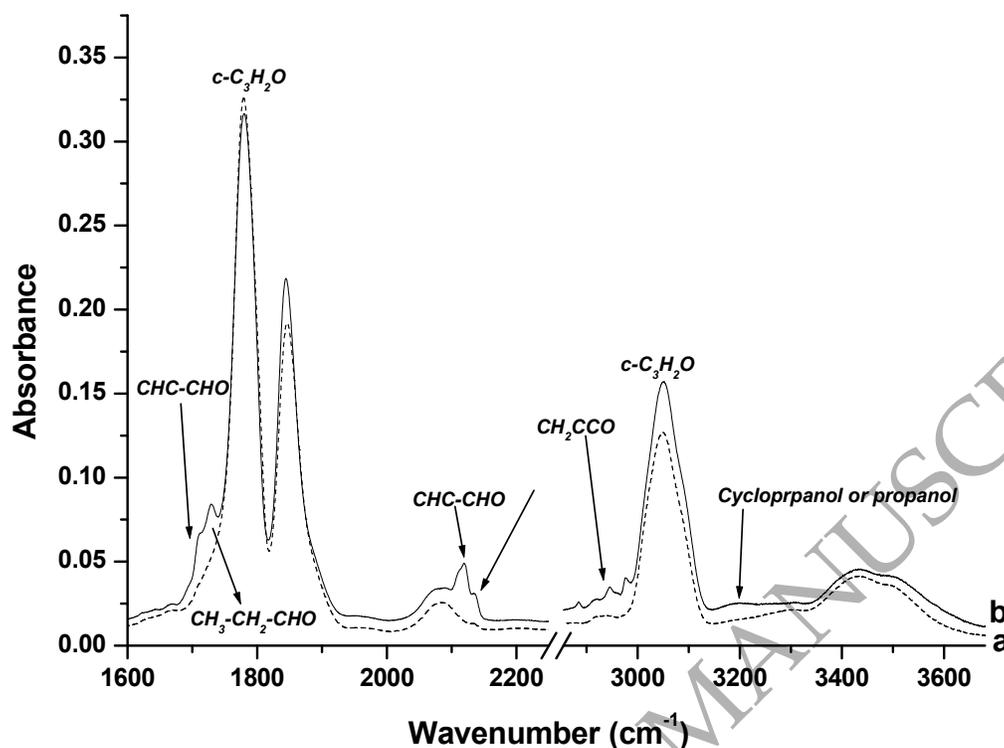


Figure 2. $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ bulk reaction at 10 K. Co-injection of (a) $c\text{-C}_3\text{H}_2\text{O}$ and H_2 . (b) $c\text{-C}_3\text{H}_2\text{O}$ and H/H_2 .

In order to identify the products of the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction in the solid state, three reference spectra of propanal (figure 3b), propynal (figure 3c), and propenal (figure 3d) were recorded and compared to the difference spectrum of $c\text{-C}_3\text{H}_2\text{O}$ ice after and before H bombardment (figure 3a). We notice that the new IR signals appearing at 1393.4, 1730.5, 2885.3, 2975.4 and 2945.3 cm^{-1} are in good agreement with the IR signatures of solid propanal ($\text{CH}_3\text{CH}_2\text{CHO}$). Similarly, the IR signatures of solid propynal (HCC-CHO) of figure 3c are in good agreement with the new IR signals detected after H bombardment of $c\text{-C}_3\text{H}_2\text{O}$ ice around 1700 and 2100 cm^{-1} and corresponding to CO and $\text{C}\equiv\text{C}$ stretching spectral regions, respectively. In addition to the formation of propanal ($\text{CH}_3\text{CH}_2\text{CHO}$) and propynal (HCCCHO) through $c\text{-C}_3\text{H}_2\text{O} + \text{H}$, propenal (CH_2CHCHO) may also be formed under our experimental conditions as the new signal at 1712.1 cm^{-1} in figure 3a is comparable to the main ν_{CO} signal of solid propenal. Finally, as mentioned above, $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ co-injection

experiment leads to the same reaction products as those obtained for the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ surface reaction performed through H bombardment of the $c\text{-C}_3\text{H}_2\text{O}$ ice, but with higher efficiency. We note that for the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ co-injection experiment, the signal detected around 2100 cm^{-1} has clearly two components (Figure 2b) that were less well resolved in figure 1c. The two IR signals are located at 2017.4 and 2121.0 cm^{-1} and can be attributed to propynal (HCCCHO) and propadienone (H_2CCCO), the two most stable isomers of cyclopropanone, respectively. This is in agreement with the attribution of Zasimov et al. (2021) who detected the characteristic IR signal of propadienone (H_2CCCO) around 2125 cm^{-1} .

