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# Organic Residues in Astrophysical Ice Analogs: Thermal Processing of Hydrogenated Glyoxal Ices under interstellar conditions

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## Abstract

Organic residues are considered as part of the chemical composition of the interstellar dust grains. They are formed under the extreme conditions of the interstellar medium and play an important role in exobiology. They may contain pre-biotic organic species such as amino acids, constituents of proteins and building blocks of DNA and RNA, key elements of life. By investigating the formation of organic residues in an astrophysical context, many groups have been focusing in the UV irradiation and subsequent warm-up of astrophysical ice analogues. This aims to suggest that organic residues are mainly formed in regions of molecular clouds exposed to UV light or cosmic rays. This study shows an organic residue formation involving glyoxal ice and H atoms. While the hydrogenation of glyoxal at 10 K leads mainly to small molecules such as CO and H<sub>2</sub>CO and CH<sub>3</sub>OH, we show that the heating of the hydrogenated ice in the 10–300 K temperature range leads to solid residues whose structure is similar to that of glycolaldehyde but they remain stable in solid phase at 300 K and atmospheric pressure. The analysis of the IR data shows that the organic residues formed through the thermal processing of CHOCHO + H reaction would be a mixture of hydroxypyruvaldehyde and methyl glyoxylate, two solid organics whose formation starts with an H-abstraction from glyoxal to form CHOCO<sup>•</sup> radical which recombines to <sup>•</sup>CH<sub>2</sub>OH and <sup>•</sup>OCH<sub>3</sub> radicals. These latter may be formed and trapped in glyoxal ice as secondary products from H<sub>2</sub>CO + H secondary reaction.

## **Keywords:**

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

## 1. Introduction

Since the detection of methylidyne radical CH, 80 years ago (Dunham et al. 1937), many investigations have been dedicated to the detection, formation and evolution of extraterrestrial organic molecules (Öberg 2016; McGuire 2018; Sandford et al. 2020 and references therein). Organic compounds exist in several regions of the Universe from molecular clouds of the interstellar medium (Pendleton 1997; Charnley et al. 2002) till small bodies of astronomical

interest such as meteorites (Yang & Epstein 1983; Llorca 2004) and comets (Fomenkova et al. 1994; Biver et al. 2014). It is well established that many organic molecules originate from reactions occurring on the surface of interstellar dust grains which are mainly composed of silicate, amorphous carbon and organic species (Tielens and Allamandola 1987; Draine 2003; Demyk 2011). By focusing on the formation and evolution of organic molecules on the interstellar dust grains, theoretical and experimental studies (Kimura and Kitadai 2015; Enrique-Romero et al. 2016; Redondo et al. 2017; Oba et al. 2019) aim to understand the appearance of life beginning by the formation of prebiotic molecules and their precursors such as sugars, amino acids or nucleic bases called “building blocks of life” (Kimura and Kitadai 2015).

Two types of organic compounds may be present in the interstellar dusts (Tielens and Allamandola 1987; Draine 2003, Boogert et al. 2015):

- Organics constituting the dust particles composed of PAH (Clemett et al. 1993; Tielens 2008) and other organic macromolecules trapped in silicate and carbon structures (Srama et al 2009).
- Organics present in the ices covering the surfaces of the interstellar grains (Greenberg 1989; Srama et al 2009).

The organic species trapped in the icy mantles covering the dust grain surfaces are made up of volatile molecules such as  $\text{CH}_4$  or  $\text{H}_2\text{CO}$  which may desorb into the gas phase during the sublimation of the ices when the temperature rises in excess of 100 K (Collings et al. 2004; Acharyya et al. 2018; Maté et al. 2019), while the organics constituting the interstellar dust would remain in the solid phase even when the grain temperature is higher than 300 K (Modica et al. 2014; d’Hendecourt et al. 2019). These residual products are characterized by high molecular weights and desorption temperatures higher than 300 K. The formation of residues, which contain a wide variety of “building blocks of life” such as amino acids (glycine, alanine, valine...), constituents of proteins, and such as purine and pyrimidine bases (cytosine, uracil, thymine, adenine), the building blocks of DNA and RNA, molecules capable of transporting genetic information, has already been investigated under interstellar medium conditions through the irradiation and warming-up of interstellar ice analogs (Elsila et al. 2007; Chen et al. 2008; Nuevo et al. 2008; Oba et al. 2019).

In the present paper, we have investigated the formation of organic residues by probing the thermal evolution of  $\text{CHOCHO} + \text{H}$  solid state reaction in the 10 - 300 K temperature range. Glyoxal ( $\text{CHOCHO}$ ) has not been detected in the interstellar medium (ISM) yet, however, its non-detection can be explained by three reasons:

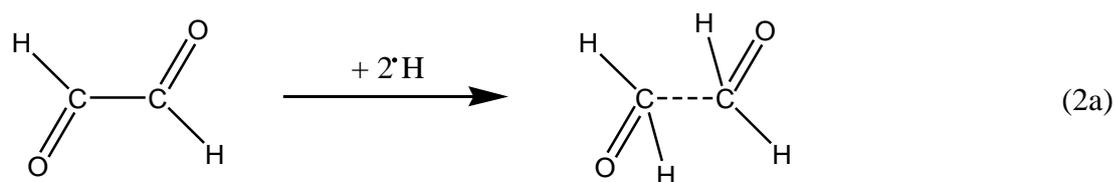
- Glyoxal exists in two forms, cis-glyoxal and trans-glyoxal. Theoretical studies have shown that the trans-glyoxal is the most stable and shows an activation energy for the trans  $\rightarrow$  cis conversion around 21 kJ.mol<sup>-1</sup> (Koch et al. 2001). However, trans-glyoxal has zero dipole moment, which makes its detection by astronomical instruments very difficult.

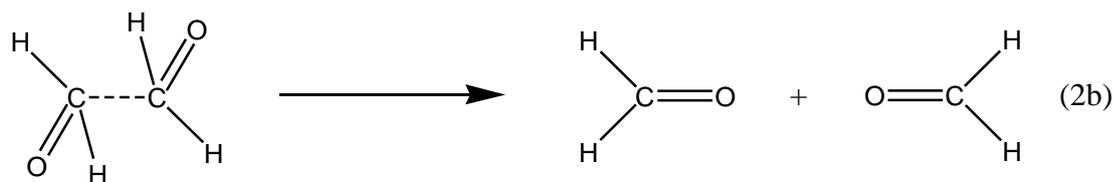
- Glyoxal would be formed on the surface of the interstellar grains by the dimerization of HCO (Wood et al. 2013), radical already detected in the ISM (Snyder, Hollis & Ulich 1976). However, recent experimental studies (Butscher et al. 2017) have shown that the HCO + HCO reaction leads rather to CO and H<sub>2</sub>CO formation while the glyoxal production is negligible. Consequently, the low amount of CHOCHO derived from HCO dimerization could be one of the reasons of glyoxal scarcity in the ISM.

