

Destruction of C₂H₄O₂ isomers in ice-phase by X-rays: Implication on the abundance of acetic acid and methyl formate in the interstellar medium

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Abstract. C₂H₄O₂ isomers, methyl formate (HCOOCH₃), acetic acid (CH₃COOH) and glycoaldehyde (HOCH₂CHO), have been detected in a lot of sources in ISM. However, their abundances are very different, with methyl formate much more abundant than the other two isomers. This fact may be related to the different destruction by ionizing radiation of these molecules. The goal of this work is experimentally study the photodissociation processes of methyl formate and acetic acid ices when exposed to broadband soft X-ray from 6 up to 2000 eV. The experiments were performed coupled to the SGM beamline in the Brazilian Synchrotron Light Source (LNLS/CNPEM) at Campinas, Brazil. The simulated astrophysical ices (12K) were monitored throughout the experiment using infrared vibrational spectroscopy. The analysis of processed ices allowed the determination of the effective destruction cross sections of the parent molecules as well as the effective formation cross section of daughter molecular species. The relative abundance between acetic acid and methyl formate ($N_{CH_3COOH}/N_{HCOOCH_3}$) in different astronomical scenarios and their column density evolution in the presence of X-rays were calculated and our results suggests that such radiation field can be one of the factors that explain the difference in the isomers C₂H₄O₂ abundances. We also quantified the daughter species after the establishment of a chemical equilibrium in the samples.

Keywords. Astrochemistry, X-rays, C₂H₄O₂, Methyl formate, Acetic acid.

1. Introduction

Of all the organic molecules detected so far in the interstellar medium, special attention has been paid to the C₂H₄O₂ isomers: methyl formate (HCOOCH₃), acetic acid (CH₃COOH) and glycoaldehyde (HOCH₂CHO). These species are involved in the synthesis of key biomolecules and they have been detected in a large variety of astronomical sources (Shiao *et al.* 2010 and references therein).

Besides the same molecular formula, the abundance of these species are quite different. To account the observed abundances of C₂H₄O₂ isomers three process must be considered for each molecule: (I) the formation pathways, (II) the desorption rates and (III) the different destruction of the molecules exposed to a radiation field. These molecules are formed in the surface of dust grains, that can be found in denser regions of clouds and protoplanetary disks. Then, in order to investigate the destruction of these molecules under a radiation field, we have to consider agents that can penetrate large column of gas, because these agents can influence the chemistry inside denser regions of protoplanetary disks and molecular clouds. X-ray and cosmic rays have low absorption cross-section, penetrating deeply inside dense molecular clouds and become an important source of

photodissociation and photoionization, even in embedded regions ISM (Pilling & Andrade 2012).

The present work examined the photodissociation of methyl formate and acetic acid frozen samples by broadband X-ray from 6 eV up to 2000 eV. The experiments were performed at 12K in attempt to minimize photodesorption processes induced by X-rays and to guarantee that photolysis products remains in the solid phase. Such low temperatures may be found in highly embedded regions of molecular clouds and some Young Stellar Objects (YSOs). The forming daughter species produced by radiolysis and the parent species were monitored by infrared spectroscopy. We also studied the difference in the isomers survival and the relative abundance in ice grain mantles and compared the experimental result with the available observational data.

2. Experimental methodology

In an attempt to simulate the photodissociation process triggered mainly by soft X-rays (broadband photon beam) on the $C_2H_4O_2$ isomers, methyl formate ($HCOOCH_3$) and acetic acid (CH_3COOH), we use a broadband soft X-ray (6-2000 eV). We utilized the facilities of the Brazilian Synchrotron Light Laboratory (LNLS) located in Campinas, Brazil. The experiments were performed using a high-vacuum portable chamber from the Laboratrio de Astroqumica e Astrobiologia (LASA/ UNIVAP) coupled to the spherical grating monochromator (SGM) beamline, which was operated in the off-focus and white beam mode, producing a wide spectral range of ionizing photons (mainly from 6 eV up to 2000 eV). The beamline details can be found elsewhere (Castro *et al.* 1997, Rodrigues *et al.* 1998).