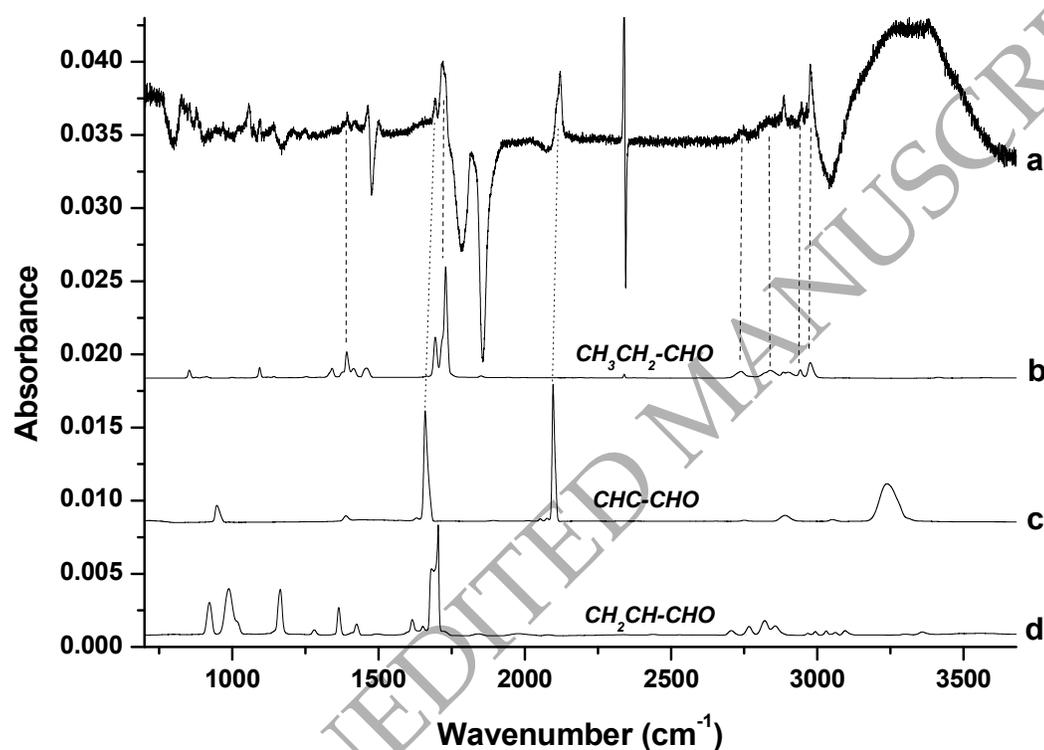


Figure 3: (a) Difference spectrum after and before H-bombardment of $c\text{-C}_3\text{H}_2\text{O}$ ice. (b) IR spectrum of pure propanal ($\text{CH}_3\text{CH}_2\text{CHO}$) ice. (c) IR spectrum of pure propynal (HCCCHO) ice. (d) IR spectrum pure propenal (CH_2CHCHO). All the spectra were recorded at 10 K.

The wide absorption band detected at 3228 cm^{-1} and corresponding to OH stretching mode shows that $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction is characteristic of the formation of an alcohol species. We suggest that cyclopropanol or propanol can be formed from the successive hydrogenation reaction of $c\text{-C}_3\text{H}_2\text{O}$ ice. Figure 4a shows the difference spectrum obtained after and before H bombardment of $c\text{-C}_3\text{H}_2\text{O}$ ice, which is compared to the IR spectra of cyclopropanol ($c\text{-C}_3\text{H}_5\text{O}$)

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C_3H_6O) and propanol ($CH_3CH_2CH_2OH$) ices formed at 10K (figure 4b and 4c). We note that the absorption band at 3228 cm^{-1} can be attributed to the OH stretching mode of $c\text{-}C_3H_5OH$ or $CH_3CH_2CH_2OH$. In the other spectral regions the characteristic IR signals of these two alcohol species are overlapped with the reactant signals between 1500 and 600 cm^{-1} and the CH-stretch signals due to propanal, between 2700 and 3000 cm^{-1} . It is important to note that Table 2 gathers tentative assignments of the species formed from the $c\text{-}C_3H_2O + H$ reaction in the solid phase. The intermolecular interactions between $c\text{-}C_3H_2O$ and the reaction products, the overlapping of absorption bands observed after hydrogenation processes could call into question all these assignments. This shows the limitations of FTIR analysis to identify complex molecules trapped in organic ices. We then used the programmed thermal desorption coupled with mass spectrometry method to exclude or confirm the formation of all these reaction products.

