LABORATORY INVESTIGATION OF X-RAY PHOTOLYSIS OF ETHANOL ICE AND ITS IMPLICATION ON ASTROPHYSICAL ENVIRONMENTS

FOTÓLISE DE GELO DE ETANOL POR RAIOS-X E SUAS IMPLICAÇÕES EM AMBIENTES ASTROFÍSICOS

Sergio Pilling[1]
Fabricio M. Freitas[2]

Abstract: Here we present experimental results on the irradiation of ethanol ice (CH_3CH_2OH) by broadband soft X-rays to simulate the effect processing of organic-rich astrophysical ices by space radiation. This molecule was detected in the interstellar medium in molecular clouds like Sagittarius B2 and towards nebulas like Orion KL. The experiments were performed at the Brazilian Synchrotron Facility LNLS/CNPEM, at Campinas, SP. The frozen sample was analyzed in-situ by infrared spectroscopy (IR) in a simulated astrophysical environment at different radiation fluences. The results show the formation of several new molecular species such as CO_2, CO, H_2O, CH_4, $CH_3(CO)CH_3$ (acetone), and CH_3COOH (acetic acid). We determined the effective destruction cross-section of ethanol ($\sim 1\times10^{-18}$ cm^2) and the formation cross-sections of the daughter species with values between 0.5 to 3.4×10^{-18} cm^2. The chemical equilibrium phase of ice was characterized and desorption yield induced by X-rays was determined (0.13 molecules $photon^{-1}$). The result helps us to understand the photolysis induced by X-rays in organic-rich ices in space environments.

Keywords: Experimental Astrochemistry; Astrophysical ices; Ethanol; X-rays; Desorption; Synchrotron Radiation.

Resumo. Neste trabalho experimental apresentamos resultados da irradiação de gelo de etanol (CH_3CH_2OH) por raios-X moles (feixe de banda larga) simulando, assim, os efeitos do processamento de gelos astrofísicos ricos em moléculas orgânica em ambientes espaciais. Esta molécula foi detectada no meio interestelar em regiões como Sagittarius B2 e Orion KL. Os experimentos foram realizados no laboratório de luz sincrotron LNLS/CNPEM em Campinas, SP. A amostra congelada foi analisada *in-situ* por espectroscopia no infravermelho (IR) em um ambiente em vácuo e foi exposta a diferentes fluências de radiação. Os resultados mostram a formação de várias novas espécies moleculares, como CO_2, CO, H_2O, CH_4, $CH_3(CO)CH_3$ (acetona) e CH_3COOH (ácido acético). Determinamos a seção de choque efetiva de destruição do etanol ($\sim 1\times10^{-18}$ cm^2). A seção de choque efetiva de formação das espécies filhas obtida teve valores entre 0,5 a $3{,}4\times10^{-18}$ cm^2. A fase de equilíbrio químico do gelo foi caracterizada e o dessorção total de moléculas pra fase gasosa, induzida por raios-X moles foi determinada (0,13 moléculas fóton-^{1}). Os resultados encontrados permite entender melhor os processos de fotólise induzidos por raios-X moles em gelos ricos em matéria orgânica em ambientes espaciais.

Palavras-chave: Astroquímica experimental; Gelos astrofísicos; Etanol; X-rays; Desorção; radiação sincrotron.

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[1] Coordenador do Laboratório de Astroquímica e Astrobiologia (LASA) da Universidade do Vale do Paraíba - Univap. E-mail: sergiopilling@yahoo.com.br.
[2] Universidade do Vale do Paraíba. E-mail: fmfreitas@gmail.com.