Briefly, the samples were deposited on a polished and clean ZnSe substrate (transparent to IR) previously cooled to 12K. For methyl formate experiment, the icy film was prepared by depositing 5 mbar of methyl formate gas during roughly 120s. For the acetic acid experiment, the sample was prepared by depositing roughly 3 mbar of acetic acid gas during around 120s. The vapor pressure of methyl formate and acetic acid at room temperature was also measured and the values were around 200 mbar and 15.5 mbar, respectively. In situ chemical analyses of the samples were performed by a portable Fourier transform infrared (FTIR) spectrometer (Agilent Inc., model Cary 630) coupled to the experimental chamber. The spectra were taken from 4000 cm^{-1} to 600 cm^{-1} with resolution of 2 cm^{-1} . The pressure inside the vacuum chamber during the irradiation process was below 10^8 mbar.

As discussed by Pilling and Bergantini (2015), the integrated photon flux in the sample, correspondent to 6-2000eV was estimated as $1.4\ 10^{14}\text{ photons cm}^{-2}\text{ s}^{-1}$ and the integrated energy flux was approximately $7.6\ 10^4\text{ erg cm}^{-2}\text{ s}^{-1}$. The photon flux profile from SGM beamline is similar to the radiation distribution of YSOs due to the large X-ray component produced by infalling material in protostars. In addition, the radiation distribution of YSOs in the soft X-ray range, as observed for T-Tauri stars (e.g., Imanishi *et al.* 2002), has a maximum around 1 keV, which is similar to the radiation spectra of the employed synchrotron beamline. In these experiment we simulated the effects of induced fast photoelectrons (keV) and slow (eV) secondary electrons, produced by X-rays, in the pure ice samples.

3. Results

The Figures 1 and 2 present the infrared spectra of methyl formate and acetic acid before (uppermost line) and after irradiation, at different irradiation times. The daughter

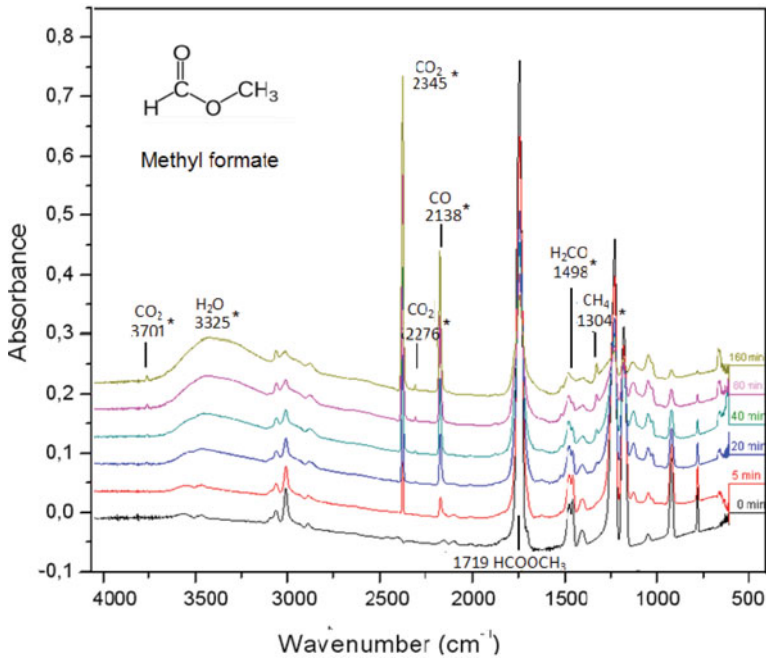


Figure 1. Infrared spectra of frozen methyl formate at 12K during isothermal irradiation with broadband soft X-ray (6 - 2000 eV) at different irradiation times. In all panels the bottom spectrum is the non-irradiated ice, and the uppermost is the spectra obtained at the maximum irradiation time (180 min).

species were not the same for the two isomers, for example, H_2CO was formed only in the methyl formate photolysis while C_2H_6 and C_5H_{10} were formed only in acetic acid photolysis (For the complete list of daughter species and the bands used to identify them see Rachid *et al.* 2017 and references therein).