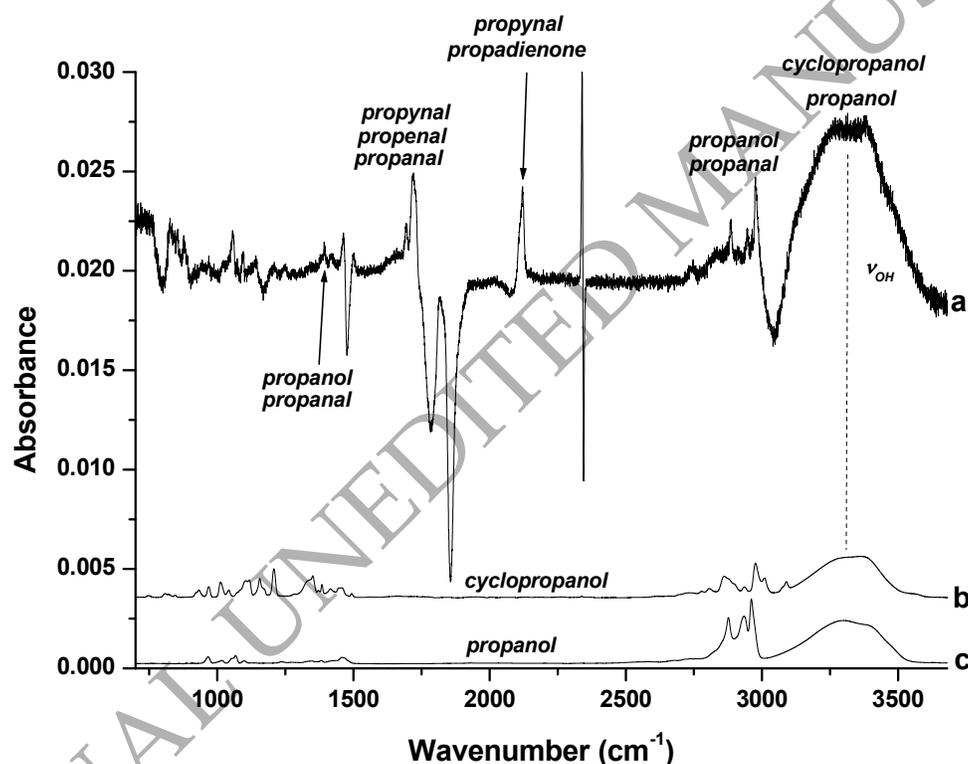


Figure 4: (a) Difference spectrum after and before H-bombardment of $c\text{-}C_3H_2O$ ice. (b) IR spectrum of pure cyclopropanol ($c\text{-}C_3H_5OH$) ice. (c) IR spectrum of pure propanol ($CH_3CH_2CH_2OH$) ice. All the spectra were recorded at 10 K.

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3.2. Mass spectrometry

First, we studied the mass spectra of cyclopropanone ($c\text{-C}_3\text{H}_2\text{O}$) and cyclopropanol ($c\text{-C}_3\text{H}_5\text{OH}$) to know the distribution of their mass fragments. The parent fragment of $c\text{-C}_3\text{H}_2\text{O}$ is located at $m/z = 54$ with a relative intensity of 48%, while its predominant fragment is located at $m/z = 26$ with a relative intensity of 100%. For $c\text{-C}_3\text{H}_5\text{OH}$, the parent and predominant fragment are observed at $m/z = 58$ and $m/z = 29$ with relative intensities of 7% and 100%, respectively.

Figure 5 presents the TPD spectra during thermal heating of cyclopropanone ice considering the fragment at $m/z = 26$, 54 and 53. We note two desorption domains for cyclopropanone in the temperatures ranges 120-170 K and 170-220 K. Between these two ranges, the $c\text{-C}_3\text{H}_2\text{O}$ ice undergoes a transition from amorphous to crystalline phase at 170 K. These TPD spectra are in good agreement with previous experimental studies on interstellar ice analogs showing that sublimation of $c\text{-C}_3\text{H}_2\text{O}$ occurs between 150 and 230 K (Aplanalp et al. 2019, Kleimeir et al. 2021).

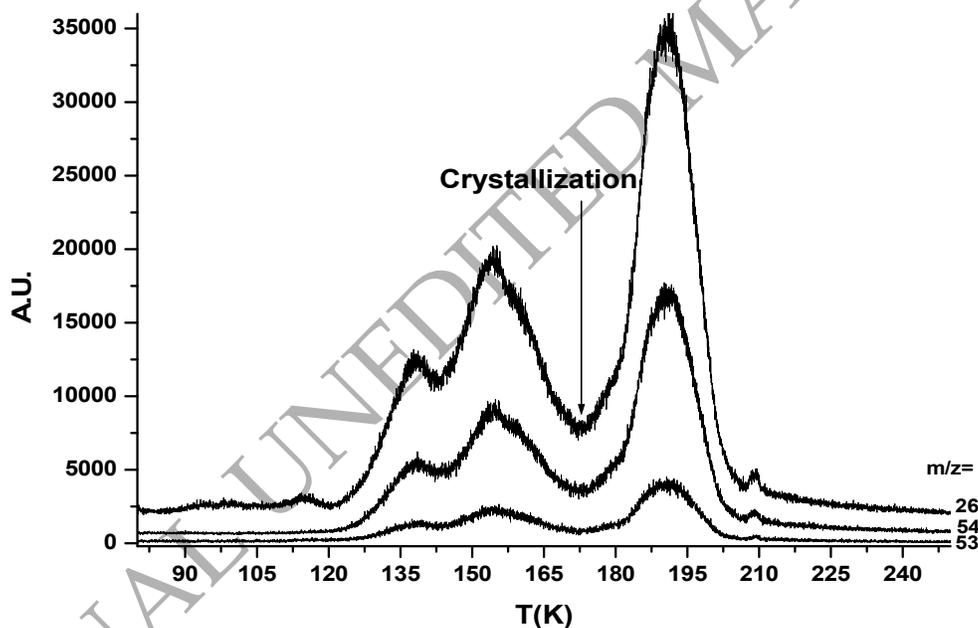


Figure 5. TPD spectra of cyclopropanone ($c\text{-C}_3\text{H}_2\text{O}$) ice formed at 10 K.