- The high reactivity of glyoxal under ISM conditions could also explain the lack of CHOCHO from the astronomical observations. Astrophysical models (Wood et al. 2013; Fedoseev et al. 2015) suggest that glyoxal interacting with hydrogen atoms would be a precursor of glycolaldehyde (CHOCH<sub>2</sub>OH) and ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH), two Complex Organic Molecules (COMs) already detected in the ISM (Hollis et al. 2000; Hollis et al. 2002).

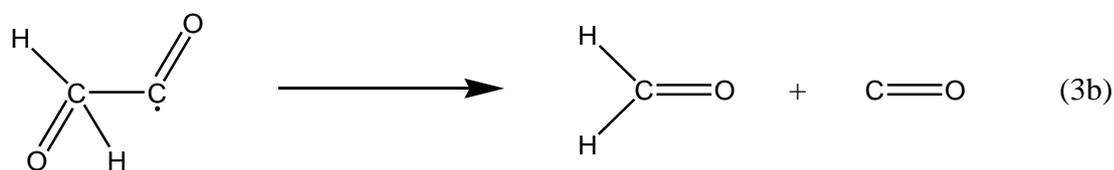
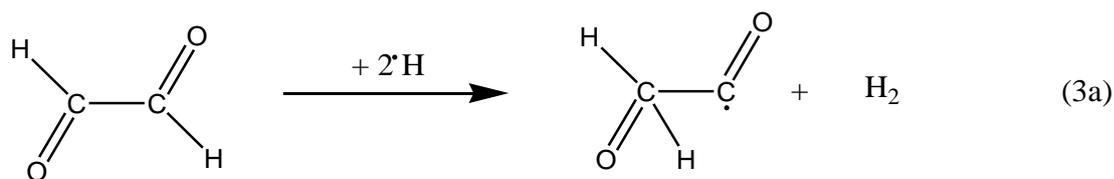


In our previous works, we carried out the hydrogenation of solid glyoxal at 10 K in order to confirm or invalidate the astrophysical models (Leroux et al. 2020). We showed that the interaction of glyoxal with H-atoms does not lead to the formation of large COMs such as glycolaldehyde and ethylene glycol. However CHOCHO + H reaction leads mainly to lighter species such as CO, H<sub>2</sub>CO and H<sub>2</sub>CO-CO a reaction intermediate where H<sub>2</sub>CO is chemically linked to CO. From this study, we have proposed two reaction pathways to describe the CHOCHO + H reaction under interstellar conditions. Due to the symmetry of the molecule, the first reaction pathway consists on a simultaneous H-addition reaction on the two carbon atoms of CHOCHO, which leads to the formation of CH<sub>2</sub>O-CH<sub>2</sub>O reaction intermediate (reaction 2a). This unstable intermediate decomposes into two molecules of formaldehyde by the C-C bond rupture (reaction 2b).





The second reaction pathway is the addition and elimination of H-atoms on CHOCHO leading to the formation of H<sub>2</sub>CO-CO (reaction 3a) reaction intermediate which decomposes in H<sub>2</sub>CO and CO (reaction 3b).



While the CH<sub>2</sub>O-CH<sub>2</sub>O reaction intermediate has not been observed under our experimental conditions, a species, stable only at temperatures lower than 100K and absorbing in the CO and H<sub>2</sub>CO spectral regions, has been tentatively assigned to the CO-H<sub>2</sub>CO reaction intermediate. However, additional theoretical (Alvarez-Barcia et al. 2018) and experimental investigations with isotopically labelled reagents should be conducted to better characterize these reaction pathways. The detection of fragments such as CO and H<sub>2</sub>CO, usually observed through radiolysis or photolysis of astrophysical ices (Gerakines et al. 1995; Hudson & Moore 1999; Krim & Jonusas 2019), during the hydrogenation of CHOCHO, would suggest the CC bond dissociation and the formation of two formyl radicals. The HCO + HCO recombination would lead then to H<sub>2</sub>CO and CO as main reaction products. However, the threshold for the formation of HCO fragments (Salter et al. 2013) from glyoxal is 290 kJ mol<sup>-1</sup>, while under our experimental conditions the H atoms are released from the atom source with energies lower than 96 kJ mol<sup>-1</sup> and which probably vanish during the interaction with the icy surface of the solid sample. Consequently, the fragmentation of glyoxal is most likely due to H-abstraction and H-addition processes. Similar results have been obtained with the hydrogenation of formic acid (Chaabouni et al. 2020) where HCOOH + H reaction leads mainly to CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>CO, and CH<sub>3</sub>OH. The authors show that the H- abstractions from HCOOH lead to CO<sub>2</sub>, while the

H-addition on the OH group leads to H<sub>2</sub>O and HCO which is immediately converted into H<sub>2</sub>CO and CH<sub>3</sub>OH.

In the present work we aim to study the influence of the temperature on the CHOCHO + H reaction from 10 to 300 K. The warming-up in the 10 - 300 K temperature range of interstellar ices containing CHOCHO and H species would mimic the evolution of COMs such as glyoxal from molecular clouds to formation of stars. Most of the laboratory studies devoted to organic residues formation are performed using UV-photolysis or particle-irradiation of interstellar ice analogs followed by thermal processing (Chen et al. 2008; Modica et al. 2014). This is the first study showing at the same time the high reactivity of glyoxal under interstellar conditions and the formation of residual products through the thermal processing of CHOCHO + H reaction carried out at 10 K.

## 2. Experimental section

Glyoxal has been prepared from trimeric glyoxal dihydrate and phosphorus (V) oxide (Wang, Arif & Gladysz 1994), and hydrogen (99.9995 per cent) was purchased from Messer. Hydroxypyruvaldehyde and methyl glyoxylate were synthesized following the synthesis of (Evans et al. 1938) and (Kelly et al. 1972), respectively.

