



Effect of the UV flux and temperature on the formation of complex organic molecules in astrophysical ices

Laura Isabel Tenelanda-Osorio^{1,2}, Alexis Bouquet¹, Olivier Mouis², and Grégoire Danger¹

¹Aix-Marseille Université, CNRS, PIIM, Marseille, France

²Aix-Marseille Université, CNRS, CNES, LAM, Marseille, France

I. Introduction

Ices throughout the ISM are exposed to different energetic processes that trigger several reactions and change the composition of the ice [1–3]. Particularly, ices in stars-forming regions can be subjected to the ultraviolet radiation that comes from the new born stars and triggers reactions in the ice. These ices are normally composed of H₂O, CO, CO₂, NH₃, methanol (CH₃OH), and traces of other molecules. Irradiation-induced reactions in these ices are a source of complex organic molecules (COM) that might later feed the building blocks of planets or other bodies that are being formed. Methanol is one of the main constituents of interstellar ices, where its abundance can go up to 30% (with respect to water) [1, 3, 4]. With this in mind, we irradiated pure methanol ice deposited at 20 and 80 K, with UV radiation during different periods of time to evaluate the effect of fluence and temperature in the abundance of volatile COMs that formed.

II. Methods

All experiments were carried out in the VAHIIA set-up [5]. Briefly, the system consists of an ultrahigh vacuum chamber connected to a GC–MS through a pre-condensation loop. The latter consists of a stainless steel loop that is immersed in liquid nitrogen for the recovery of the volatile COMs coming from the vacuum chamber. This is connected to a custom-made group of valves that allows to recover volatile COMs for their injection in the GC–MS for identification. Species recovered were identified by comparing the chromatographic peak and mass spectra with the standard database, whose retention time and mass spectrum were obtained in the system under the same conditions as the experiments.

Pure methanol was deposited on a copper plated surface attached to the tip of the cryostat in the chamber at 20 K. Six periods of time were used: 15 and 30 min, 1, 3, 8 and 24 h, for evaluating different UV fluence. Each experiment consists of five layers of 0.2 mbar of pure methanol ice each, one on top of the other. Each of these layers is irradiated during the period of time under evaluation, with a UV flux of $\sim 1 \times 10^{13}$ photons s⁻¹ cm⁻², using a flowing H₂ microwave-discharge lamp. Layers have been verified to be opaque to the UV photons, ensuring the layer(s) underneath the one being irradiated are not affected further. Once five layers are irradiated, under the same conditions, the chamber is warmed up to ~ 300 K and volatiles are recovered with the injection of Argon for transferring the sample to the pre-condensation loop. Each experiment consists of 5 layers

having received the same irradiation dose to obtain a larger quantity of products, and facilitate their detection and identification with the GC-MS. In addition, experiments were carried out at 80 K to evaluate the effect of the temperature on the abundance of volatiles formed. In this case we evaluated 30 min, 1 h and 24 h of irradiation.

III. Effect of fluence

23 molecules were identified after UV-irradiation of methanol ice. Figure 1 shows the absolute area under the total ion content curve of the molecules identified, as a function of the irradiation time. This quantity is a function of the abundance of the compound and is hereafter referred to as integrated TIC. Within functional groups, the same pattern is seen for molecules with different numbers of carbons. Aldehydes are the main functional group that forms. With the exception of formaldehyde, all of them have a similar increase up to 8h of irradiation and then even though the integrated TIC increases, the slope is smaller. Alcohols have a low yield and have a steady integrated TIC. Ethers are produced rapidly and reach high integrated TIC during the first 3-8 h but then, their formation is lower than its usage for the formation of more complex molecules and its integrated TIC drops. Dimethyl Ether (DME) has the highest integrated TIC throughout all experiments. Ketones are the main products with 4 and 5 carbons, and maintain a constant increase with the time of irradiation. Esters and ketones are the only two functional groups identified with up to 5 carbons in the chain. With the exception of methyl formate, esters have a similar pattern. During the first 3 h of irradiation the integrated TIC increases rapidly but between 3-8 h there is a recession. After, the increase is the highest.

At 8 h of irradiation several molecules display an inflection point. Aldehydes's rate of production decreases (the integrated TIC is lower than expected), while the integrated TIC of esters and ketones is higher. Special cases are formaldehyde, DME and dimetoxymethane, who fall under the detection threshold after 24 h of irradiation tends to zero, which indicates they are the main reactants to form the more complex molecules.