The evolution of the abundance of a given molecular species during the irradiation is related to the radiation fluence by:

$$A - A_0 = A_\infty(1 - e^{-\sigma_{d,f} \times F}), \quad (3.1)$$

where F is the fluence, in units of cm^{-2} , A , A_0 , and A_∞ are the areas of the infrared band related to a specific vibrational mode of a given species at a given fluence (A), for the unirradiated sample (A_0), and at the highest fluence (A_∞). In this equation, $\sigma_{d,f}$ represents the effective destruction cross section (σ_d) of parent species or effective formation cross section (σ_f) of the new formed species, both in units of cm^2 (see also Pilling and Bergantini, 2015). We measure the band area varying with the fluence and fit Equation 3.1 to calculate the effective destruction cross section of methyl formate and acetic acid when exposed to soft X-rays. The obtained values were $4.8 \times 10^{-18} \text{ cm}^2$ and $4.2 \times 10^{-18} \text{ cm}^2$ for acetic acid and methyl formate, respectively. The effective formation cross section of the formed species were also calculated by the same method and values range from $1.6 \times 10^{-18} \text{ cm}^2$.

4. Discussion

To obtain the physicochemical parameters of the $\text{C}_2\text{H}_4\text{O}_2$ isomers in conditions similar to those where they were detected, we adopted three astrophysical scenarios with different

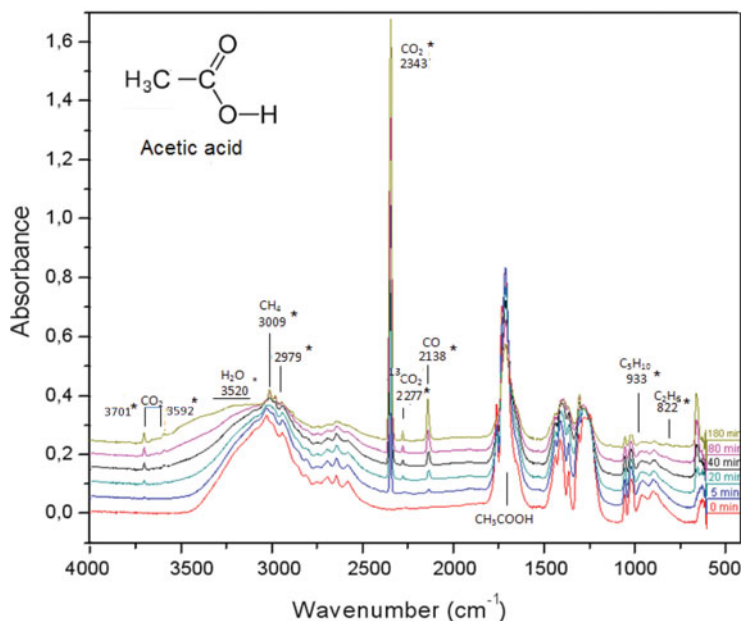


Figure 2. Infrared spectra of frozen methyl formate at 12K during isothermal irradiation with broadband soft X-ray (6 - 2000 eV) at different irradiation times. In all panels the bottom spectrum is the non-irradiated ice, and the uppermost is the spectra obtained at the maximum irradiation time (160 min).

X-ray field: a circumstellar environment (typical T Tauri stars) and two molecular clouds associated with star forming regions (e.g. Sgr B2 and W51). The modeling of soft-X-ray flux in each of these scenarios can be found in Rachid *et al.* (2017).

The half-lives of the parent species were determined following the equation:

$$\tau_{1/2} = \frac{\ln 2}{\sigma_d \times \phi} \quad (4.1)$$

where ϕ indicates the photon flux in units of photons $\text{cm}^{-2}\text{s}^{-1}$. Due to the small difference in the effective destruction cross section, the half-lives are not so different. An interesting way to see how these small differences can help to explain the relative abundances is studying the changes in the column density of the molecules as a function of time and well as the evolution of the relative column density between the two isomers in time. From the effective dissociation cross section we can calculate the X-ray photodissociation rate (k):

$$k = \sigma_d \times \phi, \quad (4.2)$$

where ϕ is the photon flux in units of $\text{cm}^{-2}\text{s}^{-1}$ and σ_d is the effective dissociation cross section, in cm^2 .

