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Reduction of unsaturated compounds under interstellar conditions: chemoselective reduction of C≡C and C=C bonds over C=O functional group

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ABSTRACT

The knowledge of the H-addition reactions on unsaturated organic molecules bearing a triple or a double carbon–carbon bond such as propargyl or allyl alcohols and a CO functional group such as propynal, propenal or propanal may play an important role in the understanding of the chemical complexity of the interstellar medium. Why different aldehydes like methanal, ethanal, propynal and propanal are present in dense molecular clouds while the only alcohol detected in those cold regions is methanol? In addition, ethanol has only been detected in hot molecular cores. Are those saturated and unsaturated aldehyde and alcohol species chemically linked in molecular clouds through solid phase H-addition surface reactions or are they formed through different chemical routes? To answer such questions, we have investigated a hydrogenation study of saturated and unsaturated aldehydes and alcohols at 10 K. We prove through this experimental study that while pure unsaturated alcohol ices bombarded by H atoms lead to the formation of the corresponding fully or partially saturated alcohols, surface H-addition reactions on unsaturated aldehyde ices exclusively lead to the formation of fully saturated aldehyde. Such results show that in addition to a chemoselective reduction of C≡C and C=C bonds over the C=O group, there is no link between aldehydes and their corresponding alcohols in reactions involving H atoms in dense molecular clouds. Consequently, this could be one of the reasons why some aldehydes such as propanal are abundant in dense molecular clouds in contrast to the non-detection of alcohol species larger than methanol.

Key words: astrochemistry – methods: laboratory – solid state – techniques: spectroscopic – ISM: molecules.

1 INTRODUCTION

More than 160 molecules have been detected in dense molecular clouds of the interstellar medium (ISM). Reactions involving hydrogen atoms reacting with different astrochemical relevant species on the icy interstellar grain at temperatures around 10 K have been often proposed to have a crucial role in the production of some of those detected molecules (Hiraoka et al. 2002; Hidaka et al. 2004; Watanabe et al. 2004; Dulieu et al. 2010; Krim et al. 2010). However, at very low temperature, hydrogen atoms could not react with compounds bearing an unsaturated functional group to lead to the corresponding more saturated derivatives when the

activation barriers of the reactions cannot be passed over. Consequently, an important part of the understanding of the chemistry of the ISM could be given by a better knowledge of what is reduced and what is not reduced in lab simulations concerning unsaturated compounds already observed in the ISM. Some detected molecules could thus find a possible way for their formation while the lack of reaction with hydrogen for some other species could demonstrate that another chemical pathway has to be found to explain their presence in this medium.

Many studies have been devoted to the reaction of hydrogen atoms with carbon monoxide or formaldehyde with the aim to form methanol or both of its radical precursors (CH_3O and CH_2OH) (Hiraoka et al. 1994; Watanabe & Kouchi 2002, Fuchs et al. 2009; Pirim & Krim 2011). Unambiguously, hydrogen atoms react with formaldehyde, the simplest aldehyde. Is this reduction reaction of

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a carbonyl group still occurring with substituted derivatives? For derivatives with a carbon–carbon (CC) double or triple bond, is this unsaturated group more or less easily reduced than the carbonyl group? Both questions pushed us to study the hydrogenation of unsaturated aldehydes to know if the H-addition reactions could propose an origin to the observation of saturated aldehyde, the propanal (Turner 1991; Hollis et al. 2004; Hollis et al. 2006) or saturated alcohols (Ball et al. 1970; Zuckerman et al. 1975; Hollis et al. 2002) or, at the opposite, could demonstrate that they cannot be formed through those reaction pathways. From astronomy observations, propynal has been observed in the ISM (Irvine et al. 1988) while propenal has been tentatively detected (Hollis et al. 2004). The synthesis of propynal in the ISM would start from C_3O (Irvine et al. 1988) and the chemoselective hydrogenation of the latter, proposed by Hollis et al. (2004), would form propenyl and propanal. In fact, among the partially saturated compounds, propanal has been detected (Hollis et al. 2004) while neither allyl nor propargyl alcohols have been found. On the other hand, although methanol and ethanol are abundant in the ISM (Bisschop et al. 2007), propanol ($CH_3CH_2CH_2OH$) is still missing in the list of detected molecules. In this context, reactions of hydrogen radicals with the unsaturated derivatives under ISM conditions are thus the key for a better understanding of their chemistry. As mentioned earlier, the H-addition reactions in solid phase have been investigated by different groups on simple astrochemical relevant species to quantify the formation of saturated species such as CH_3OH and CH_3NH_2 from hydrogenation of simple molecules like CO, H_2CO and HCN (Watanabe et al. 2003; Theule et al. 2011). However, in some of those studies the reaction products are probed and quantified only in gas phase by mass spectroscopy from the temperature programmed desorption (TPD). This gas phase detection method has been adopted as the IR signals of the reaction products formed and trapped in solid phase which might either be under the limit of detection or overlap with the IR signals of the reactants. Nevertheless, the characterization of reaction products from the TPD makes it impossible to confirm whether the products detected by mass spectroscopy are actually formed in solid phase through a hydrogenation process or during the TPD of the solid samples. Consequently, only an accurate IR analysis of the reactant ices before and after H-bombardment remains the single possibility to show if an H-addition reaction would take place in solid phase at very low temperature mimicking the surface reaction of the icy interstellar grains.

Here, we report the solid phase H-addition reactions on propynal (HC≡CCHO), propenal (H_2C=CH–CHO, acrolein), propanal (CH_3CH_2CHO) and also on unsaturated alcohols such as propargyl (HC≡CCH$_2$OH) and allyl alcohol (H_2C=CHCH$_2$OH). Fig. 1 shows the possible reaction pathways for successive H-addition reactions on unsaturated compounds.

2 EXPERIMENTAL SECTION

Hydrogen gas is purchased from Messer, with a purity of 99.9995 per cent. Propargyl alcohol, allyl alcohol, propanol, propenal and propanal were purchased from the Aldrich company. Propynal was synthesized by oxidation of propargyl alcohol following the procedure of Sauer (1963). Our solid samples have been prepared under ultrahigh vacuum in a chamber maintained at 10^{-9} mbar, where pure alcohol and aldehyde ices have been formed by condensing the saturated or unsaturated corresponding alcohol or aldehyde vapour on a highly polished, Rh-plated copper mirror maintained at 10 K using a closed-cycle helium cryogenerator (Sumitomo cryogenics F-70). At room temperature, the vapour pressures of aldehydes are
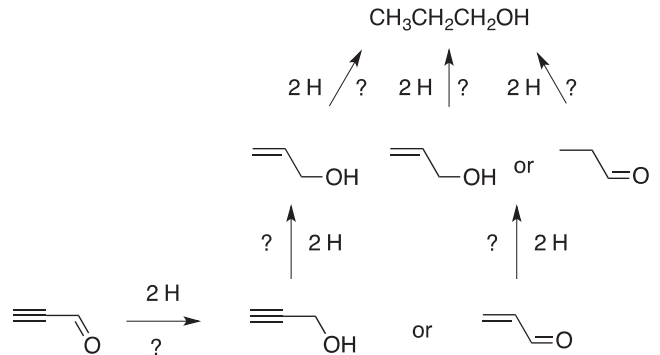

Figure 1. Possible reaction pathways for the hydrogenation processes of unsaturated compounds: HC≡CCH$_2$OH, H_2C=CHCH$_2$OH, HC≡CCHO, H_2C=CH–CHO, CH_3CH_2CHO.