CHOCHO + H solid sample preparations at 10 K have been described in our previous study (Pirim & Krim 2011; Leroux et al. 2020). In brief, gaseous glyoxal is introduced in a ramp and co-injected with hydrogen atoms on a Rh-plated copper mirror maintained at 10 K and located in an ultrahigh vacuum chamber maintained at 10<sup>-10</sup> mbar. The hydrogen atoms are formed by the dissociation of molecular hydrogen using a microwave driven atomic source (SPECS, PCS-ECR). The source is operated in a mode where the particles released are largely thermalised (<1 eV). The H-atoms are injected at an optimum pressure of 10<sup>-5</sup> mbar in the chamber with a ratio H/H<sub>2</sub> around 15 per cent measured with a Quadrupole Mass Spectrometer (QMS - Hidden Analytical) by monitoring the H and H<sub>2</sub> mass signals with the microwave discharge on and off. The microwave discharge has been modified by adding to its output a curved teflon tube which allows additional thermalisation of the species released from the atomic source and also to block the light from the plasma discharge to avoid possible photo-irradiation processing during the H-bombardment of our samples. Using a leak valve, glyoxal is injected at 9 × 10<sup>-9</sup> mbar with a flux of 2 μmol min<sup>-1</sup> while the H-atom flux estimated from the amount of molecular hydrogen injected during the co-injection experiment is around 10<sup>17</sup> atoms cm<sup>-2</sup> s<sup>-1</sup>. The ratio between glyoxal and H-atoms is equal to 150 during the co-injection experiment. The samples are

formed at 10 K using a closed-cycle helium cryogenerator (Sumitomo cryogenics F-70) and heated from 10 to 300 K using a programmable temperature controller (Lakeshore 336). CHOCHO + H solid state reaction is monitored at different temperatures by recording infrared spectra of (CHOCHO + H/H<sub>2</sub>) ices in the mid-infrared (IR) spectral region 4000 – 500 cm<sup>-1</sup> with a resolution of 0.5 cm<sup>-1</sup>, using a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer in the transmission-reflection mode with an incidence angle of 8° with respect to the normal to the substrate surface. By coupling temperature programmed desorption (TPD), mass spectrometry and IR spectroscopy we have characterized the reaction products derived from glyoxal hydrogenation occurring at 10 K and followed by thermal processing in the 10-300 K temperature range.

### 3. Results and discussions

Figure 1 shows the IR spectra resulting from CHOCHO + H/H<sub>2</sub> co-injection at 10 K (figure 1b) followed by a sample heating at 100 and 130 K (figures 1d and 1f). In order to highlight the reaction products due to CHOCHO + H solid state reaction at 10, 100 and 130 K, we have recorded under the same experimental conditions the IR spectra for a reference experiment consisting on CHOCHO + H<sub>2</sub> co-injection at 10 K (figure 1a) followed by a sample heating at 100 and 130 K (figures 1c and 1e). The comparison between figures 1a and 1b shows that at 10 K, CHOCHO + H reaction leads mainly to CO, H<sub>2</sub>CO and CO-H<sub>2</sub>CO, in addition to CH<sub>3</sub>OH which may be formed as a secondary product resulting from the hydrogenation of formaldehyde (Leroux et al. 2020). The results of the thermal processing at 100 and 130 K of (CHOCHO + H/H<sub>2</sub>) and (CHOCHO + H<sub>2</sub>) solid samples are presented in figures (1d,1c) and (1f,1e), respectively. The IR features at 1452 and 2115 cm<sup>-1</sup> corresponding to the CO-H<sub>2</sub>CO reaction intermediate disappear completely at 100 K, highlighting its reactivity or its desorption. However stable species such as CO, H<sub>2</sub>CO which would desorb around 30 K (Acharyya and al. 2018) and 110 K (Noble et al. 2012), respectively, remain trapped in CHOCHO ice. Additionally, we notice that between 100 and 130 K, the absorption bands of glyoxal and those of CO and H<sub>2</sub>CO become sharp and decrease in intensity. These spectral changes are due to glyoxal ice crystallization which is effective from 100K and where the IR signals of the species trapped in the ice become very narrow and sharp, and then easily detectable.

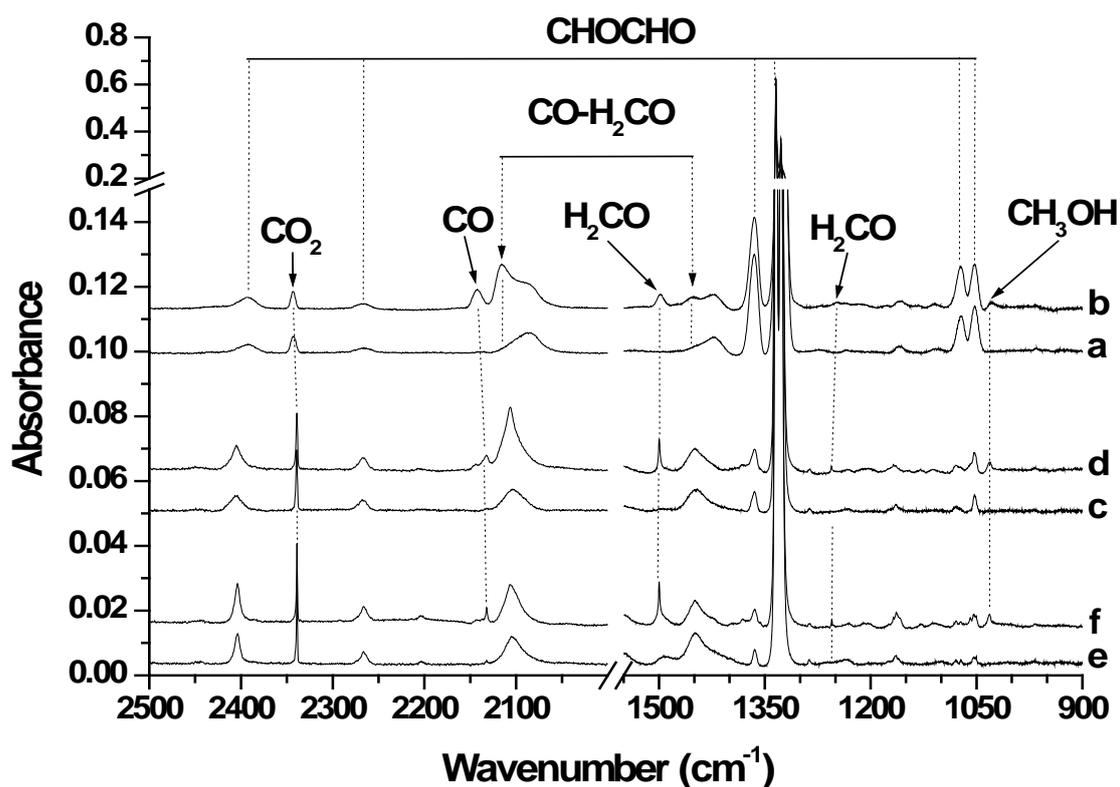


Figure 1: Co-injection experiment at 10 K: a) CHOCHO + H<sub>2</sub>. b) CHOCHO + H/H<sub>2</sub>.  
 Sample heating at:  
 - 100 K: c) CHOCHO + H<sub>2</sub>. d) CHOCHO + H/H<sub>2</sub>.  
 - 130 K: e) CHOCHO + H<sub>2</sub>. f) CHOCHO + H/H<sub>2</sub>.