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1 INTRODUCTION

Ethanol (CH_3CH_2OH), one of the simplest alcohols, was first in detected in space toward the region of Sagittarius B2 molecular cloud by Zuckerman et al. (1975). Later, it was also detected in the submillimeter spectrum of the molecular cloud towards G34.3 + 0.15 (Millar et al*.,* 1995). More recently, ethanol has been also detected in other objects such as toward the Orion KL region (Pearson et al*.,* 1997) and several molecular clouds towards the galactic center (Requena-Torres et al., 2006). Besides the gas-phase findings, this species has been studied in the solid phase in relevant ice matrices by comparison with FTIR transmission spectroscopy (Schriver et al., 2007; Van Scheltinga et al*.,* 2018)

Millar et al*. (*1995) concluded that such a large abundance of ethanol must be formed efficiently by grain surface chemistry. One explanation is that grains could hold an appreciable amount of ethanol ice, which is released to the gas-phase when a newborn star heats the surrounding gas and dust. Ethanol molecules evaporated from ice mantles can then participate in subsequent gas-phase reactions in those regions (Charnley et al., 1995).

Here, we present results from the experiments of the irradiation of solid ethanol in the presence of broadband soft X-rays (6 to 2000 eV), in an attempt to simulates radiation induced chemistry ethanol-rich ices presented in the interstellar medium, and interplanetary medium and other space environments. The same technique employed in this article was useful for analyzing the destruction/formation of other molecules in LASA/UNIVAP´s experiments such as the irradiation of SO_2 ice at 12 K (Bonfim et al., 2017), pure $HCOOCH_3$ ice at 12 K (Rachid et al., 2017), a binary ice mixture N_2:CH_4 (19:1) at 12 K (Vasconcelos et al., 2017), a quaternary ice mixture H_2O:CO_2:NH_3:SO_2 (10:1:1:1) at two different temperatures (50 K and 90 K) (Pilling & Bergantini, 2015), CH_3OH pure ice at 12 K bombarded by soft X-rays (6 to 2000 eV) and by fast electrons (4.9 keV) (Freitas & Pilling, 2022) and CH_3CN pure ice at 13 K bombarded by soft X-rays (6 to 2000 eV) (Carvalho & Pilling, 2020a).

2 METHODOLOGY

The current experiment was conducted employing a LASA/UNIVAP´s portable vacuum chamber coupled to the SGM beamline of the Brazilian Synchrotron Light Source (LNLS/CNPEM). We operate the beamline in off-focus (beam size ~0.5 cm^2 to fully illuminate the sample) and broadband mode to simulate the effects caused by broadband soft X-rays with a small fraction of UV photons (6 to 2000 eV) in an icy sample. The average flux was 1×10^{14} photons cm^{-2} s^{-1}. The pressure in the main chamber was below 2×10^{-8} mbar. More details were given by Pilling and Bergantini (2015). Briefly, gaseous CH_3CH_2OH was slowly deposited into a clean ZnSe substrate crystal couple to helium closed-cycle cryostat connected to the vacuum chamber, through a capillary tube for about 5 minutes forming ice with ~1.1 μm of initial thickness.

The icy sample's chemical changes were monitored by transmittance infrared spectroscopy (Agilent Cary-630 Portable FTIR). The infrared (IR) spectra obtained has a resolution of 2 cm^{-1} and a spectral range of 4000 cm^{-1} to 800 cm^{-1}.

From the analysis of the band area in the IR spectra together with the knowledge of IR band-strength of the assigned molecular species (Hudgins et al., 1993; Bennett & Kaiser, 2007; Bouilloud et al*.,* 2015; Hudson & Moore, 2018) we determined the column density of the molecular species (or molecular abundances) following the methodology described by Pilling et al*.* (2010a; 2010b; 2011). The column density of pure ethanol ranges from 2.9×10^{18} molecule cm^{-2} (initial value) to 1.7×10^{18} molecule cm^{-2} (final value after irradiation). The ice was irradiated with broadband soft X-rays during 240 minutes (Fluence = 1.9×10^{18} cm^{-2}) at a constant temperature of 12 K.