Table 1. Amounts of deposited species (μmol).

Propargyl alcohol (HC≡CCH$_2$OH)	0.30 ± 0.08
Allyl alcohol (H_2C=CHCH$_2$OH)	1.0 ± 0.2
Propanol ($H_3CCH_2CH_2OH$)	0.20 ± 0.05
Propynal (HC≡CCHO)	3.1 ± 0.5
Propenal (H_2C=CH–CHO)	10 ± 1
Propanal (CH_3CH_2CHO)	4.0 ± 0.6

approximately (Stull, 1947) a few hundred mbars (propanal, 422 mbar; propenal, 290 mbar) while those of alcohols are one order of magnitude lower (propanol, 20 mbar; allyl alcohol, 28 mbar). The glass flasks containing the pure organic compounds are kept in cooling baths formed by a mixture of liquid nitrogen and methanol, to maintain the temperature of the aldehydes or the alcohols as low as –50°C, in order to control the amount of deposited material. Afterwards, the frozen compounds are partially evaporated by increasing the temperature of the cooling bath between −50 and 5°C to introduce in an 80 cm^3 ramp, less than 10 mbar of vapour gas that is subsequently injected into the high vacuum chamber to form the organic ices by condensation on to the mirror sampler. The pressure in the ramp is measured with a digital Pirani gauge. Knowing the volume of the injection ramp, the amount of deposited material is evaluated from the decrease of the pressure in the ramp during the deposition of the sample. Pure organic ices have been formed at 10 K and characterized by infrared spectroscopy. The amounts of the organic species deposited have been chosen to obtain thick ices (few tens of micrometres) for a better vibrational mode characterization and also in order to increase the yield of the H-addition reaction and thus to have the upper limit of the reaction products (Watanabe et al. 2003). Table 1 lists the amounts of deposited organic species.

Following the solid sample depositions, the ices have been bombarded during 45 min by atomic hydrogen generated with a flux of about 10^{15} atoms cm^{-2} s^{-1} from a microwave discharge (SPECS, PCS-ECR) into H_2 gas with H_2-dissociation yields about 15 per cent (Pirim & Krim 2011). The flux of H atoms has been estimated from the amount of molecular hydrogen injected during the H-bombardment while the H_2-dissociation yield has been measured using a Quadrupole Mass Spectrometer (QMS – Hidden Analytical). The samples are analysed before and after H-bombardments by recording infrared spectra between 5000 and 500 cm^{-1}, with a resolution of 0.5 cm^{-1}, using a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer, in the transmission–reflection mode with an incidence angle of 8°.
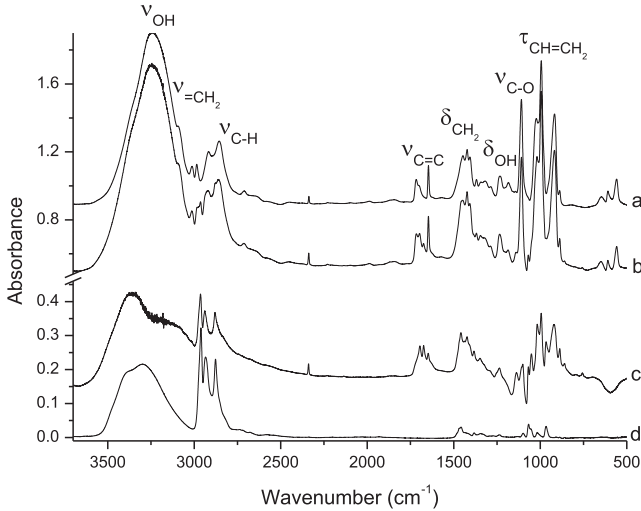
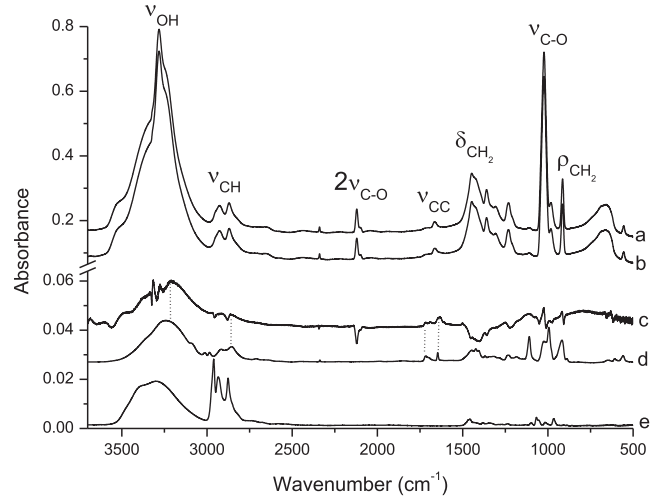**Figure 2.** (a) Deposition of 1.0 μmol of allyl alcohol ($H_2C=CHCH_2OH$) on a mirror maintained at 10 K. (b) Hydrogenation of solid allyl alcohol ($H_2C=CHCH_2OH$) at 10 K. (c) Difference spectrum: spectrum (b) − spectrum (a). (d) Deposition of 0.2 μmol of pure propanol ($H_3C-CH_2CH_2OH$) on a mirror maintained at 10 K.