During the CHOCHO + H/H<sub>2</sub> sample heating between 10 and 130 K, no new reaction products due to the thermal processing of CHOCHO + H solid state reaction have been detected. Besides CO and H<sub>2</sub>CO whose IR features are clearly separated from those CHOCHO ice, we did not detect any new IR signal which may be assigned to a new given reaction product. Such new reaction products signals could be trapped in CHOCHO ice but they would have their IR signatures hidden by the absorption bands of glyoxal. This shows the limit of the IR analysis when reagents and products absorb in the same spectral regions. In order to highlight reaction products other than CO and H<sub>2</sub>CO, we have used the temperature programmed desorption (TPD) coupled to spectrometry to list all the species formed in the solid phase and which may release in the gas phase. The desorbing species are then identified by comparing the desorption temperatures and fragmentation patterns. This is what we did in our previous study (Leroux et al. 2020) to show that the only species desorbing from CHOCHO + H/H<sub>2</sub> ices are CO, H<sub>2</sub>CO and CHOCHO at 30, 93 and 177 K. There is no trace of species such as CHOCH<sub>2</sub>OH or HOCH<sub>2</sub>CH<sub>2</sub>OH which would desorb at 195 and 214 K, respectively (Butscher et al. 2015).

However the simultaneous analysis of the mass signals and IR data during the heating of CHOCHO + H/H<sub>2</sub> sample in the 190-300 K temperature range reveals the formation of organic residues while no volatile heavier COMs are detected. Figure 2 shows the heating of CHOCHO + H/H<sub>2</sub> sample between 160 and 200 K. We notice that species such as H<sub>2</sub>CO remain trapped in glyoxal ice till 160 K and they disappear entirely at 165 K. The CHOCHO IR signals decrease considerably between 160 and 170 K and vanish completely at 185 K.

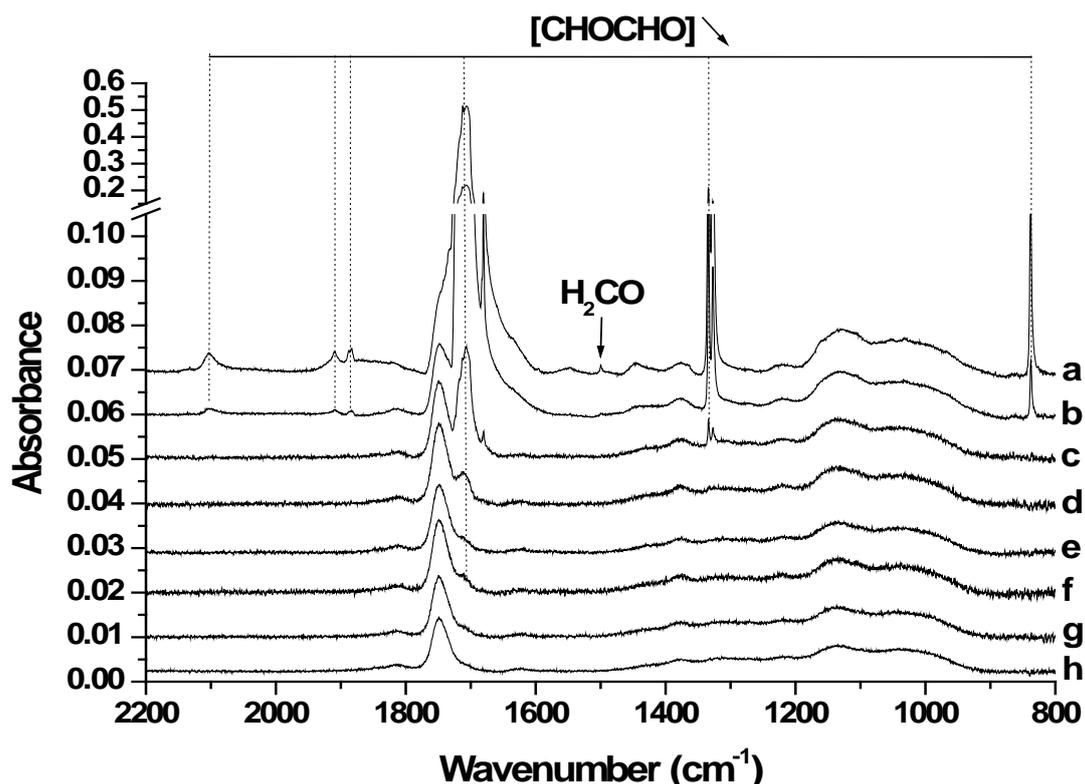


Figure 2: Emergence of organic residues during the CHOCHO + H/H<sub>2</sub> sample heating between 160 and 190 K: (a) 160 K; (b) 165 K; (c) 170 K; (d) 175 K; (e) 180 K; (f) 185 K; (g) 190 K and (h) 200 K.

The disappearance of H<sub>2</sub>CO at 165 K is followed by the decrease of CHOCHO signals and the appearance of IR features, in the 2000-1700 cm<sup>-1</sup> spectral region, which may correspond to a C=O functional group of residual products formed during the thermal heating of CHOCHO + H/H<sub>2</sub> sample and which remain stable beyond 300 K. In addition to this new absorption band located in the C=O functional group spectral region, these residues show other IR features in the 1200-900 and 3700-2700 cm<sup>-1</sup> spectral regions corresponding to the C-O and OH functional groups, respectively. Figure 3 shows the IR spectra of the residual products during the sample heating between 200 and 300 K, in the 4000-900 cm<sup>-1</sup> spectral region. The residues formed under our experimental conditions show four characteristic spectral regions which may

correspond to OH, CH, C=O and C-O functional groups and although the intensities of the absorption bands decrease during the sample heating, these residual products remain in solid state even at room temperature.