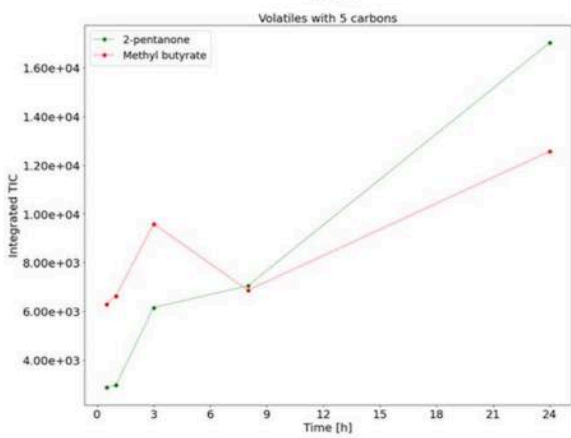
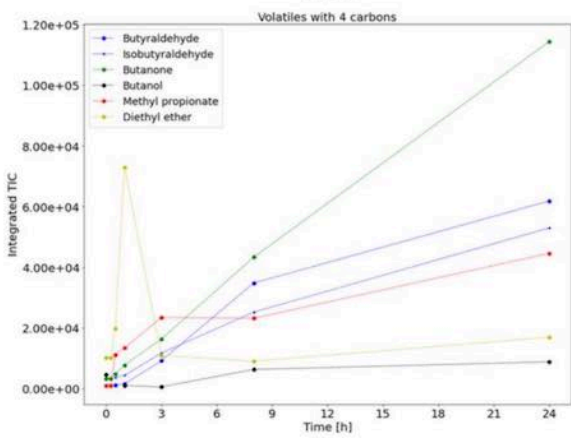
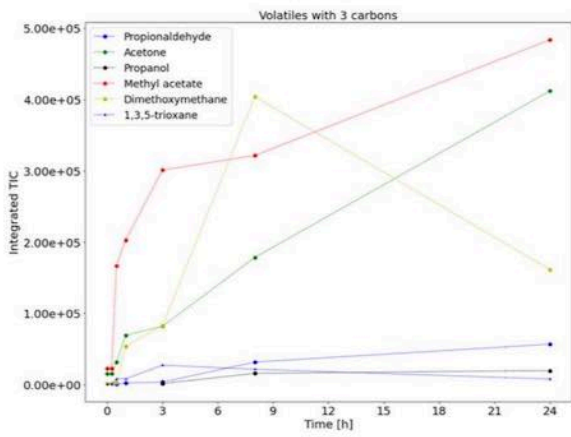
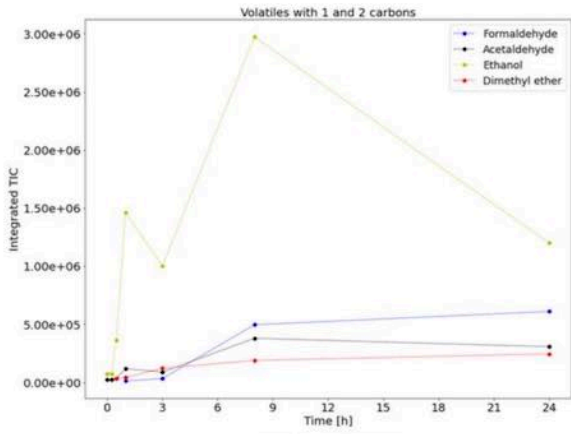


Fig. 1. Integrated TIC of volatiles formed after UV-irradiation at 20 K. Aldehydes: blue, ethers: yellow, alcohol: black, ketones: green, esters: red.

IV. Effect of temperature

At 80 K there is a reduction in diversity and integrated TIC of products, and there is no common pattern to describe the functional groups as in section III. Propanol, DME and 1,3,5-trioxane are not identified at anytime. Aldehydes are identified only after 24 h of irradiation, except for isobutyraldehyde that appears at all times. Alcohols and Ethers have a lower yield. Ketones are still produced at all times with constant yield, which suggest an efficient mechanism of formation.

References

- [1] S. Maity, R. I. Kaiser, and B. M. Jones, *Physical Chemistry Chemical Physics*, vol. 17, no. 5, pp. 3081–3114, 2015.
- [2] P. de Marcellus, C. Meinert, I. Myrgorodska, L. Nahon, T. Buhse, L. L. S.d’Hendecourt, and U. J. Meierhenrich, *PNAS*, vol. 112, no. 4, pp. 965–970, 2015.
- [3] D. Paardekooper, J.-B. Bossa, and H. Linnartz, *Astronomy & Astrophysics*, vol. 592, p. A67, 2016.
- [4] A. Bergantini, S. Góbi, M. J. Abplanalp, and R. I. Kaiser, *The Astrophysical Journal*, vol. 852, no. 2, p. 70, 2018.
- [5] N. Abou Mrad, F. Duvernay, P. Theulé, T. Chiavassa, and G. Danger, *Analytical chemistry*, vol. 86, no. 16, pp. 8391–8399, 2014