In addition to cyclopropanone as the main reactant, Table 3 summarizes the desorption temperatures and characteristic mass fragments of potential products of the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction, and which have already been discussed during our IR analysis study, such as propanal, propenal, propynal, cyclopropanone, propanol, and cyclopropanol.

Table 3. Characteristic m/z values of cyclopropanone and potential products of $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction, associated with their desorption temperatures. Relative intensities of the mass fragments are shown in parentheses.

Species	desorption Temperature	m/z	reference
Cyclopropanone	150-230 K	54 (48%) 53 (11%)	Present work
propynal	125-155 K	54 (60%) 53(100%)	Abplanalp & Kaiser. 2019
Propanal	125 K	58 (100%) 57 (30%)	Qasim et al. 2019
Propenal	123-173K	56 (100%) 55 (70%)	Abplanalp & Kaiser. 2019
cyclopropanone	90 – 133 K	56 (15%) 42 (15%)	Abplanalp & Kaiser. 2019
propanol	155 K	59 (4%) 60 (2%)	Qasim et al. 2019
cyclopropanol	171 K	58 (7%) 57 (32%)	Present work

In order to characterize all products formed by the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction in the solid state at 10 K, we analyzed the TPD of hydrogenated cyclopropanone ices, based on the mass data and desorption temperatures of table 3. Figure 6 shows the TPD signals of organics species that are released into the gas phase upon heating the solid sample and can be attributed to the desorption of many reaction products already characterized through our IR analysis.

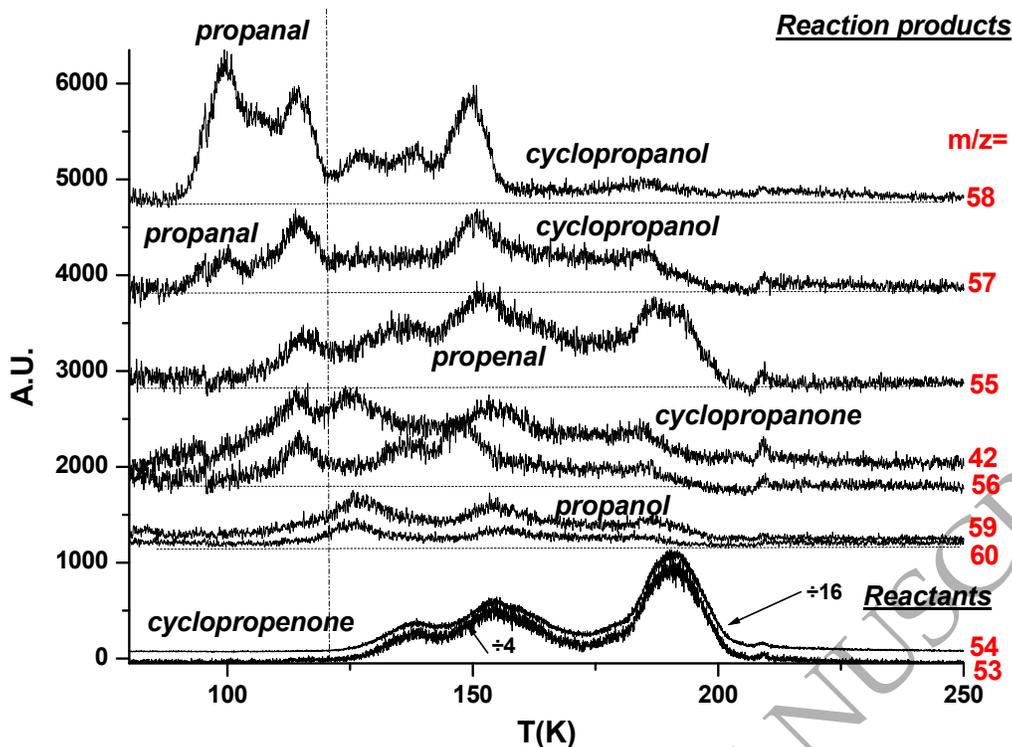


Figure 6. TPD spectra of hydrogenated cyclopropenone ($c\text{-C}_3\text{H}_2\text{O} + \text{H}$) ices formed at 10 K. The TPD signal at $m/z = 54$ and 53 of the reactant $c\text{-C}_3\text{H}_2\text{O}$ are divided by 16 and 4, respectively, to be comparable with TPD signal of the products.