3 RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of un-irradiated and irradiated ethanol (after 240 minutes of soft X-ray irradiation), presented in the panels a and b, respectively. The main IR bands are indicated in the figures. In the case of ethanol the main observed bands were: the -C-C- stretch at 879.8 cm^{-1}, the stretch -C-O- at ~1051 cm^{-1}, the -C-H rocking at 1090.5 cm^{-1}, and the -O-H stretch at the 3391 cm^{-1}.

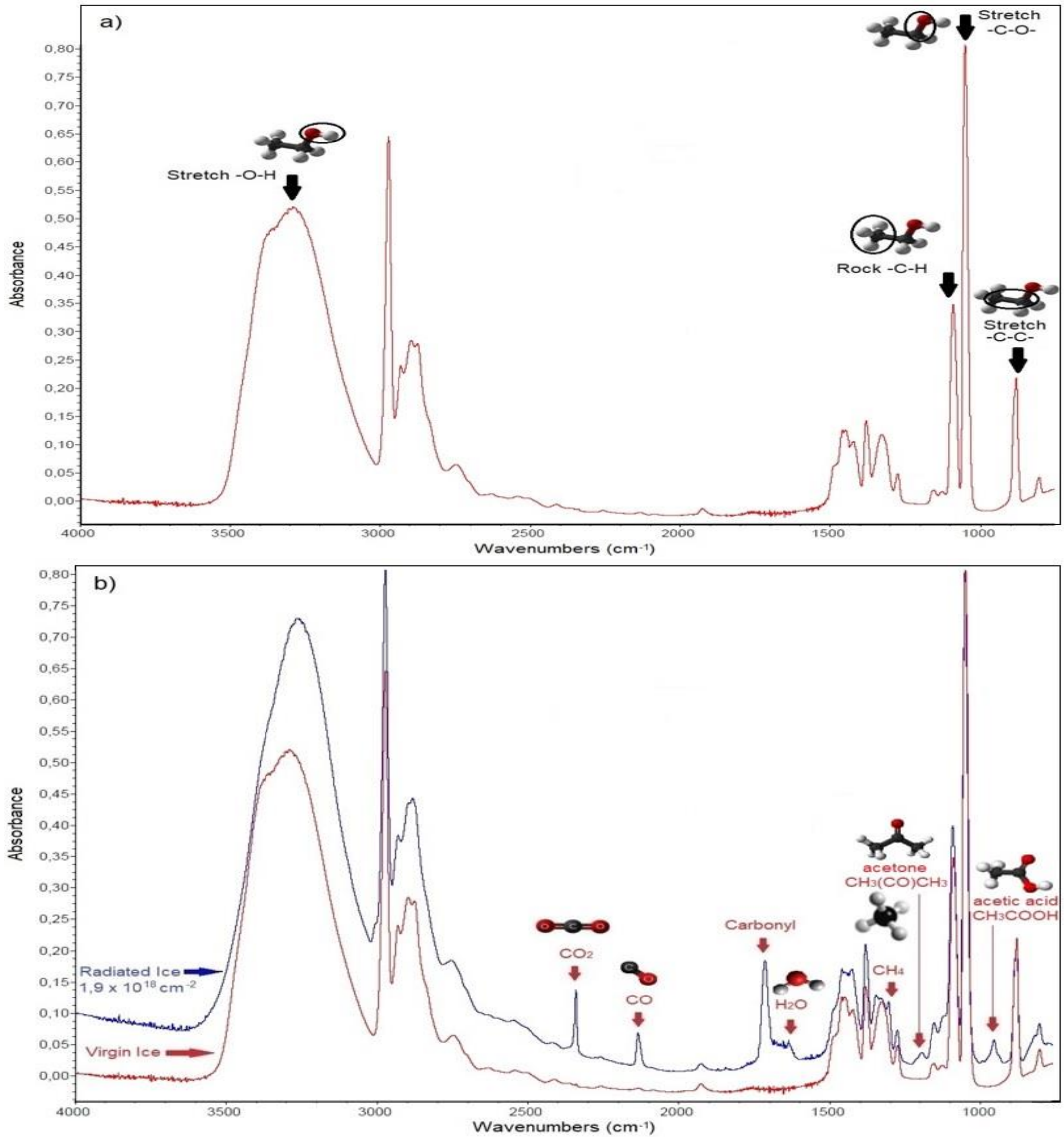
The new IR bands associated with the new produced molecular species as results of irradiation of ethanol are also indicated in panel b. Details of the eventual reaction routes triggered by the incoming radiation in the ethanol ice will be presented in future publication with the application of the PROCODA code (e.g. Pilling et al*.,* 2022; Carvalho et al. 2022).