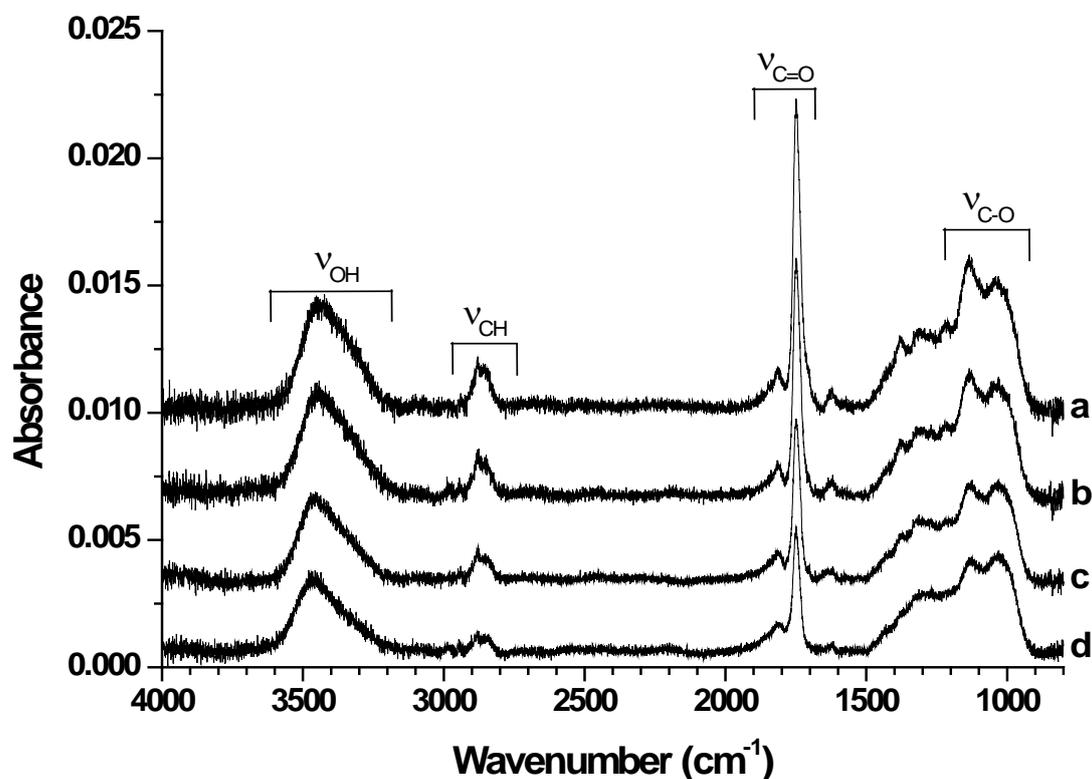


Figure 3: Evolution between 200 and 300 K of the organic residues formed during the thermal heating of CHOCHO + H/H<sub>2</sub> sample. Heating at: (a) 200 K, (b) 225 K, (c) 250 K, (d) 300 K.

Although the residual products formed during the heating of CHOCHO + H/H<sub>2</sub> sample are in the solid phase at room temperature, we have compared their IR spectrum recorded at 300 K to that of glycolaldehyde (CHOCH<sub>2</sub>OH) ice recorded at 10 K (Figure 4). In fact, as for the residual products, CHOCH<sub>2</sub>OH has similar functional groups such as OH, CH, C=O and C-O.

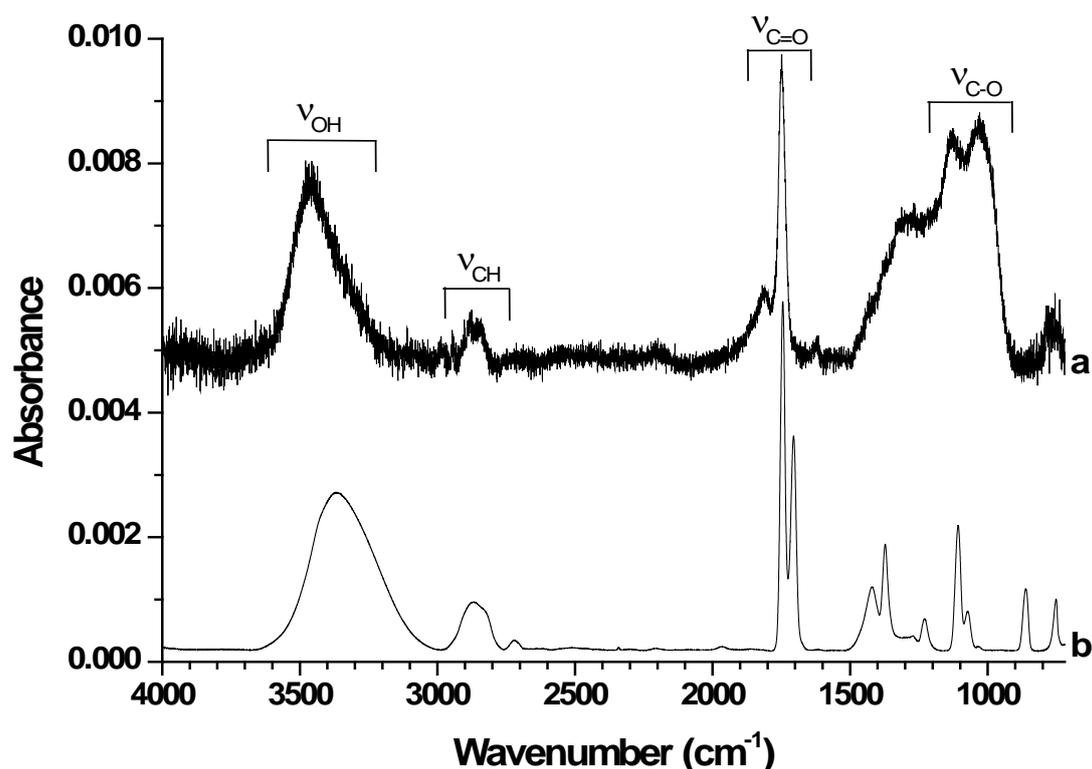


Figure 4: IR spectrum of: (a) the organic residues derived  $\text{CHOCHO} + \text{H}/\text{H}_2$  sample formed at 10 K and heated to 300 K, (b) Deposition of pure glycolaldehyde ( $\text{CHOCH}_2\text{OH}$ ) on a substrate maintained at 10 K. The signal of this reference spectrum is divided by 100 to have the intensity of the  $\nu_{\text{C=O}}$  band comparable to that of the organic residues.