From figure 6 the TPD profile of $m/z = 57, 58$ reveals three sublimations events at 90-120 K, 120-160 K and 160-200 K temperature ranges. These two mass fragments are characteristic of propanal and cyclopropanol which may desorb, based on the data on table 4 at 125 and 171 K, respectively. Therefore, in the temperature range 90-120 K, signals at $m/z = 57, 58$ with relative intensities $I_{58} > I_{57}$ confirm the formation of propanal, a species which has already be evoked during our IR analysis. Desorption of propanal continues between 120 and 160 K, when the cyclopropenone ice begins to sublimate. In the temperature range 160-200 K, the relative intensities of the fragments at $m/z = 58$ and 57 are reversed and the fact that $I_{57} > I_{58}$ suggests that cyclopropanol ($c\text{-C}_3\text{H}_5\text{OH}$) is also formed and desorbs between 160 and 200 K.

Based on the data in table 3, the TPD signals of the mass fragments at $m/z = 60$ and 59 , appearing between 120 and 200 K in figure 6 and with $I_{59} \sim 2 I_{60}$, are consistent with formation of propanol during the hydrogenation of cyclopropanone.

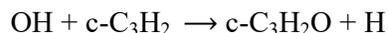
Abplanalp et al 2015 showed that propenal and cyclopropanone desorb in the 123 - 173 K and 90 - 133 K temperature ranges, respectively. Propenal is characterized by mass fragments at $m/z = 56$ (100%) and 55 (70%), while cyclopropanone is characterized by mass fragments at $m/z = 56$ (15%) and 42 (15%). Figure 6 shows that the TPD signals of the mass fragments at $m/z = 56$ and 42 have almost the same intensity in the 97 - 120 K and 160 - 200 K temperature ranges which may be attributed to release into the gas phase of cyclopropanone before and during desorption of hydrogenated cyclopropanone ice, respectively. Similarly, mass fragments at $m/z = 56$ and 55 appearing in the 110 - 200 K temperature range could be assigned to the formation of propenal. However the relative intensities of these two TPD signals are not in agreement with the data of table 3, where the signal of the fragment at $m/z = 56$ (100%) should be slightly higher than that at $m/z = 55$ (70%). This discrepancy could be due to the fact that $c\text{-C}_3\text{H}_2\text{O}$ ice has in its mass fragments distribution a mass fragment at $m/z = 55$ (4.5%). Finally, for propynal (HCCCHO), one the main product we detected in our IR spectra during the hydrogenation of cyclopropanone, its desorption is expected to take place between 122 and 155 K but its characteristic signals from its mass fragments at $m/z = 53$ (100%) and 54 (60%) are overlapped by those of cyclopropanone ($c\text{-C}_3\text{H}_2\text{O}$) ice.

4. Discussion

By coupling FTIR spectroscopy and TPD mass spectrometry, we have investigated the $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ solid state reaction through two different experimental methods. We show that cyclopropanone reacts with hydrogen atoms under interstellar medium conditions leading to propanal ($\text{CH}_3\text{CH}_2\text{CHO}$), $c\text{-C}_3\text{H}_4\text{O}$ (cyclopropanone), propenal (CH_2CHCHO), propynal (HCCCHO), propadienone (CH_2CCO), cyclopropanol ($c\text{-C}_3\text{H}_6\text{O}$) and propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$).

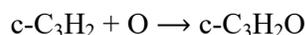
The formation pathways of $c\text{-C}_3\text{H}_2\text{O}$, using propenylidene as a precursor, have been the subject of much research. Propenylidene (C_3H_2) of interest for astrochemistry, is observed in two isomeric forms: cyclic and linear. In 1985, Matthews and Irvine showed that cyclopropenylidene ($c\text{-C}_3\text{H}_2$) was the only ubiquitous species in the galaxy. Later, Cernicharo et al 1991 showed that the linear form of propenylidene ($l\text{-C}_3\text{H}_2$) can also be observed in TMC-1. Cyclopropenylidene plays an important role in the formation of cyclopropanone ($c\text{-$

C₃H₂O). Petries et al. (1995) proposed that the cyclopropenone could be formed from the OH + c-C₃H₂ reaction.

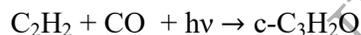


Using DFT calculations, Loison et al. (2016) found that this reaction proceeds without energy barriers. However, no experimental studies have been conducted to confirm such a mechanism.

Diekens et al. (2001) suggested that the reaction between c-C₃H₂ and atomic oxygen or molecular oxygen leads also to cyclopropenone, based on the abundance of all three species in the Sagittarius B2(N) spatial region.