The changes of molecular abundances as a function of radiation fluency (destruction or production) were evaluated by the analysis of infrared area evolution with fluence using the equation:

$$S(F) - S_0 = S_\infty \times [1 - \mathrm{EXP}(-\sigma_{d,f} \times F)] \ [cm^{-1}] \qquad [1]$$

where S(F), S_0 and S_∞ are the band areas of the infrared spectrum, at a given fluence F, at the beginning of the experiment (virgin sample) and at the highest fluence (named terminal experimental fluence), respectively. In this equation, F is the radiation fluence, in units of cm^{-2} and $\sigma_{d,f}$ represents the effective formation cross section (σ_f) new-formed species or the effective destruction cross section (σ_d) parent species, both in units of cm^2 (Pilling & Bergantini, 2015).

Figure 1 - a) The infrared spectrum of the virgin ethanol ice at 12 K showing its main vibrational modes. b) Overlap of the virgin ethanol ice (red line) and irradiated ice spectra after 240 minutes (Fluence = 1.9 x10^{18} cm^{-2}) of exposure soft X-rays (6 to 2000 eV).



Source: The authors.

Figure 2 presents the subtracted band area (proportional to the molecular abundances) as a function of fluence. Lines are the best fits employing equation 1. The values for the effective cross section determined are also shown. The upper panel (positive values) presents the new produced species due to irradiation with broadband soft X-rays (6 - 2000 eV) and the lower panel (negative values) presents the destruction (or dissociation) of parts of the ethanol molecule (by quantifying the decreasing of bands associated with its respective vibration modes). The formation cross section of the carbonyl (functional group composed of a carbon atom double-bounded to an oxygen atom) was 1.1×10^{-18} cm^2 but, as this group is present in two observed daughter species ($CH_3(CO)CH_3$, and CH_3COOH) and possible other molecules like acetaldehyde and formaldehyde, it was not discussed in this manuscript. The uncertainty in the fluency and in the subtracted band area are around 20% due to small decrease of flux of the beam line with time as discussed by Pilling and Bergantini (2015).

Figure 2 - Evolution of the difference band areas of identified ethanol daughter species (upper panel) and four ethanol band areas (bottom panel) during the experiment irradiated with soft X-rays as a function of fluence.