These organic residues are characterized by a wide absorption band located between 3250 and 3700  $\text{cm}^{-1}$  and characteristic of the OH functional group. Two peaks are detected in the C=O spectral region at 1812 and 1749  $\text{cm}^{-1}$ , in addition to two signals at 1132 and 1033  $\text{cm}^{-1}$  which may be assigned to the C-O bonds. The absorption band observed between 2944 and 2862  $\text{cm}^{-1}$  may be attributed to the C-H stretching mode while the shoulder around 1320  $\text{cm}^{-1}$  would be assigned to the C-H bending modes. Table 1 draws a tentative assignment of the main IR absorption bands of the organic residues formed under our experimental conditions.

The comparison between the IR Spectra of the residual products and glycolaldehyde ice shows that there is a structural analogy between the two solid samples. The IR signal corresponding to the C=O stretching mode of glycolaldehyde ice is located at 1745  $\text{cm}^{-1}$  while that of the organic residues is at 1749  $\text{cm}^{-1}$ . The IR spectrum of the residual products shows two absorption bands between 2750 and 3700  $\text{cm}^{-1}$  which have the same shape and intensity as for the OH and CH absorption bands of glycolaldehyde ice. There are also two bands in the 1100-1000  $\text{cm}^{-1}$  region which, although thinner in the IR spectrum of glycolaldehyde ice, are similar to those

observed in the IR spectrum of the residues. However, this structural analogy between the two solid samples would not allow to assign the residual solid to glycolaldehyde ice, because the former remains solid at 300 K whereas the latter desorbs around 190 K (Hudson et al. 2005).

Table 1: Assignments and intensities of main IR absorption bands of the organic residues (vs: very strong, s: strong, w: weak)

Vibration mode	Position (cm <sup>-1</sup> )	Intensity
O-H stretch	3464	s
C-H stretch	2944	w
C-H stretch	2862	w
C=O stretch	1812	w
C=O stretch	1749	vs
C-H bend	1320	s
C-O stretch	1132	s
C-O stretch	1033	s

Consequently, the residual products we form under our experimental conditions are therefore composed of OH functional groups and one or more functions involving a C=O bond (such as carboxylic acid, aldehyde, ketone, ester). The first hypothesis is that the C=O and O-H groups are on the same carbon, which means that the organic residues would be carboxylic acids. Five acids from two to four carbons have been selected as potential candidates (Figure 5). The most likely acids that could be formed would contain 2 carbon atoms such as:

- (i) acetic acid which is one of the simplest carboxylic acids.
- (ii) oxalic acid and glyoxylic acid which have a structure close glyoxal with two C=O functional groups.
- (iii) glycolic acid and diglycolic acid which have a CH<sub>2</sub> functional group.

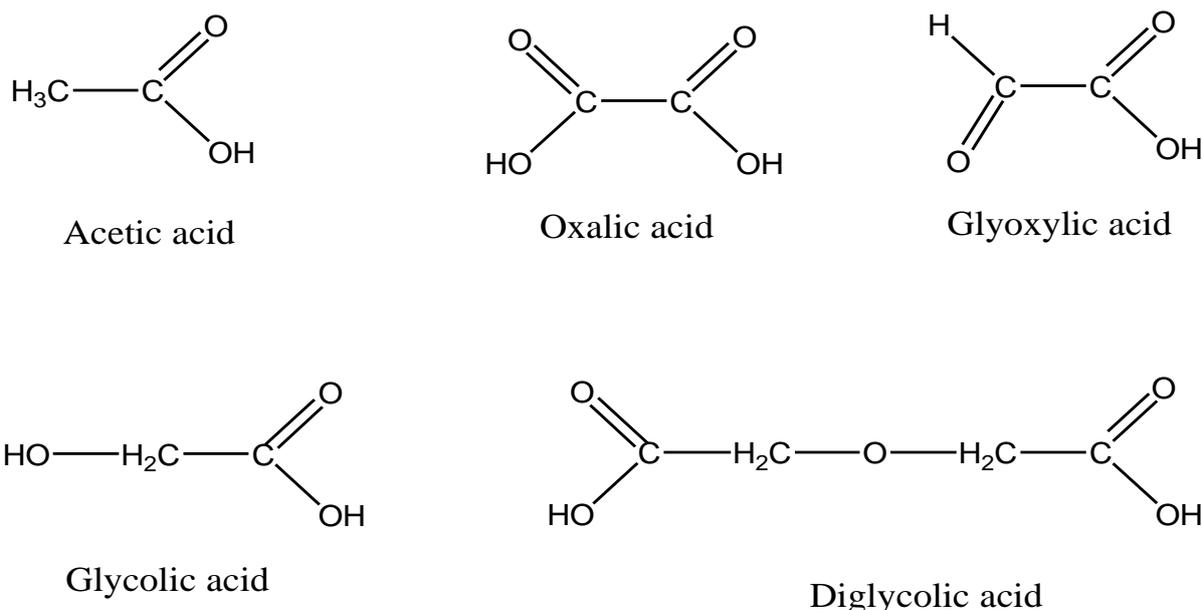


Figure 5: Potential carboxylic acid candidates for the organic residues

The residual products, we form through the thermal processing of CHOCHO + H reaction carried out at 10 K and heated to 300 K, are solid at room temperature and atmospheric pressure and consequently they cannot be aliphatic acids. The saturated aliphatic acids such as acetic acid, formic acid, propanoic acid, butanoic acid... are not solid at room temperature and atmospheric pressure. In fact, the melting point of acetic acid (ethanoic acid) is 290 K, while those of methanoic (formic acid), propanoic and butanoic acids are 282, 252 and 268 K, respectively (Kippling and Tester 1952, McDonald et al. 1959, Johnson and Cole 1951, Dreisbach and Martin 1949, Kohler et al. 1981, Radwan and Hanna 1976). Four other acids with higher melting points (Wilhoit and Shiao 1964; Bradley et al 2014) have been proposed as potential candidates for the residual products: oxalic acid (mp: 464 K), glyoxylic (mp: 353 K), glycolic acid (mp: 348 K) and diglycolic acid (mp: 416 K). Table 2 lists the IR spectral positions of the OH, CH, C=O and C-O functional groups of the residues we form and those of the four acids we propose.