3 RESULTS

3.1 H-addition reaction on unsaturated alcohols involving double or triple CC bonds: the case of allyl ($H_2C=CHCH_2OH$) and propargyl ($HC\equiv CCH_2OH$) alcohols

3.1.1 Hydrogenation of allyl alcohol ($H_2C=CHCH_2OH$)

Fig. 2(a) shows the infrared spectrum of pure allyl alcohol ($H_2C=CHCH_2OH$) ice formed on a mirror maintained at 10 K, with OH and CH stretching modes located in 3600–2500 cm^{-1} spectral region, C=C and C–O vibrations at 1644 and 1110 cm^{-1}, respectively and CH$_2$, OH and CH=CH$_2$ deformations at 1430, 1240 and 994 cm^{-1}, respectively (Dostert et al. 2016). After IR-analysis, the allyl alcohol ice has been bombarded during 45 min by H atoms. The result of the H-bombardment is shown in Fig. 2(b) where new signals appear clearly at 2965, 2932 and 2877 cm^{-1}, illustrating a clear transformation of allyl alcohol ice under H exposition. To better characterize such a transformation, Fig. 2(c) shows the difference spectrum before and after H-bombardment. The difference spectrum can be compared to a reference spectrum of propanol ice (Fig. 2d) obtained by condensing 0.2 μmol of pure propanol. Comparison between Figs 2(c) and (d) shows that the hydrogenation of allyl alcohol ice leads mainly to the reduction of the C=C double bond to form the saturated propanol ($H_3C-CH_2CH_2OH$). If we suppose that for a given species deposited at 10 K, the sticking probability on the 1 cm^2 cold mirror of our sampler is 1, we can then deduce the amount of propanol formed in solid phase through $H_2C=CHCH_2OH + 2H \rightarrow H_3C-CH_2CH_2OH$ reaction. In fact, the infrared intensity of the signal of the 0.20 ± 0.05 μmol deposited propanol is almost 1.5 times higher than that of the propanol ice formed by hydrogenation of $H_2C=CHCH_2OH$. Thus, we estimate that less than 0.13 μmol of $H_3C-CH_2CH_2OH$ could be formed by bombarding a thick ice of allyl alcohol during 45 min with H atoms. Nevertheless, the decrease of $H_2C=CHCH_2OH$ signal could not be quantified due to the overlapping absorption bands of the reactant and product. However, in some spectral regions as those at 1200–1000 cm^{-1} and 800–500 cm^{-1} (Fig. 2c), the signal of the bombarded allyl alcohol ice decreases by almost 15 per cent. From

Figure 3. (a) Deposition of 0.30 μmol of propargyl alcohol ($HC\equiv CCH_2OH$) on a mirror maintained at 10 K. (b) Hydrogenation of solid propargyl alcohol at 10 K. (c) Difference spectrum: spectrum (b) − spectrum (a). (d) Deposition of pure allyl alcohol ($H_2C=CHCH_2OH$) on a mirror maintained at 10 K (signal divided by approximately 60 in comparison with that of Fig. 2a). (e) Deposition of 0.20 μmol of pure propanol ($H_3C-CH_2CH_2OH$) on a mirror maintained at 10 K (signal divided by approximately 10 in comparison with that in Fig. 2d).

these first results, we can conclude that even though propanol is not yet detected in the ISM, its abundance could be linked to that of unsaturated allyl alcohol ($H_2C=CHCH_2OH$) as follows:

$$H_2C = CHCH_2OH + 2H \rightarrow H_3C - CH_2CH_2OH.$$

3.1.2 Hydrogenation of propargyl alcohol ($HC\equiv CCH_2OH$)

Similar experiments have been carried out with the unsaturated propargyl alcohol ($HC\equiv CCH_2OH$) to highlight the triple CC bond reduction by H-addition in solid phase at 10 K. Figs 3(a) and (b) show the infrared spectra of the propargyl alcohol ice before and after H-bombardments, respectively, while Fig. 3(c) shows the resulting difference spectrum. To analyse the consequences of the H-bombardment on propargyl alcohol ice, two references spectra have been added, in Figs 3(d) and (e), corresponding to unsaturated allyl alcohol ($H_2C=CHCH_2OH$) and saturated propanol ($CH_3CH_2CH_2OH$) ices, respectively.

In order to see whether the H-reduction of the triple CC bond in propargyl alcohol ($HC\equiv CCH_2OH$) would lead to the formation of a double or a single CC bond, the difference spectrum (Fig. 3c) is compared to the two reference spectra (Figs 3d and e). We notice that the difference spectrum, derived from the hydrogenation process of solid propargyl alcohol, is more consistent with the IR signatures of solid allyl alcohol (3d) rather than with those of solid propanol (3e). This can be noted from the spectral region between 3600 and 2500 cm^{-1}, where the shapes of the absorption bands corresponding to OH and CH stretching modes, in the difference spectrum (Fig. 3c) and in that of solid allyl alcohol (Fig. 3d), are almost similar. However, they differ from those observed in the spectrum of solid propanol (Fig. 3e), which shows three specific structured absorption signals at 2965, 2932 and 2877 cm^{-1}. On the other hand, analysis in the spectral region ranged between 2000 and 1200 cm^{-1} confirms such a point, where the signals shown in the difference spectrum (3c) are more reliable to those corresponding to solid allyl alcohol (Fig. 3d) than to those of solid propanol (Fig. 3e).

Here, we can also estimate the amount of allyl alcohol formed through $HC \equiv CCH_2OH + 2H \rightarrow CH_2 = CHCH_2OH$ reaction by comparing the intensity of the signals in the difference spectrum (3c) to those of solid allyl alcohol obtained by condensing 1 μmol of $H_2C = CHCH_2OH$ at 10 K. In Fig. 3(d), the signal of solid allyl alcohol is divided by 60 in comparison with that of Fig. 2(a). Thus, approximately less than 1/60 μmol of $H_2C = CHCH_2OH$ could be formed by H-addition on a thick ice of propargyl alcohol. We estimate from the decreasing IR signals in Fig. 3(c) that only 5 per cent of $HC \equiv CCH_2OH$ molecules are consumed during the hydrogenation process. Consequently, as a second conclusion of this study, we note that the hydrogenation of solid propargyl alcohol ($HC \equiv CCH_2OH$) would lead mainly to the formation of allyl alcohol $CH_2 = CHCH_2OH$:

$$HC \equiv CCH_2OH + 2H \rightarrow CH_2 = CHCH_2OH$$
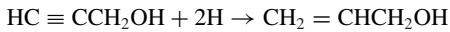
3.2 H-addition reactions on unsaturated aldehydes involving double or triple CC bonds and CO functional group: the case of propanal (CH₃CH₂CHO), propenal (H₂C=CHCHO) and propynal (HC≡CCHO)

We present in this part the hydrogenation of species containing a single, double or triple CC bond and a CO double bond, in order to see whether the H atom attack takes place preferably on the multiple CC bonds as observed earlier in the case of the hydrogenation of unsaturated alcohols or on the CO function which it would correspond to the reaction pathway to transform aldehydes into alcohols. We have then carried out similar studies of hydrogenation of solid aldehydes involving single, double or triple CC bonds: pure propanal (CH_3CH_2CHO), propenal ($H_2C = CHCHO$) and propynal ($HC \equiv CCHO$) ices.