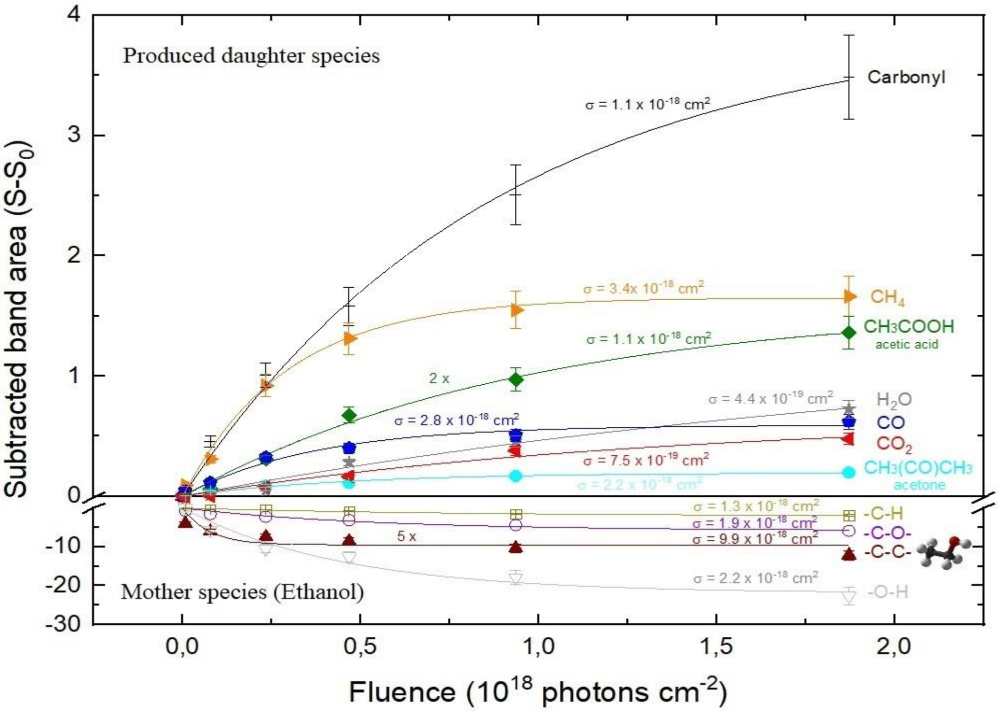


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Table 1 presents the effective destruction cross sections of pure ethanol (from different vibrational modes) and effective formation cross section of new products (CO_2, CO, H_2O, CH_4, $CH_3(CO)CH_3$, and CH_3COOH), due to the irradiation by soft X-rays. The term effective employed here describes the average values of this physicochemical parameter since the embedded molecules have different chemical environments within the ice; additionally, the effective cross sections varies with radiation fluence. Such variable chemical scenario during the irradiation phase also induces a variation in the efficiency of chemical routes, as a function of radiation fluence, and the term effective was employed also in an attempt to handle this issue.

The -C-C- stretch was considered here to represent the effective destruction of ethanol ice due to the break between the two carbons (ethanol´s “backbone”; see also Portugal et al., 2014). This effective destruction cross section ($\sim 1 \times 10^{-18}$ cm^2) is half the value obtained with pure methanol ($\sim 2.1 \times 10^{-18}$ cm^2) using the same experimental conditions (Freitas & Pilling, 2020). The term "effective" was used to consider the fact that the average values of the cross sections, as well as the molecular yields, depend on the chemical environments in the icy sample (surrounding molecules). Therefore, such parameters may have different values locally. In addition, the sample composition also changes during the experiments and an effective value is a way to handle this issue.

Following the methodology described by Pilling et al. (2019) and Carvalho and Pilling (2020a), by considering the mass conservation criterium, we determined by employing the column mass (the column density multiplied by the molecular mass of the considered species) of the observed species and estimated the column mass of the non-observed (or unknown) species and the desorption column mass, as well as, the desorption yield. To determine the desorption yield it was also assumed that, although we could not observe all the produced daughter species, the desorbed mass of the non-observed species (calculated in terms of column mass) should have the same proportion of the desorbed mass of observed species in the IR spectrum. The considered value for desorption yield (Y) in this work was 0.13 molecule photons^{-1}, a value which satisfies the mass conservation criterium and also the equilibrium chemistry criteria that should exist in the ice at larger radiation fluences (see also Pilling et al*.,* 2022). The desorption yield found in this experiment is 0.7 times the desorption yield determined in a previous investigation carried out with methanol, employing the same ionizing agent, experimental chamber, ice temperature and methodology (Freitas & Pilling, 2020).

Table 1 - Effective destruction cross sections of pure ethanol (determined from different vibrational modes) and the effective formation cross section of the new products due to the irradiation of ethanol ice at 12K by soft X-rays.