Using the calculated values of k and considering a first-order reaction we can calculate the evolution of the column densities of each molecule when exposed to different X-ray field:

$$N(t) = N_0 e^{-kt} \quad (4.3)$$

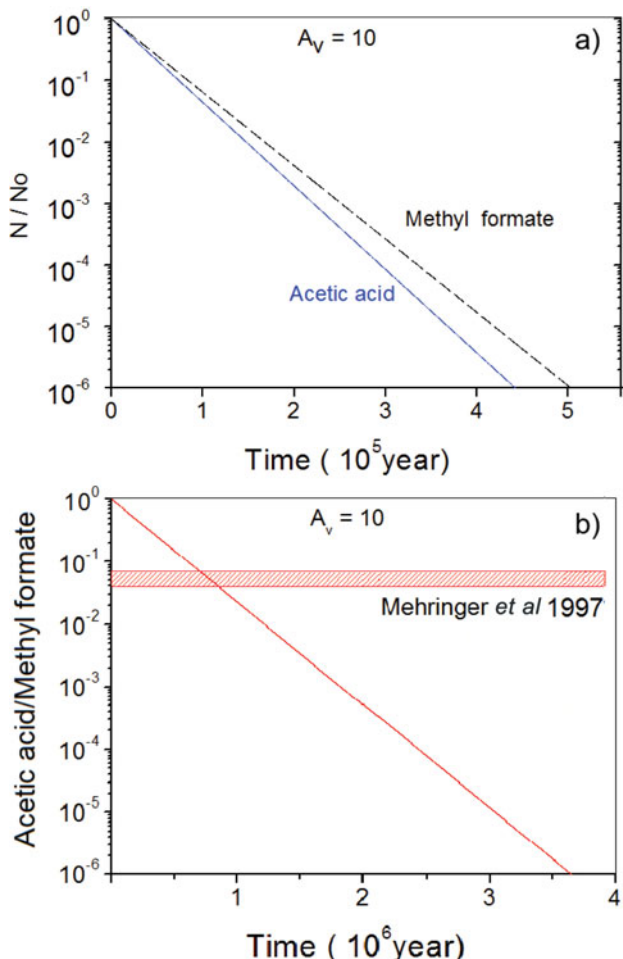


Figure 3. a) Evolution of the column density ($N(t)/N_0$) for methyl formate (dashed black line) and acetic acid (blue line) for a scenario similar to the giant molecular cloud Sgr B2 at $A_v = 10$; b) Abundances ratio ($N_{CH_3COOH}/N_{HCOOCH_3}$) evolving in time. Horizontal red bar shows the observed values in Sgr B2 (Mehring *et al.* 1997)

where k is the constant rate, in s^{-1} , N_0 is the initial column density and $N(t)$ is the column density in time, both in molecules cm^{-2} .

Using $N(t)$, we calculated the relative abundance ($N_{CH_3COOH}/N_{HCOOCH_3}$) evolving in time for different visual extinction. Figure 3a present the temporal evolution of the column density ($N(t)/N_0$) for acetic acid and methyl formate, at $A_v = 10$, in a X-ray radiation field similar to those found in Sgr B2, following Equation (4.3). Figure 3b shows the relative abundance between these two species in time. The red dashed bar shows the observed value of the relative abundance in Sgr B2 (Mehring *et al.* 1997).

We also considering the attenuation of the X-ray flux in order to simulate the effects of this radiation in inner parts of the clouds and protoplanetary disks. For simplification, we assume that all photons in the 6–2000 eV range are equally attenuated by the gas/dust. The attenuation of the photon flux as a function of the visual extinction is given by (adapted from Mendoza *et al.* 2013):

$$\phi_x(A_v) = \phi_x(A_v = 0)e^{-2.3 \times 10^{-2} A_v} \quad (4.4)$$

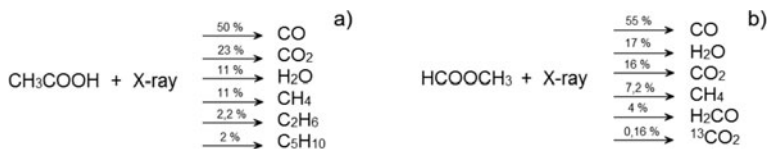


Figure 4. Main products from methyl formate photodissociation by broadband soft X-ray (6-2000eV) and their branching ratios of a) Acetic acid and b) Methyl formate

where A_v is the visual extinction, ϕ_x ($A_v = 0$ mag) is the non-attenuated flux in units of photons $\text{cm}^{-2} \text{s}^{-1}$.