3.2.1 Hydrogenation of propanal (CH₃CH₂CHO)

As mentioned earlier, propanal (CH_3CH_2CHO) has been detected in the ISM since 2004 (Hollis et al. 2004). In such a situation, could this aldehyde species be the source of propanol ($H_3C - CH_2CH_2OH$) through $CH_3CH_2CHO + 2H$ reaction? To answer this question, Figs 4(a) and (b) show the infrared spectra of solid propanal before and after H-bombardments, respectively. The two spectra are similar showing structured signals between 3000 and 2750 cm^{-1} corresponding to CH stretching modes, a very huge absorption band at 1730 cm^{-1} characteristic of the CO functional group and three sets of signals between 1500 and 750 cm^{-1} corresponding to CH₃ bending and rocking modes (Dostert et al. 2016). Fig. 4(c) shows the resulting difference spectrum and as a reference, the spectrum of solid propanol is presented in Fig. 4(d), since the obvious reaction product for a hydrogenation reaction of an unsaturated aldehyde such as propanal should be propanol. However, as shown in Figs 4(c) and (d), the hydrogenation of propanal does not lead to the formation of propanol. The difference spectrum (Fig. 4c) does not show any slight similarity with that of solid propanol (Fig. 4d). In fact, in the difference spectrum of Fig. 4(d) characterizing the H-bombardment of solid propanal, we notice that the CO absorption band remains unchanged and simultaneously, while the CH stretching signals slightly decrease those corresponding to the CH₃ bending and rocking modes increase. Such behaviours could be attributed to a transformation of the structure of solid propanal under H-atom exposure (Accolla et al. 2011). However, we do not detect any new signal that could be attributed to a new reaction product such as propanol or propanal fragments. These results show that the
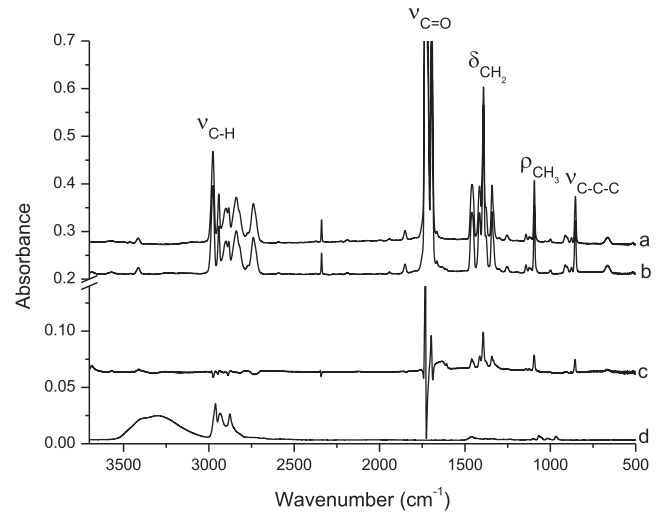
Figure 4. (a) Deposition of 4 μmol of propanal (CH_3CH_2CHO) on a mirror maintained at 10 K. (b) Hydrogenation of solid propanal at 10 K. (c) Difference spectrum: spectrum (b) − spectrum (a). (d) Deposition of 0.2 μmol of pure propanol ($H_3C - CH_2CH_2OH$) on a mirror maintained at 10 K (signal divided by approximately 10 in comparison with that of Fig. 2d).
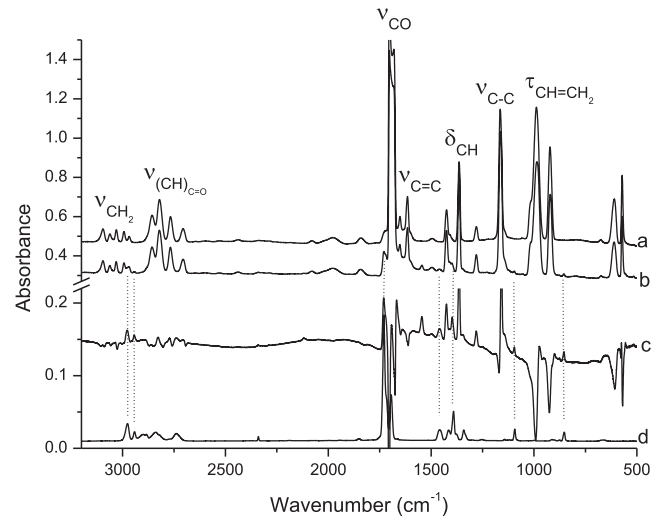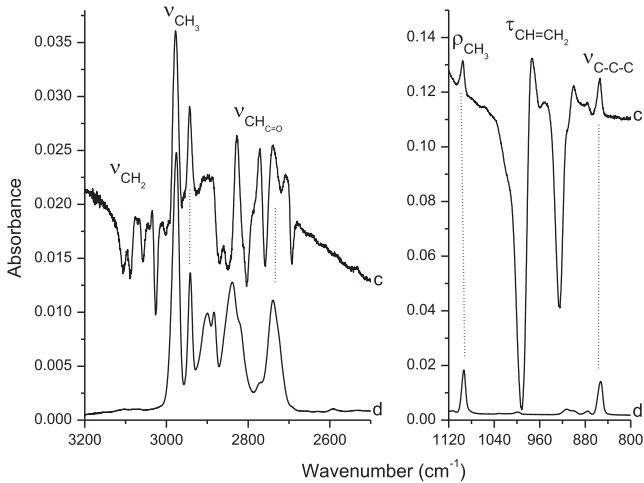

Figure 5. (a) Deposition of 10 μmol of propenal ($H_2C = CHCHO$) on a mirror maintained at 10 K. (b) Hydrogenation of solid propenal at 10 K. (c) Difference spectrum: spectrum (b) − spectrum (a). (d) Deposition of 4 μmol of propanal $CH_3 - CH_2CHO$ on a mirror maintained at 10 K (signal divided by approximately 10 in comparison with that of Fig. 4a).

$CH_3CH_2CHO + 2H$ reaction could not be a source of transformation of propanal (CH_3CH_2CHO) into propanol ($CH_3CH_2CH_2OH$), and propanal seems to be stable under H attacks. This may be one of the reasons why propanal is highly abundant in some molecular clouds where one of the predominant reactions is the surface H-addition.