In addition to the two mechanisms mentioned above, Ahmadvand et al. (2014) proposed a third possible pathway for cyclopropenone formation in the interstellar medium, involving carbon monoxide and acetylene. They showed that the CO + C₂H₂ reaction has high barrier energy and is unfavorable at low temperatures. On the other hand, the c-C₃H₂ + O₂ reaction has no barrier and represents a likely mechanism for the interstellar formation of c-C₃H₂O. Despite the high barrier for the CO + C₂H₂ reaction, Zhou et al 2008 conducted laboratory experiments on the chemistry of non-equilibrium grain ice under interstellar conditions, and showed the formation of c-C₃H₂O at the grain surface via an addition of CO to C₂H₂. They showed that involving excited states, propynal can be formed from the CO-C₂H₂ complex via HCO---CCH radical interactions.

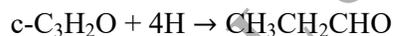
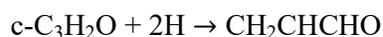
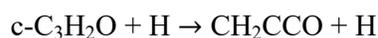
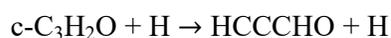


Recently, Kleimeir et al. (2021) confirmed the formation of c-C₃H₂O and HCCCHO by exposure of CO + C₂H₂ ices to ionizing radiation with 5 keV electrons at 5 K. In addition, Zasimov et al. (2021) reported the results of X-ray irradiation of isolated 1:1 C₂H₂...CO complexes in solid gas matrices (Ar, Kr, and Xe) at 5 K. They revealed the formation of the three C₃H₂O isomers: cyclopropenone, propynal and propadienone.

Using DFT calculations and NAUTILUS chemical model, Loison et al. (2016) studied the formation and loss of the three $\text{H}_2\text{C}_3\text{O}$ isomers. They showed that the chemistry of these species mainly involves reactions in the gas phase. Propynal, cyclopropenone and propadienone are formed through the reactions $\text{O} + \text{C}_3\text{H}_3$, $\text{OH} + \text{c-C}_3\text{H}_2$ and $\text{OH} + \text{l-C}_3\text{H}_2$, respectively, while the destruction reactions of cyclopropenone are as follows:



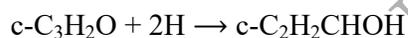
Although gas-phase experiments are needed to confirm all these reaction pathways, organic species such as cyclopropenone may also be trapped in icy grains and, unlike heavy radicals, the mobility of H atoms on grain surfaces would induce the transformation and loss of $\text{c-C}_3\text{H}_2\text{O}$. In the present study, we show that the reaction mechanisms involved in $\text{c-C}_3\text{H}_2\text{O} + \text{H}$ solid phase reaction depend on the hydrogen number and are completely different from those involving OH , H_3^+ , H_3O^+ or HCO^+ in the gas phase. $\text{c-C}_3\text{H}_2\text{O} + \text{H}$ surface reaction leads to propynal (HCCCHO), propadienone (CH_2CCO), the two stable isomers of $\text{c-C}_3\text{H}_2\text{O}$, propenal (CH_2CHCHO), cyclopropanone ($\text{c-C}_3\text{H}_4\text{O}$) and propanal ($\text{CH}_3\text{CH}_2\text{CHO}$)



For the formation of all these species during the hydrogenation of $\text{c-C}_3\text{H}_2\text{O}$, the functional group CHO of $\text{c-C}_3\text{H}_2\text{O}$ is not reduced and except for cyclopropanone ($\text{c-C}_3\text{H}_4\text{O}$), the opening of $\text{c-C}_3\text{H}_2\text{O}$ ring takes place during successive H-addition and H-abstraction processes.

The formation of propynal (HCCCHO) and propadienone (CH_2CCO) involves only one H atom. The addition of H can take place on the carbon of the CHO group, which induces an

opening of the *c*-C₃H₂O ring associated with an abstraction of an H atom from the C=C group leading to the formation of HCCCHO. Similarly, when the attack of the H atom takes place on one of the two carbons of the HC=CH group of *c*-C₃H₂O, it induces an opening of the *c*-C₃H₂O ring associated with an abstraction of an H-atom from the central carbon of the chain. Such a mechanism leads to the formation of propadienone (CH₂CCO). The simultaneous H-addition reactions on the two carbons of the CHO and C=C groups would also induce an opening of the *c*-C₃H₂O ring leading to the formation of propenal (CH₂CHCHO). In the same the simultaneous H-addition on the two carbons C=C group would only reduce *c*-C₃H₂O to cyclopropanone (*c*-C₃H₄O). Finally, propenal that was detected in our mass and IR spectra can be formed by secondary hydrogenation of propynal (HCCCHO) and propenal (CH₂CHCHO). We have already shown in previous studies (Jonusas et al. 2017) that CH₂CHCHO + 2H and HCCCHO + 4H efficiently lead to propanal (CH₃CH₂CHO) and that propanal remains stable under H-attacks. A theoretical study by Zaverkin et al. (2018) for the CH₃CH₂CHO + H reaction showed that a cycle of H-abstraction and H-addition reactions leads to a zero transformation balance of propanal and that this reaction cannot be an efficient source of propanal conversion to propanol. This brings us back to the explanation of the formation of the two alcohols that we have detected under our experimental conditions. We have demonstrated that both cyclopropanol (*c*-C₃H₆O) and propanol (CH₃CH₂CH₂OH) can be formed after H bombardement of *c*-C₃H₂O ice at 10K. As mentioned above the formation of propanol during the *c*-C₃H₂O + H reaction does not mean that propanol is produced as secondary product via the CH₃CH₂CHO + H reaction but other reaction pathways should be proposed. In this context, our hypothesis that two possible pathways for *c*-C₃H₂O + H can occur:



As shown in figure 7, once *c*-C₂H₂CHOH (cyclopropenol) and *c*-C₃H₄O (cyclopropanone) are formed by *c*-C₃H₂O + 2H reaction, they may be converted into cyclopropanol through the reduction of C=C and CO group, respectively. The resulting cyclopropanol can be stabilized in the ice or react through ring opening to form a bi-radical species (figure 7). Barluenga et.al (1983) showed that cyclopropanol is highly reactive and that low energy can induce its ring opening and the formation of propanal. Under our experimental conditions, the excess energy released during the *c*-C₂H₂CHOH + 2H and *c*-C₃H₄O + 2H reactions would induce the

opening of cyclopropanol to form a bi-radical species as shown in figure 7. In the absence of H atoms, the bi-radical converts to propanal while in the presence of 2H atoms, it leads to the formation of propanol.

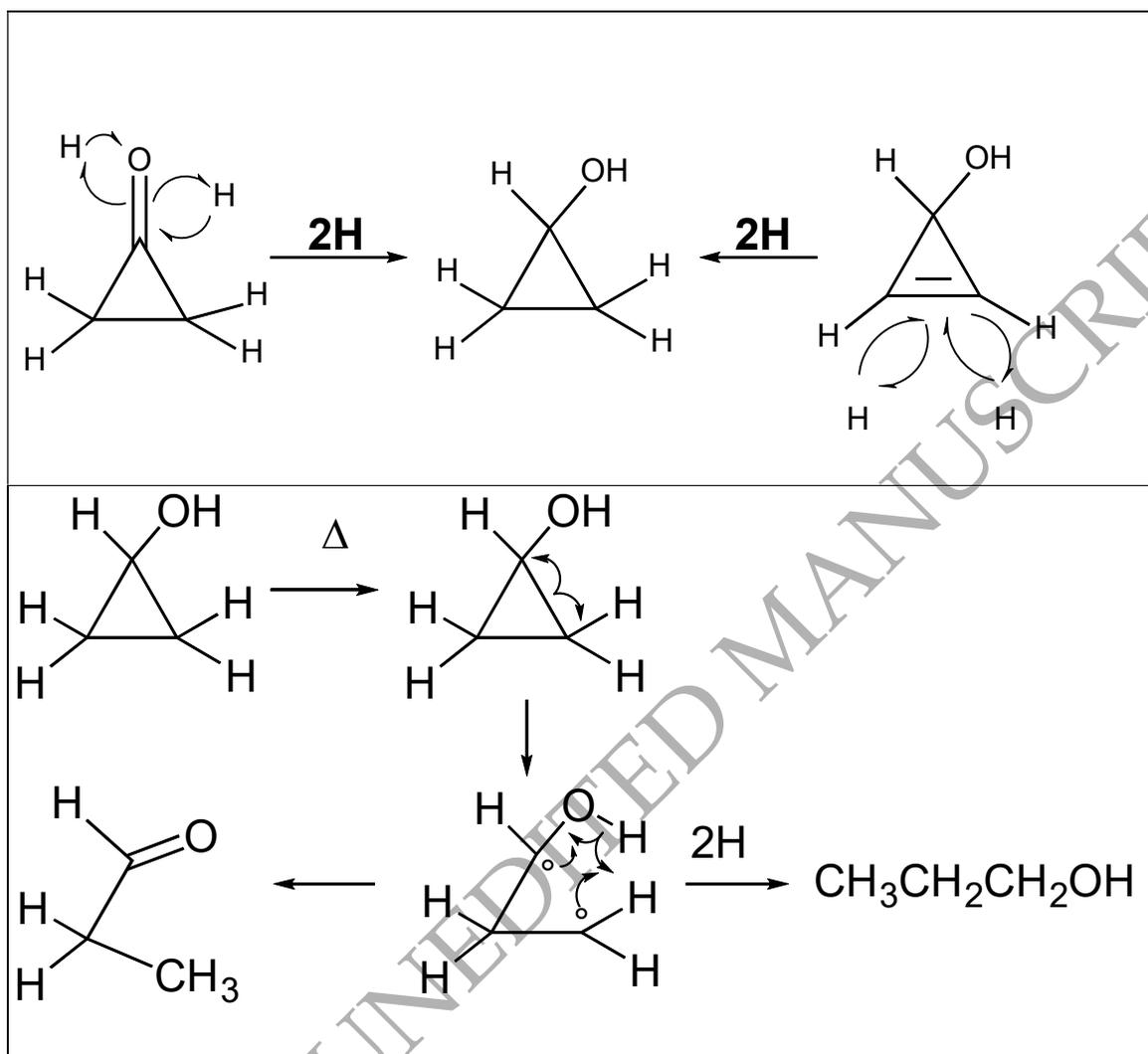


Figure 7: Conversion of $c\text{-C}_2\text{H}_2\text{CHOH}$ (cyclopropanol) and $c\text{-C}_3\text{H}_4\text{O}$ (cyclopropanone) into cyclopropanol and mechanism of formation of propanal and propanol upon ring opening of cyclopropanol ($c\text{-C}_2\text{H}_2\text{CHOH}$)

Cyclopropanone, propynal, propenal, propanal, propanol have already been detected in the interstitial medium, in contrast to propadienone, cyclopropanone, cyclopropanol and cyclopropanol. However, it is interesting to note that from the solid state reaction $\text{H} + c\text{-C}_3\text{H}_2\text{O}$, all these species can be formed involving hydrogen addition and/or abstraction processes and different numbers of hydrogen atoms. Figure 8 shows the evolution

mechanisms of propenone interacting with H-atoms under the conditions of the interstellar medium according to the products detected in this study.

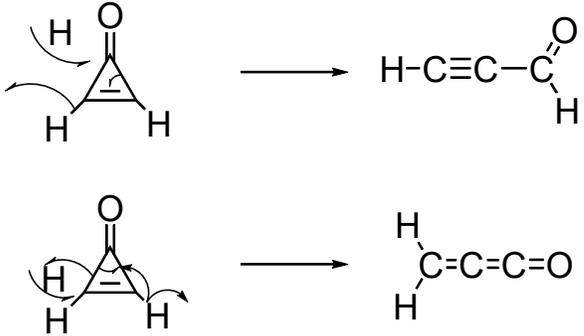
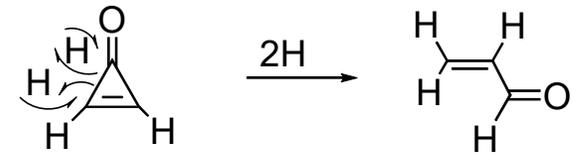
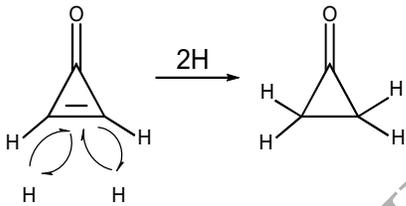
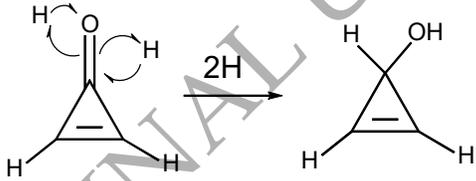