Table 2: Spectral positions of OH, CH, C=O and C-O functional groups in 4 acids compared to those of the residues formed under our experimental conditions  
(source: Spectral Database of Organic Compounds SDBS)

Vibration mode	O-H stretch	C-H stretch	C=O stretch	C-O stretch
<b>Organic Residues</b>	<b>3464</b>	<b>2944, 2862</b>	<b>1749</b>	<b>1132, 1033</b>
Oxalic acid	3424	-	1685	1263, 1126
Glyoxylic acid	3360	2990	1740	1207, 1104, 1043
Glycolic acid	3297	2940	1729	1264, 1086
Diglycolic acid	3027	2926	1746	1196, 1151, 1043

The residual products we form have a characteristic C=O absorption band ( $1749\text{ cm}^{-1}$ ) whose spectral position fits only that of glyoxylic acid ( $1740\text{ cm}^{-1}$ ) and diglycolic acid ( $1746\text{ cm}^{-1}$ ). This would exclude oxalic acid ( $1685\text{ cm}^{-1}$ ) and glycolic acid ( $1729\text{ cm}^{-1}$ ) as potential candidates of the organic residues. However, glyoxylic acid ( $1740\text{ cm}^{-1}$ ) and diglycolic acid ( $1746\text{ cm}^{-1}$ ) have their OH spectral position at  $3360$  and  $3027\text{ cm}^{-1}$  while the OH band of the residual products is located at  $3464\text{ cm}^{-1}$  and this would reject the diglycolic acid from the acids list we propose. Consequently, the only acid which would slightly fit the residual products could be the glyoxylic acid ( $1740\text{ cm}^{-1}$ ) whose structure is similar to glyoxal where an H atom is substituted by an OH group. Such an acid has its C=O and O–H functional groups on the same carbon atom but it shows at atmospheric pressure a relative low melting point ( $353\text{ K}$ ) similar to that of glycolaldehyde ( $370\text{ K}$ ) and it cannot be considered as one of the residues we form. Another hypothesis is that the C=O and O-H functional groups are not on the same carbon atom. Even without considering long chains of carbon atoms, many molecules may correspond to this description. A sorting is done by taking into account the structure of the reagent which is the starting molecule (glyoxal: CHOCHO) and the possible radicals formed during the CHOCHO + H/H<sub>2</sub> reaction. We found that at  $10\text{ K}$ , the main reaction products are CO, H<sub>2</sub>CO, CO-H<sub>2</sub>CO intermediate and CH<sub>3</sub>OH as a secondary product. Thus, the presence of CH<sub>3</sub>OH resulting from the hydrogenation of H<sub>2</sub>CO indicates also the presence of  $\cdot\text{CH}_2\text{OH}$  and  $\cdot\text{OCH}_3$  (Hiraoka et al. 1999; Fuchs et al. 2009; Hama & Watanabe 2013) as intermediates in the CHOCHO + H/H<sub>2</sub> solid sample.



The trapping of such intermediates in glyoxal ice would lead to two potential candidates for the organic residues: the hydroxypyruvaldehyde and methyl glyoxylate (Figure 6).

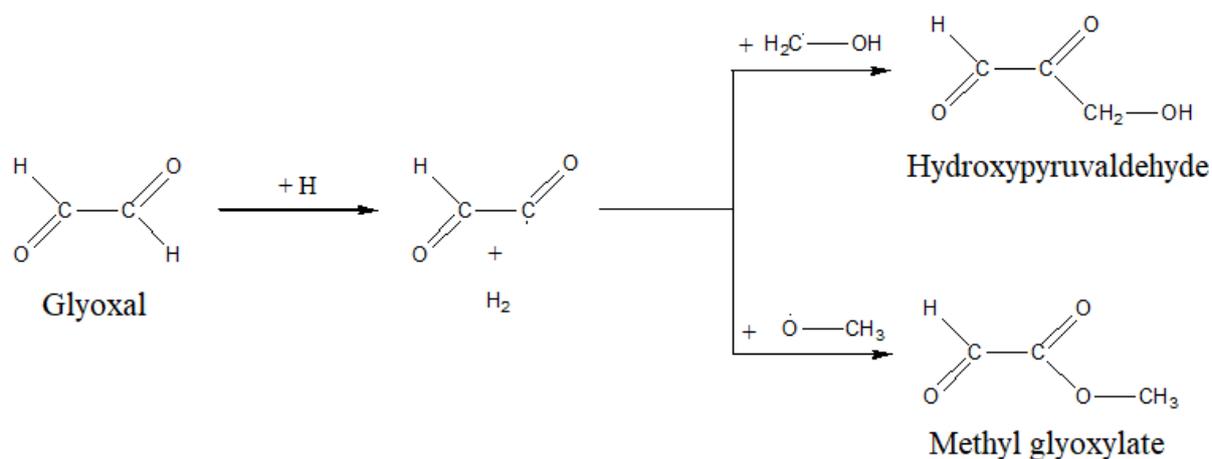


Figure 6: Reaction pathways for the formation of the organic residues.

The formation of these two organic residues would start with a hydrogen abstraction from the glyoxal to form the radical  $\text{CHOCO}$  which may recombine to  $\cdot\text{CH}_2\text{OH}$  or  $\cdot\text{OCH}_3$  radicals to form  $\text{CHOCOOCH}_3$  and  $\text{CHOCOCH}_2\text{OH}$ , respectively.

Hydroxypyruvaldehyde is characterized by C=O, CH and CH<sub>2</sub> functional groups in addition to ketone and alcohol functions. Methyl glyoxylate is characterized by aldehyde and ester functions. The hypothesis is that the residual products formed during the thermal processing of  $\text{CHOCHO} + \text{H}/\text{H}_2$  ice would be a mixture of these two organic compounds which are solid at room temperature and atmospheric pressure. We have synthesized and recorded at room temperature, using a KBr disk, the IR spectra of hydroxypyruvaldehyde and methylglyoxylate in order to get a comparison between these two solid species and the residual products.