3.2.2 Hydrogenation of propenal (H₂C=CHCHO)

Similarly to the previous hydrogenation experiments, propenal ice has been bombarded during 45 min with H atoms. Fig. 5(a) shows the infrared signatures of solid propenal characterized by two sets of signals around 3000 cm^{-1} corresponding to CH stretching modes, two signals around 1700 cm^{-1}, features of C=O and C=C stretching modes, and three sets of signals between 1500 and 500 cm^{-1}

Figure 6. Zoom of Figs 5c and d, in two spectral regions, 3200–2500 cm^{-1} and 1100–800 cm^{-1}: (c) Difference spectrum: spectrum (Fig. 5b) − spectrum (Figs 5a and d). Deposition of propanal CH$_3$–CH$_2$CHO on a mirror maintained at 10 K (signal divided by approximately 10 in comparison with that of Fig. 4a).

corresponding to CH$_2$ bending modes, in addition to the C–C stretching signal at 1161 cm^{-1} (Dostert et al. 2016). Fig. 5(b) illustrates the results of the hydrogenation of solid propenal and Fig. 5(c) shows the corresponding difference spectrum after and before H-bombardment. In these latter figures, new signals appear at 2975, 2938, 2890 cm^{-1} in the CH stretching region, at 1730 cm^{-1} in the C=O stretching region and at 1458, 1397, 1342, 1092 and 855 cm^{-1} in the bending mode region. Those new signals fit exactly the IR signatures of solid propanal CH$_3$–CH$_2$CHO as shown in Fig. 5(d). We thus conclude that the hydrogenation of unsaturated propenal CH$_2$=CHCHO containing a double C=C bond and a CO functional group leads only to the reduction of the double C=C into C–C single bond to form propanal CH$_3$–CH$_2$CHO and consequently, this reaction cannot be a source of formation of alcohol species:

$$H_2C = CHCHO + 2H \rightarrow CH_3CH_2CHO.$$

In addition to the signals appearing after H-bombardments of solid propenal which are easily assignable to propanal CH$_3$–CH$_2$CHO (CH and CO signals around 3000 and 1700 cm^{-1}, respectively, Figs 5b and c), Fig. 6 compares the difference spectrum before and after H-bombardment to the IR signatures of solid propanal in two different spectral regions: 3200–2500 and 1100–800 cm^{-1}. From this figure, we notice a decrease of propenal signal, estimated around 8 per cent and due to the C=C bond reduction through H$_2$C=CHCHO + 2H $\rightarrow$ CH$_3$CH$_2$CHO reaction. More specifically, while signals involving C=C vibrational modes such as ν_{CH2} and $\tau_{CH=CH2}$ disappear, those involving C–C vibrational modes such as ρ_{CH3} and $\nu_{C–C–C}$ appear and can be attributed to solid propanal. Comparison between the IR intensities in the difference spectrum (5c and 6c) and those of solid propanal obtained by condensing of 4 μmol of CH$_3$CH$_2$CHO at 10 K (in Figs 5d and 6d, the signal of solid propanal is divided by 10 in comparison with that of Fig. 4a) shows that approximately 4/10 μmol of CH$_3$CH$_2$CHO could be formed by H-addition on a thick ice of H$_2$C=CHCHO.

3.2.3 Hydrogenation of propynal (HC≡CCHO)

Figs 7(a) and (b) show the infrared spectra of solid propynal before and after H-bombardments, respectively. From Fig. 7(a)
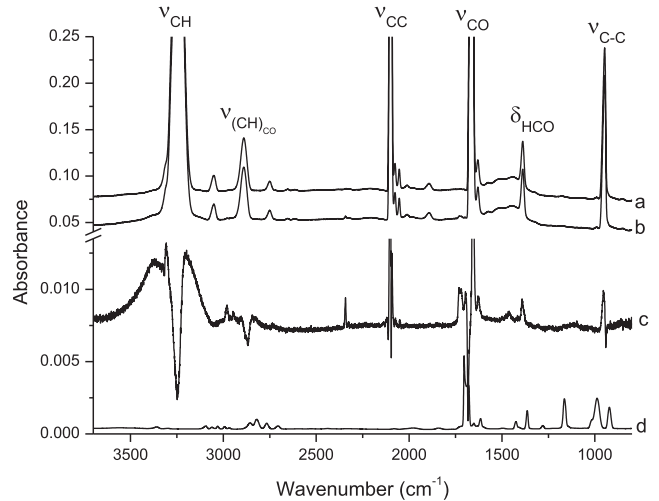

Figure 7. (a) Deposition of 3.1 μmol of pure propynal (HC≡CCHO) on a mirror maintained at 10 K. (b) Hydrogenation of solid propynal at 10 K. (c) Difference spectrum: spectrum (b) − spectrum (a). (d) Deposition of 10 μmol of pure propenal (H$_2$C=CHCHO) on a mirror maintained at 10 K (signal divided by approximately 600 in comparison with that of Fig. 5a).

characterizing the solid propynal, we note two sets of signals around 3000 cm^{-1} corresponding to CH stretching modes, three signals at 2100, 1660 and 947 cm^{-1} attributed to C≡C, C=O and C–C stretching modes, respectively and the HCO bending mode located at 1388 cm^{-1} (Klarde & Kremer 1977). Fig. 7(b) shows the results of the hydrogenation of solid propynal, while Fig. 7(c) illustrates the difference spectrum after and before H-bombardments. As a reference, the spectrum of solid propenal (H$_2$C=CHCHO) is presented in Fig. 7(d), supposing that the hydrogenation of a triple C≡C bond might lead to the formation of a C=C double bond, thus the propenal species. From the previous observations, we have already shown that the hydrogenation of HC≡CCH$_2$OH leads to CH$_2$=CHCH$_2$OH and the CO function remains unchanged for the H$_2$C=CHCHO + 2H reaction.

Although the difference spectrum (Fig. 7c) shows a small decrease of propynal (HC≡CCHO) signal estimated around 1.5 per cent, due to HC≡CCHO + 2H reaction, the new signals appearing at 2975, 1730, 1458 and 1397 cm^{-1} do not show any similarity with the IR absorption signals of solid H$_2$C=CHCHO (Fig. 7d), suggesting that the hydrogenation of propynal may lead to the formation of another chemical species rather than propenal. In fact, the new species formed during the hydrogenation process is propanal resulting from a direct transformation of the triple C≡C bond into a single C–C bond.