Molecular species (vibration mode)	**Wavenumber (cm^{-1})**	**σ_d (cm^2)**	**σ_f (cm^2)**
Ethanol (stretch -O-H)	3391	2.2×10^{-18}	-
Ethanol (rock -C-H)	1091	1.3×10^{-18}	-
Ethanol (stretch -C-O-)	1051	1.9×10^{-18}	-
Ethanol (stretch -C-C-)*	880	$\sim 1 \times 10^{-18}$	-
CO_2	2342	-	7.5×10^{-19}
CO	2136	-	2.8×10^{-18}
H_2O	1657	-	4.4×10^{-19}
CH_4	1301	-	3.4×10^{-18}
$CH_3(CO)CH_3$	1200	-	2.2×10^{-18}
CH_3COOH	839	-	1.1×10^{-18}

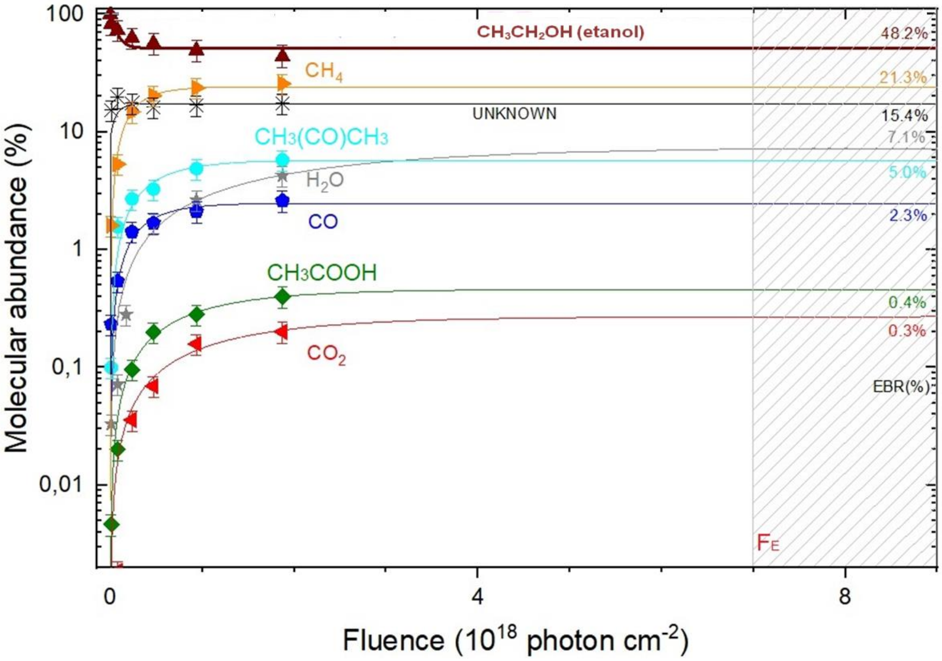
* Considered as ethanol reference band for the effective destruction cross section (ethanol´s “backbone”).

Source: The authors.

Figure 3 presents the evolution of the molecular abundances, in percentage, of the molecular species present in irradiated ice sample, as a function of broadband soft X-rays fluence. The hashed rectangle bar indicates the region of the chemical equilibrium (CE). From this fluency onwards the chemical composition of the sample practically does not change during the processing by the ionizing radiation. Additional details on the CE phase can be obtained elsewhere (e.g. Rachid et al*.,* 2017; Vasconcelos et al*.,* 2017; Pilling et al., 2019)). The values listed inside the hashed rectangle bar are the abundances in the chemical equilibrium also named as equilibrium branching ratio (EBR). In this figure, it is easy to observe that the evolution of molecular abundances tends to reach a plateau at larger fluences, indicating the appearing of this CE phase. In the current experiment, this occurs at fluences of about $F_E \sim 7\times10^{18}$ photons cm^{-2}. The lines observed in this figure are the best-fit model employing a slightly modified version of equation (1), written in terms of column density instead difference band area, up to the fluences 9×10^{18} photons cm^{-2} to show the appearing of an horizontal plateau (the chemical equilibrium phase).