H + c-C ₃ H ₂ O	mechanisms	number of H atoms involved
	H-addition And H-abstraction	0
	H-addition	2
	H-addition	2
	H-addition	2

Figure 8: Evolution mechanisms of propenone interacting with H-atoms under the conditions of the interstellar

5. Conclusion

In the present work, we performed under interstellar medium conditions $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction in the solid phase, monitored by FTIR spectroscopy and mass spectrometry. Our main results are as follows:

1. $c\text{-C}_3\text{H}_2\text{O} + \text{H}$ reaction could be an important source of alcohols such as cyclopropanol and propanol. Cyclopropanol ($c\text{-C}_3\text{H}_6\text{O}$) can be formed from a successive hydrogenation reaction of $c\text{-C}_3\text{H}_2\text{O}$ ice. Then, upon ring opening of $c\text{-C}_3\text{H}_6\text{O}$, propanal ($\text{CH}_3\text{CH}_2\text{CHO}$) is favored in the absence of hydrogen atoms, while propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) can be formed in the presence of two hydrogen atoms.
2. The formation of propynal (HCCCHO) and propadienone (CH_2CCO) involves only one H atom. The addition of H can take place on the carbon of the CHO group or on that of C=C group, which induces an opening of the $c\text{-C}_3\text{H}_2\text{O}$ ring associated with an abstraction of an H-atom leading to HCCCHO and CH_2CCO , two isomers of $c\text{-C}_3\text{H}_2\text{O}$.
3. The simultaneous H-addition reactions on the two carbons of the CHO and C=C groups would also induce an opening of the $c\text{-C}_3\text{H}_2\text{O}$ ring leading to the formation of propenal (CH_2CHCHO).
4. The simultaneous H-addition on the two carbons C=C group would only reduce $c\text{-C}_3\text{H}_2\text{O}$ to cyclopropanone ($c\text{-C}_3\text{H}_4\text{O}$).

Data availability

The data of this paper will be shared on reasonable request to the corresponding author.

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