To confirm such a suggestion, Figs 8(c) and d show a zoom in the 2000–1100 cm^{-1} and 3100–2600 cm^{-1} spectral regions of Figs 7(c) and (d), and Fig. 8(e) corresponds to solid propanal. We notice, from Fig. 8, that in addition to the decrease of the signal at $\nu_{CH(C=O)}$ and $\nu_{C=O}$ of propynal, the new signals appearing at 2975, 2946, 2738, 1730, 1458, 1397 and 1092 cm^{-1}, after H-bombardment of propynal ice, are in good agreement with the IR signatures of the solid propanal (Fig. 8e) rather than with those of solid propenal (8d). Comparison between the IR intensities in the difference spectrum (8c) and those of solid propanal from Fig. 8(e), where the IR signal due the condensation of 4 μmol of CH$_3$–CH$_2$CHO is divided by 400, allows an estimation of the amount of propanal formed by hydrogenation of propynal. In such a situation, approximately less than 4/400 μmol of CH$_3$CH$_2$CHO could be formed
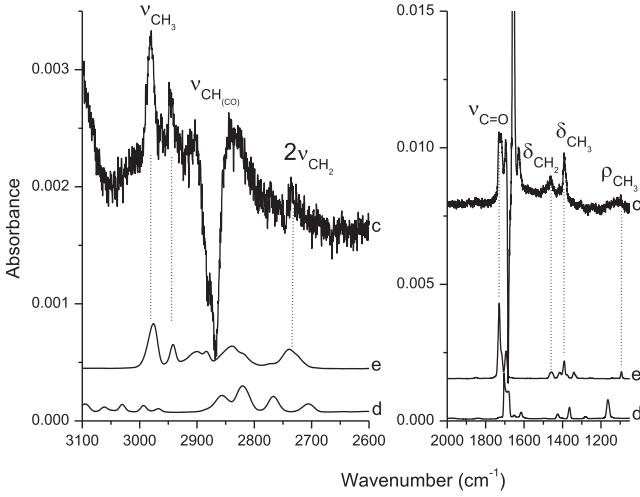
Figure 8. Zoom of Figs 7c and d, in two spectral regions, 3200–2500 cm^{-1}. (c) Difference spectrum: spectrum (Fig. 7b) − spectrum (Figs 7a and d). Spectrum of solid propenal formed at 10 K (signal divided by 600 in comparison with that of Fig. 5a). (e) Spectrum of solid propanal CH$_3$–CH$_2$CHO formed at 10 K (signal divided by approximately 400 in comparison with that of Fig. 4a).

by H-addition on a thick ice of HC≡CCHO. Such a direct transformation of propynal into propanal without observing propenal as intermediate might be due to the fact that H$_2$C=CHCHO + 2H → CH$_3$CH$_2$CHO reaction could be kinetically faster than HC≡CCHO + 2H → H$_2$C=CHCHO.

4 DISCUSSION

The efficiency of a hydrogenation reaction, carried out by bombarding solid samples by H atoms, should depend on the thickness of the ice sample, the energy barrier of the H-addition reaction and the flux of the H atoms (Hiraoka et al. 1994, Watanabe & Kouchi 2002, Watanabe et al. 2003; Fuchs et al. 2009). In the present study, as all the ices formed under our experimental conditions are thick and are exposed to the same amount of H atoms, the yield of the studied hydrogenation reactions would depend more on the energy barriers of a given reaction than on the reactant concentrations. However, the concentration of the reactants and the products can be evaluated from the IR spectrum analysis. The integrated intensities

of the absorption bands of the reactant and the products can be calculated and corresponding column densities n (molecules cm^{-2}) might be deduced knowing the IR absorption band strength (A cm molecule^{-1}) for a given species X trapped in the solid sample:

$$n = \frac{\ln 10 \int I(v) \, dv}{A} \frac{\cos(8°)}{2}.$$

The integral term is the band area or the integrated intensity of an absorption band (cm^{-1}) of given chemical species X. The correction factor ln 10 cos(8°)/2 takes into account our IR experimental condition measurements (Bennett et al. 2004). Still, in order to have an order of magnitude of the concentrations of the species involved in solid phase, the band strength (A) for a given trapped species X should be known. This is the case for simple molecules such as CO, CH$_3$OH, H$_2$CO, HCN but not for relatively larger molecules investigated in this study. For this reason, we have first estimated the band strengths of different absorption bands of HC≡CCH$_2$OH, H$_2$C=CHCH$_2$OH, H$_3$C−CH$_2$CH$_2$OH, HC≡CCHO, H$_2$C=CH–CHO, CH$_3$−CH$_2$CHO pure ices, by taking into account the exact amount of the vapour pressures of the deposited species and by supposing that the sticking probability on the cold surface (1 cm^2) of our sampler is one. Table 2 lists the calculated band strengths A_{OH}, A_{CH}, $A_{C=O}$, $A_{C=C}$, $A_{C≡C}$, corresponding to OH, CH, CO and CC absorption bands for the studied alcohols and aldehydes.

We note, from Table 2, that CH band strengths of propynal are twice that of propanal and four times that of propenal. On the other hand, the CO band strength of CH$_3$CH$_2$CHO is 1.4 times higher than that of HC≡CCHO but nearly 23 times higher than that of H$_2$C=CH–CHO, which will make it easier to detect species such as propynal and propanal rather than propenal. Furthermore, while the OH band strengths of the three alcohols have the same order of magnitude, the CH band strength of propanol is almost five times higher than that of H$_2$C=CHCH$_2$OH and HC≡CCH$_2$OH. Knowing the band strengths of those aldehydes and alcohols, we can deduce the column densities (molecules cm^{-2}) of the different species formed during the hydrogenation processes. Table 3 gathers the column densities of a given reaction product Y though X + H → Y successive H-addition reaction.

From Table 3, we notice that even though the hydrogenation reactions of HC≡CCH$_2$OH and H$_2$C=CHCH$_2$OH involve two successive H-additions, the comparison between the amounts of the obtained reaction products shows that the H$_2$C=CHCH$_2$OH + 2H

Table 2. Calculated band strengths (in cm molecule^{-1}) A_{OH}, A_{CH}, $A_{C=O}$, $A_{C=C}$, $A_{C≡C}$.

Species (X)	n ($\times10^{17}$)	A_{OH} ($\times10^{-16}$)	A_{CH} ($\times10^{-17}$)	$A_{C=O}$ ($\times10^{-17}$)	$A_{C=C}$ ($\times10^{-17}$)	$A_{C≡C}$ ($\times10^{-17}$)
Propargyl alcohol (HC≡CCH$_2$OH)	1.8 ± 0.5	8 ± 2	4 ± 1			0.5 ± 0.1
Allyl alcohol (H$_2$C=CHCH$_2$OH)	6.0 ± 1	4 ± 1	5 ± 1		1.3 ± 0.3	
Propanol (H$_3$CCH$_2$CH$_2$OH)	1.2 ± 0.3	6 ± 2	22 ± 6			
Propynal (HC≡CCHO)	19 ± 3		1.6 ± 0.2	1.0 ± 0.2	0.9 ± 0.1	
Propenal (H$_2$C=CH–CHO)	60 ± 6		0.4 ± 0.1	0.06 ± 0.01	0.6 ± 0.1	
Propanal (CH$_3$CH$_2$CHO)	24 ± 4		0.8 ± 0.1	1.4 ± 0.2		

n: column density (molecules cm^{-2}).
Spectral regions for band strength calculations:
Propargyl alcohol – ν_{OH}: 3700–2995 cm^{-1}, ν_{CH}: 2995–2710 cm^{-1}, ν_{CC}: 1760–1616 cm^{-1}.
Allyl alcohol – ν_{OH}: 3609–3031 cm^{-1}, ν_{CH}: 2966–2738 cm^{-1}, ν_{CC}: 1751–1607 cm^{-1}.
Propanol – ν_{OH}: 3593–3006 cm^{-1}, ν_{CH}: 3006–2766 cm^{-1}.
Propynal – ν_{CH}: 3393–3110 cm^{-1}, ν_{CC}: 2135–2030 cm^{-1}, ν_{CO}: 1697–1608 cm^{-1}.
Propenal – ν_{CH}: 3142–2941 cm^{-1}, ν_{CC}: 1715–1664 cm^{-1}, ν_{CO}: 1663–1600 cm^{-1}.
Propenal – ν_{CH}: 3142–2941 cm^{-1}, ν_{CC}: 1715–1664 cm^{-1}, ν_{CO}: 1663–1600 cm^{-1}.
Propanal – ν_{CH}: 3026–2680 cm^{-1}, ν_{CO}: 1747–1705 cm^{-1}.