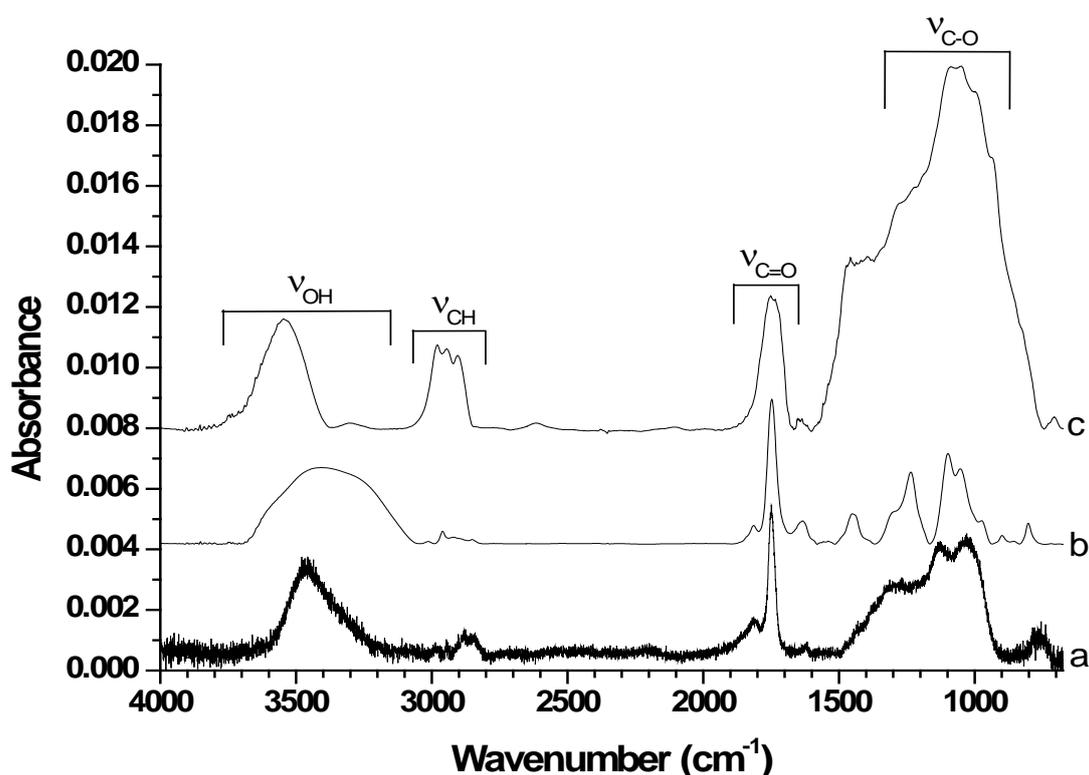


Figure 7: IR Spectrum at room temperature and atmospheric pressure of (a) the organic residues (b)  $\text{CHO}(\text{CO})\text{OCH}_3$  (methyl glyoxylate) and (c)  $\text{CHOCOCH}_2\text{OH}$  (hydroxypyruvaldehyde).

Figure 7 shows the IR spectra of the residual products, hydroxypyruvaldehyde and methyl glyoxylate recorded at room temperature and atmospheric pressure. The three spectra show a great similarity where the CO functional group of the residual products is located at  $1749\text{ cm}^{-1}$  while that of  $\text{CHOCOCH}_2\text{OH}$  and  $\text{CHO}(\text{CO})\text{OCH}_3$  is at  $1747$  and  $1746\text{ cm}^{-1}$ , respectively, indicating a spectral position difference of only 2 to  $3\text{ cm}^{-1}$ . In addition, methylglyoxylate has a band at  $1810\text{ cm}^{-1}$ , also observed in the IR spectrum of the residual products at  $1812\text{ cm}^{-1}$ . The comparison between the three IR spectra of figure 7 suggests that the IR spectrum of the residual products would be a combination of the two IR spectra of hydroxypyruvaldehyde and methyl glyoxylate. Consequently, among the organic molecules that may be formed through the thermal processing of  $\text{CHOCHO} + \text{H}$  reaction carried out at  $10\text{ K}$ , hydroxypyruvaldehyde and methyl glyoxylate mixture would correspond to the residual products we detect under interstellar conditions and it could be part of the composition of the interstellar grains. The formation of hydroxypyruvaldehyde and methyl glyoxylate under interstellar conditions is due

to the recombination of radicals formed during the  $\text{CHOCHO} + \text{H}/\text{H}_2$  solid state reaction and which may be induced by thermal processing, during the heating of the sample.

In the interstellar medium, dust particles are composed of carbon and silicon, elements generated firstly in stars and supernova explosions. C- and Si-bearing molecules such as graphite and silicate are present in variable amounts in the interstellar dust grains (Tielens and Allamandola 1987; Draine 2003). The spectral analysis of these two components of dust grains is performed in different spectral regions:

- 9.7 and 18  $\mu\text{m}$  characteristic of Si-O stretching and O-Si-O bending modes of silicate minerals, respectively.

- 3.4  $\mu\text{m}$  characteristic of CH stretching of aliphatic hydrocarbons (Pendleton et al. 1994; Mennella et al. 2003; Siebenmorgen et al. 2014).

As mentioned in the introduction part, dust grains serve as a support of accretion for many volatile molecules which form at low temperatures the icy mantles of the interstellar grains (Greenberg et al. 1995; Srama et al 2009). When the temperature rises in excess of 200 K, the most volatile part of the interstellar ices desorbs while the less volatile part, the solid materials, would enter into the composition of the dust and its growth (Greenberg et al. 1995). Using UV irradiation or high energy particles and subsequent warm-up of interstellar ice analogs (Modica et al. 2014; Greenberg et al. 1995; d’Hendecourt et al. 2019), laboratory experiments have already shown that such solid residues, which can be considered as organic interstellar dusts created in situ in molecular clouds and not derived from stars explosions, would be formed preferentially in photo-dominated regions (PDRs) of the ISM. Our results show that reactions involving H-atoms and glyoxal molecules could also be a source of residual products. Consequently, residues or organic dusts could be formed in dark molecular clouds without UV or cosmic rays involvement.

#### 4. Conclusion

Organic residues play an important role in the chemistry of the interstellar medium. These solid residues are known to contain several pre-biotic molecules such as amino acids, nucleic bases, sugars. . . which may involve in molecules carrying the genetic information. Although their formation has been investigated by numerous groups, mainly through UV-photolysis or particle-irradiation of interstellar ice analogues followed by thermal processing, we show for the first time a new reaction pathway which leads to residual species through  $\text{CHOCHO} + \text{H}$  solid state reaction. This study demonstrates that the co-injection  $\text{CHOCHO} + \text{H}/\text{H}_2$  at 10K

followed by a sample heating leads to CO, H<sub>2</sub>CO, and CH<sub>3</sub>OH species which remain trapped in CHOCHO ice in 10–160K temperature range. The sublimation of glyoxal ice when the temperature rises in excess of 200K leads to residual products which remain stable in solid phase at room temperature and atmospheric pressure. We show that the residues formed under our experimental conditions would be a mixture of hydroxypyruvaldehyde and methylglyoxylate formed by CH<sub>2</sub>OH + CHOCO and CH<sub>3</sub>O + CHOCO radical combination, respectively. While CHOCO radical results from H abstraction from glyoxal (CHOCHO + H → CHOC<sup>•</sup>O + H<sub>2</sub>), CH<sub>2</sub>OH, and CH<sub>3</sub>O radicals are formed and trapped in CHOCHO ice as secondary products due to secondary hydrogenations of formaldehyde (H<sub>2</sub>CO + H → C<sup>•</sup>H<sub>2</sub>OH / O<sup>•</sup>CH<sub>3</sub>).

### Data availability

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

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