The comparison between the current results with a previous investigation on methanol ice at 12 K irradiated by X-rays employing the same methodology (Freitas & Pilling, 2020) shows that destruction of ethanol is higher (roughly 5 times) than the determined for the methanol. Additionally, the produced set of new species due to the incoming radiation is different within these ices. For example, in the methanol experiment the daughter species acetone and acetic acid were not observed. It is worth mentioning that the effective formation cross-section of CO and CO_2 was higher in the ethanol ice experiment.

Figure 3 - Evolution of the molecular abundances, in percentage, of the molecular species present in irradiated ice sample, as a function of broadband soft X-rays fluence. The hashed rectangle indicates the region of the chemical equilibrium (no further modification in the ice happens).



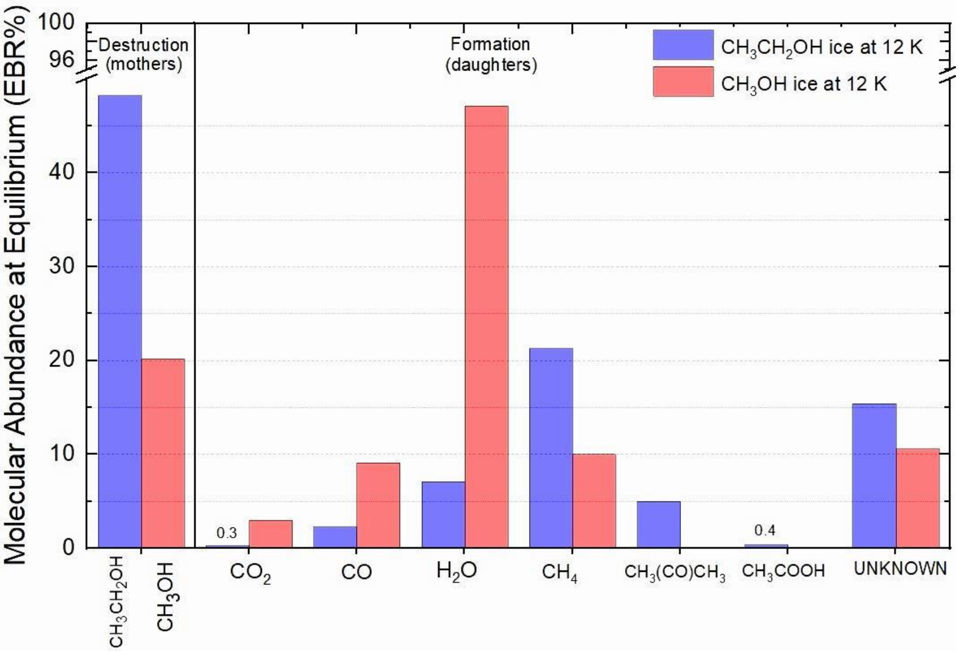
Source: The authors.

Figure 4 presents a comparison between the molecular abundances determined at the CE phase in the experiments employing pure ethanol ice (this work) and pure methanol ice (Freitas & Pilling, 2020), both ices irradiated with broadband soft X-rays and recorded with the same instrumentation. The comparison shows that the proportion of parent species is more significant in ethanol sample. In contrast, the formation of H_2O is considerably higher in pure methanol. Based on the observations, the proportion unknown, species in the ethanol experiment, should be enriched in oxygen atoms due to the low production of observed species containing this atom, such as CO_2, CO and H_2O in this sample. Finally, the absence of acetone and acetic acid, daughter species not observed in the methanol experiment, indicates that the reaction routes to produce this species are highly dependent of ethanol or its main products.