We observed that at moderate visual extinction, the observed relative abundances of Sgr B2 could be reached after an exposition to X-ray radiation of nearly 10^6 years. For high values of visual extinction (highly embedded ices), the observed relative abundances of Sgr B2 could be reached after an exposition to X-ray radiation of approximately 10^8 years. Considering that a typical molecular cloud has an age of approximately 10^7 years, the time to reach the observed relative abundances in such radiation field can be reached for some value of visual extinction between 10 and 300 magnitudes (considering only the effects of X-ray photodissociation). This result indicates that maybe the X-ray photodestruction of methyl formate and acetic acid in the inner part of Sgr B2 can help to explain the difference in abundances of these two isomers.

We performed the same analysis for different values of the X-ray field and visual extinction. We concluded that considering an YSO scenario the differences in the abundances can also be better explained taking into account the X-ray photodestruction of the molecules in highly embedded regions. In the case of W51, we find that the exposed time to X-ray has to be long to reach the observed values of visual extinction, this can be due to an underestimation of the X-ray field in our model. For more details of the analysis and the models see Rachid *et al.* (2017).

In this work we could also quantify the daughter species through the Equilibrium Branching Ratio of the formed species (EBR). The EBR is the relative abundance of the daughter species after the system reaches chemical equilibrium (that is, the regions in the difference area graph where the column densities of formed/destroyed species don't vary so much). These parameters are important and can be used as input of astrochemical modeling of the gas and ice phase chemistry. The EBR of each formed species can be calculated by the following expression:

$$EBR(\%) = \frac{n_i}{\sum n_i} \times 100(\%), \quad (4.5)$$

where n_i is the column density of the species i and $\sum n_i$ is the sum of the column density of the identified species. The column density (N) of a species can be determined using the area of a band in the infrared spectra:

$$N = \frac{2.3}{A} \int Abs_\nu d\nu, \quad (4.6)$$

where A is the band strength for the used band and Abs_ν is the absorption at a given frequency. The integral in this equation gives the band area. Figure 4a and 4b give the EBR of the identified species for acetic acid and methyl formate, respectively. The main photodissociation product is CO (EBR > 50% of the assigned species), for both isomers, that is also the major product of dissociation in gas phase (Fantuzzi *et al.* 2011).

5. Conclusions

In this work, we present the results of experimental investigation of the effects of broadband X-rays with energy from 6 to 2000 eV (plus fast electrons, low energy secondary electrons and a minor component of VUV photons) on frozen methyl formate and acetic acid thin films (at 12K). Our main result and conclusions are as follows:

New molecules produced during photolysis were identified on the basis of their characteristic infrared absorption bands.

The effective dissociation cross section of methyl formate and acetic acid were determined: $4.2 \times 10^{-18} \text{ cm}^2$ and $4.8 \times 10^{-18} \text{ cm}^2$, respectively. This difference in the half-lives implies in great difference in the survival of molecules in large scales of time.

We calculated the evolution of column density and the of the relative abundances ($N_{\text{CH}_3\text{COOH}}/N_{\text{HCOOCH}_3}$) considering an X-ray field similar to the one existent at the main sources where the $\text{C}_2\text{H}_4\text{O}_2$ isomers were observed (around YSOs and in molecular clouds) to analyze their survival. We conclude that the photodissociation induced by X-ray in highly embedded ices can account for the relative abundance of methyl formate and acetic acid in regions with high visual extinction.

We determined the equilibrium branching ratios (EBR) from methyl formate and acetic acid. The main photodissociation product is CO (EBR > 50% of the assigned species), for both isomers.

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