Table 3. Column densities of Y species formed through $X + H \rightarrow Y$ reaction.

Deposited species (X)	Nature of Y species formed through $X + H \rightarrow Y$ reaction	Y column densities (molecules cm^{-2}) ($\times 10^{17}$)
HC≡CCH$_2$OH	H$_2$C=CHCH$_2$OH	0.10 ± 0.02
H$_2$C=CHCH$_2$OH	H$_3$CCH$_2$CH$_2$OH	0.8 ± 0.2
H$_3$CCH$_2$CH$_2$OH	–	–
HC≡CCHO	CH$_3$CH$_2$CHO	0.06 ± 0.01
H$_2$C=CH–CHO	CH$_3$CH$_2$CHO	2.3 ± 0.3
CH$_3$CH$_2$CHO	–	–

reaction is eight times more efficient than the HC≡CCH$_2$OH + 2H reaction. We conclude that the reaction HC≡CCH$_2$OH + 2H should get an energy barrier relatively higher than that of H$_2$C=CHCH$_2$OH + 2H and this may explain the low amount of allyl alcohol formed when HC≡CCH$_2$OH ices are exposed to H atoms. Consequently, the low yield of the HC≡CCH$_2$OH + 2H → CH$_2$=CHCH$_2$OH reaction may prevent a complete reduction of the C≡C triple bond of propargyl alcohol.

Similarly, the transformation of the H$_2$C=CH–CHO aldehyde into CH$_3$CH$_2$CHO seems to be very efficient as it leads to the formation of a huge amount of propanal (2.3×10^{17} molecules cm^{-2}). However in the case of HC≡CCHO hydrogenation, we directly observed a total reduction of the triple C≡C bond and there was no evidence for the detection of H$_2$C=CH–CHO as a reaction intermediate. We conclude that H$_2$C=CH–CHO + 2H reaction should not have an energy barrier or at least, it would show an activation energy lower than that of HC≡CCHO + 2H, and thus as soon as the H$_2$C=CH–CHO is formed through HC≡CCHO + 2H reaction, it is transformed into propanal. These results are in good agreement with the interstellar observations where propynal and propanal are abundant in molecular clouds while the detection of propenal has never been confirmed (Turner 1991; Hollis et al. 2004).

On the other hand, by comparing the results of the CC bond reductions in alcohols and aldehydes, we would point out that the non-detection of propanol from HC≡CCH$_2$OH + 4H reaction would be due to the fact that the energy barrier of H$_2$C=CHCH$_2$OH + 2H reaction should be higher than that of H$_2$C=CH–CHO + 2H.

In the case of the unsaturated aldehydes species, we also show that there is no link between large aldehydes and their corresponding reduced alcohols via successive hydrogen additions occurring in solid phase at cryogenic temperatures.

Even though many studies have proposed the existence of links between aldehydes species and their corresponding alcohols in the interstellar grains (Hollis et al. 2002) taking as examples the CO + H and H$_2$CO + H surface reactions (Hiraoka et al. 2002; Hidaka et al. 2004; Watanabe et al. 2004; Krim et al. 2010), the solid phase hydrogenation reaction of the simplest aldehyde H$_2$CO to form CH$_3$OH would be an exception. We show in this study that propanal does not react with H atoms under interstellar conditions to form propanol and this is consistent with the fact that CH$_3$CH$_2$CHO is highly abundant in space while CH$_3$CH$_2$CH$_2$OH is still not detected.

Consequently the presence of aldehydes and their corresponding alcohols, very often not in the same interstellar regions (Hollis et al. 2002), does not mean that alcohol species are necessarily produced on icy mantles in the ISM via aldehydes + H reaction. Other reaction pathways should be proposed and taken into account to explain the formation of alcohols detected in hot cores. In this context, some experimental studies have already shown that complex species such
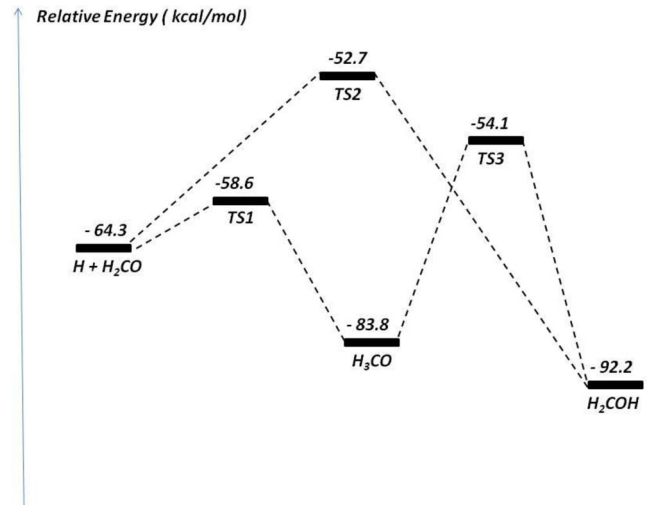
Figure 9. Relative energies of H$_2$COH and H$_3$CO and transitions states for H + H$_2$CO reaction according to Xu et al. (2015). TS1 and TS2 are the transitions states that lead to the reaction products H$_3$CO and H$_2$COH. TS3 is the transition state between the two isomeric forms H$_3$CO and H$_2$COH.

as large alcohols found in the ISM might be formed through high-energy radiations of ice analogues (Moore & Hudson 1998).