Astrophysical implications

According to the current experiment, methane (CH_4) is one of the more abundant new produced species (21% at the chemical equilibrium). We can then suppose that species like species like the volatile ices CH_4, CO, CO_2 that dominate Pluto's surface (Grundy et al., 2016) and that are also observed in Neptune Satellite Triton (Owen et al*.,* 1993), could have been produced from astrophysical ices enriched by ethanol in our Solar system. Additionally, this same argument can be also applied for acetone (5% at the chemical equilibrium), and for acetic acid (0.4% at the chemical equilibrium), both observed in giant molecular cloud Sagittarius B2 (Combes et al*.,* 1987, Mehringer et al*.,* 1997) where ethanol was also detected (Zuckerman et al*.,* 1975; Requena-Torres et al., 2006).

Figure 4 – Comparison between the molecular abundance at the chemical equilibrium of CH_3OH (Freitas & Pilling, 2020) and CH_3CH_2OH (this work) in the experiments carried out with broadband soft X-rays (6 - 2000 eV), both at 12 K and employing the same instrumentation.



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As pointed by Pilling et al*.,* (2019) and Carvalho and Pilling (2020b), by knowing the fluence to reach chemical equilibrium at lab we can also estimate the timescale to reach chemical equilibrium (TS_E) in space environments. The estimated timescale for ethanol ices at 12 K, exposed to solar VUV and soft X-rays, hypothetically present at the Saturn orbit (at 9.5 AU; photon flux of 8×10^9 cm^{-2} s^{-1}; (Gueymard, 2004; Pilling & Bergantini, 2015)) was around 30 years. In the case of ices at Triton orbit (~30 AU; photon flux of 9×10^6 cm^{-2} s^{-1}; (Gueymard, 2004; Pilling & Bergantini, 2015)) and KBOs typical orbit (~40 AU; photon flux of 5×10^3 cm^{-2} s^{-1}; (Gueymard, 2004; Pilling & Bergantini, 2015)), the estimated TS_E values were ~3×10^4 and ~4×10^7 years. We also estimate the TS_E for hypothetical ethanol rich ices at 12 K outside the solar system in the presence of incoming soft-X rays, for comparison purpose.

Finally, the TS_E for ethanol-rich ices at 12 K illuminated by X-rays at the distance of 3 lightyears (~2×10^5 AU) from the supermassive Black Hole in the center of our Galaxy, Sagittarius A* (photon flux of 5×10^3 cm^{-2} s^{-1}; Barrière et al*.,* 2014; Quataert, 2002) was around 4×10^7 years.

CONCLUSION

In this work, we present experimental results on the irradiation of ethanol ice (12 K) employing broadband soft X-rays (6-2000 eV) in an attempt to simulate the processing of astrophysical ices enriched by organic molecules, by ionizing radiation in space environments. The experiments were performed at the Brazilian Synchrotron facility LNLS/CNPEM and the sample analysis was conducted employing IR spectroscopy (FTIR). The main conclusions were:

i) New molecular species were produced during bombardment (CO_2, CO, H_2O, CH_4, $CH_3(CO)CH_3$, and CH_3COOH) The mass of unknown species was estimated by considering mass conservation in the system and molecular desorption. The desorption yield is estimated to be around 0.13 molecules per photon.

ii) The effective destruction cross section for ethanol due to the employed broadband X-rays is around $\sim 1 \times 10^{-18}$ cm^2. The effective formation cross-section of the daughter species were between 0.5 to 3.4×10^{-18} cm^2. The formation cross-section of CO in the current experiment is higher than the observed in previous experiment employing methanol with same methodology.

iii) The main photolysis product at chemical equilibrium (at large fluence) was CH_4 (21.3%) followed by the H_2O and $CH_3(CO)CH_3$ (7.1% and 5.0%, respectively).

iv) Timescales to reach the chemical equilibrium phase (TS_E) for pure ethanol ice irradiated by broadband soft X-rays (6 – 2000 eV) were estimated for some astrophysical environments.

This study helps to better clarify the effects of ionizing radiation on ethanol rich ices as well as the equilibrium chemistry phase that happens in icy surfaces in spaces and also corroborates that radiation induced chemistry by broadband soft X-rays plays an important role in astrophysical environments.

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