In order to understand why formaldehyde is reduced into methanol by H-addition reaction and not larger aldehydes such as propanal and propenal, we have first analysed, from a theoretical point of view, the key step of CH$_3$OH formation which is H + H$_2$CO reaction (Xu et al. 2015). Many theoretical models have already shown that H + H$_2$CO reaction leads to the formation of H$_3$CO which is converted by tunnelling into a more stable radical H$_2$COH. Afterwards, the H$_2$COH or both radicals would react with H atoms to form methanol. Fig. 9 shows the relative energies of H$_2$COH and H$_3$CO and transition states for H + H$_2$CO reaction. The energy barrier for the H$_2$CO + H → H$_3$CO reaction is 5.7 kcal mol^{-1} while that of H$_2$CO + H → H$_2$COH is 11.6 kcal mol^{-1}. H$_2$COH radical is 8.4 kcal mol^{-1} more stable than H$_3$CO and this relative stability between the two radicals allows the isomeric conversion H$_3$CO → H$_2$COH. It would play an important role, as we will specify later, in the formation of methanol by successive H-addition on H$_2$CO.

Even though there is no theoretical model for the hydrogenation of larger aldehydes such as propanal, propenal and propynal, Kwon et al. (2002) investigated the potential energy surface of the O(^{3}P) + C$_3$H$_5$ reaction, where H$_2$C=CH–CHO was formed and reacted with H atoms to form three radicals H$_2$C–CH$_2$–CHO, H$_2$C=CH–CH$_2$O and H$_2$C=C–CH$_2$OH. The former one is due to the reduction of the C=C bond of propenal while the two latter ones, similar to H$_3$CO and H$_2$COH from H$_2$CO + H reaction, should play the key role for the formation of the allyl alcohol species from H$_2$C=CH–CHO + H reaction.

Fig. 10 shows the relative energies of H$_2$C–CH$_2$–CHO, H$_2$C=CH–CH$_2$O and H$_2$C=C–CH$_2$OH. First, the reduction of the C=C bond of propenal may take place through H + H$_2$C=CH–CHO → H$_2$C–CH$_2$–CHO reaction which is exothermic by 31.3 kcal mol^{-1} and has a low-energy barrier of 7.2 kcal mol^{-1}. Afterwards, the H$_2$C–CH$_2$–CHO radical may react with an additional H atom through a hydrogen attack on the carbon atom to form propanal (H$_3$C–CH$_2$–CHO), a scenario that has been validated by our experimental results.
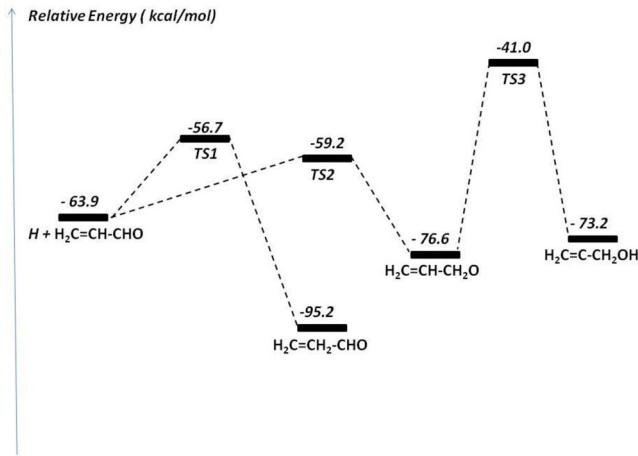
Figure 10. Relative energies of $H_2C=CH_2$–CHO, $H_2C=CH$–CH_2O and $H_2C=C$–CH_2OH and transitions states for H + $H_2C=CH$–CHO reaction according to (Kwon et al. 2002). TS1 and TS2 are the transitions states that lead to the reaction products $H_2C=CH_2$–CHO and $H_2C=CH$–CH_2O. TS3 is the transition state between the two isomeric forms $H_2C=CH$–CH_2O and $H_2C=C$–CH_2OH.

The reduction of the C=O function would start by the H + $H_2C=CH$–CHO reaction which would lead to the formation of $H_2C=CH$–CH_2O radical, an intermediate of $H_2C=CHCH_2OH$ alcohol. This reaction is exothermic by 12.7 kcal mol^{-1}, has a low-energy barrier of 4.7 kcal mol^{-1} and may easily occur under our experimental conditions.

Conversely to the formation of H_3CO and its conversion by tunnelling $H_3CO \rightarrow H_2COH$ into the corresponding stable isomer CH_2OH which would open two different routes for the formation of methanol though H_3CO + H and CH_2OH + H, the radical $H_2C=CH$–CH_2O, more stable by 3.4 kcal mol^{-1} than its corresponding isomer $H_2C=C$–CH_2OH, would not be converted into $H_2C=C$–CH_2OH by tunnelling. Thus without providing an external energy to the system, there is only one route for the formation of $H_2C=CHCH_2OH$ alcohol, which is $H_2C=CH$–CH_2O + H reaction where an H atom would attack the oxygen atom of $H_2C=CH$–CH_2O. In such a situation, the oxygen atom $H_2C=CH$–CH_2O is probably engaged with neighbouring molecules though hydrogen bonding, preventing the formation of the OH function. $H_2C=C$–CH_2OH + H reaction would be more favourable than $H_2C=CH$–CH_2O + H, as the H attack would occur on the central carbon. We conclude that in order to form $H_2C=CHCH_2OH$ by successive H-addition reaction on $H_2C=CH$–CHO, we should support the $H_2C=C$–CH_2OH + H reaction rather than $H_2C=CH$–CH_2O + H. This would occur only by inducing a conversion of the stable radical $H_2C=CH$–CH_2O into the less stable one $H_2C=C$–CH_2OH by providing, to the system, an external energy higher than 35.6 kcal mol^{-1}. This is consistent with our experimental results proving that the reduction of a CC bond may occur just by H-addition reaction however the transformation of aldehydes species into alcohols cannot take place through aldehydes + H solid phase reaction and it would probably require further energy to occur.

5 CONCLUSION

The hydrogenation of the simplest aldehyde H_2CO to form CH_3OH would not justify the existence of links between other aldehydes species and their corresponding alcohols in icy mantles on the inter-

stellar grains. Propynal and propanal have been observed in the ISM where H-addition reactions are predominant while neither propargyl or propanol alcohols have been detected. In this context, we have investigated the hydrogenation process of alcohols and aldehydes involving triple, double and single CC bonds under ISM conditions for a better understanding of their chemistry. Pure aldehyde and alcohol ices formed at 10 K have been bombarded by H atoms and the yield of the reactions has been measured *in situ* in solid phase by infrared spectroscopy. We show through this experimental study that unsaturated alcohols can be reduced to fully or partially saturated alcohols, while unsaturated aldehydes such as propynal and propenal are exclusively reduced to fully saturated aldehyde, propanal. We also show that there is no link between large aldehydes and their corresponding reduced alcohols via successive H addition occurring in solid phase at cryogenic temperatures. Consequently the presence of aldehydes and saturated alcohols, very often not in the same interstellar regions, does not imply that alcohol species are necessarily produced on icy grains via aldehydes + H reactions. Thus, rather than H thermal reactions, other energetic reactions should be taken into account to explain the formation pathways of alcohol species detected in hot cores.

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