

# A study of methyl formate in astrochemical environments

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## ABSTRACT

Several complex organic molecules are routinely detected in high abundances towards hot cores and hot corinos. For many of them, their paths of formation in space are uncertain, as gas-phase reactions alone seem to be insufficient.

In this paper, we investigate a possible solid-phase route of formation for methyl formate (HCOOCH<sub>3</sub>). We use a chemical model updated with recent results from an experiment where simulated grain surfaces were irradiated with 200-keV protons at 16 K, to simulate the effects of cosmic ray irradiation on grain surfaces.

We find that this model may be sufficient to reproduce the observed methyl formate in dark clouds, but not that found in hot cores and corinos.

**Key words:** astrochemistry – stars: formation – ISM: abundances – ISM: molecules.

## 1 INTRODUCTION

Methyl formate (HCOOCH<sub>3</sub>) is the simplest example of an ester. It is derived from the formic acid (HCOOH), where a methyl group is attached to the carboxyl group. It is an important organic complex molecule that was first detected by Brown et al. (1975) towards the Sgr B2(N), the richest molecular source in the Galaxy located in the Galactic Centre giant cloud Sgr B2. It is considered to play a key role in understanding the origin of life because it leads to the synthesis of bio-polymers. Methyl formate has two structural isomers, glycolaldehyde (HCOCH<sub>2</sub>OH) and acetic acid (CH<sub>3</sub>COOH), but it has been reported that this molecule is the most abundant among these isomers (Hollis et al. 2001). Particularly, its column density in the Orion hot core was derived to be  $9.4 \times 10^{15} \text{ cm}^{-2}$  by Ikeda et al. (2001), and this value was confirmed by Sakai et al. (2007). Methyl formate has also been detected in the G31.41+0.31 hot molecular core (HMC); its column density is observed to be  $3.4 \times 10^{18} \text{ cm}^{-2}$  around this region. Cazaux et al. (2003) observed methyl formate in the hot core around the protostellar object IRAS 16293–2422. Hence, methyl formate seems to be ubiquitous in star-forming regions.

Several studies have been carried out on methyl formate to understand its formation mechanisms, but it is still debated whether complex organic molecules form on dust icy mantles during the cold phase, on grains during the warm-up phase or in the gas phase. Despite a large activation energy barrier between protonated methanol and formaldehyde (Horn et al. 2004), Garrod & Herbst (2006) found that the latter route of formation is viable during the icy mantle sublimation phase. Moreover, very recently, Laas et al. (2011) have proposed two Fischer esterification (the acid-catalyzed reaction of a

carboxylic acid with an alcohol to give an ester) pathways that occur during the warming-up phase, involving protonated formic acid and methanol and protonated methanol and neutral formic acid, respectively. Both reactions have two channels that correlate to cis- and trans-protonated methyl formate. They emphasized that methanol photodissociation branching ratios and warm-up time-scales influence the relative ratios between these two geometries.

The possibility that more complex species are formed at low temperatures on surfaces has been investigated before (e.g. Charnley 1997, 2001; Herbst & van Dishoeck 2009), and in particular methyl formate production on dust surfaces was first proposed by Herbst (2005): CO, C and O lead to the formation of CH<sub>3</sub>O and HCO radicals, both known as methyl formate precursors. Based on this pathway and using energetic electrons at 10 K, laboratory experiments were performed by Bennett & Kaiser (2007) in order to produce methyl formate and estimate the rate coefficients for this reaction. Different experiments involving methyl formate were also performed by Gerakines, Schutte & Ehrenfreund (1996) and Öberg, Bottinelli & van Dishoeck (2009), which obtained this molecule after ultraviolet (UV) photolysis of pure methanol and CO:CH<sub>3</sub>OH ice mixtures. Recently, a laboratory study by Modica & Palumbo (2010) has suggested a new solid-state route of formation for this molecule. By using infrared spectroscopy in the 4400–400 cm<sup>-1</sup> range for *in situ* monitoring the sample during the experiments, they simulated a cosmic ion irradiation on a binary mixture containing CH<sub>3</sub>OH and CO ice: methyl formate was therefore released to the gas phase after sublimation of these icy samples.

In this paper, we include the Modica & Palumbo (2010) experiments in our chemical model UCL\_CHEM (Viti et al. 2004b), by extrapolating from the experiments a new rate coefficient for the methyl formate formation on grains. Our purpose is to investigate whether surface reactions during the cold phase *alone* can account for the observed abundances of methyl formate in massive

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star-forming regions and around low-mass stars. In Section 2, we describe the experimental procedure; physical and chemical details of the chemical model are summarized in Section 3. In Section 4, we qualitatively model four different sources, and present our findings.

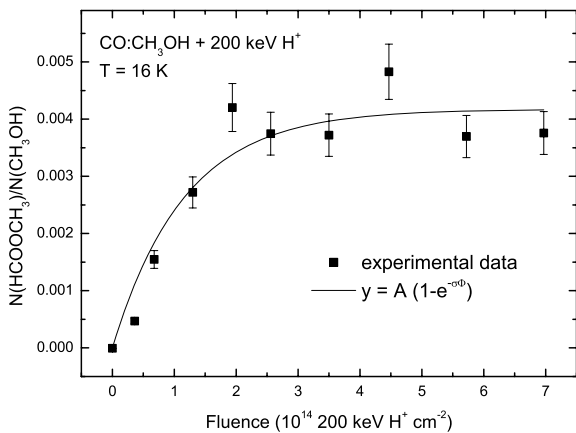
## 2 EXPERIMENTS

Experiments have been performed in the Laboratory of Experimental Astrophysics in Catania (Italy). Solid samples were prepared and irradiated in a stainless steel vacuum chamber where pressure is kept below  $10^{-7}$  mbar. The gas mixture to be investigated was injected into the chamber through a needle valve where it froze on to the substrate (Si or KBr) placed in thermal contact with the tail section of a cryostat (10–300 K). After deposition, the samples were bombarded by 200-keV  $H^+$  ions. Ions are obtained from an ion implanter interfaced with the vacuum chamber. The beam used produces current densities in the range from 0.1 to a few  $\mu A cm^{-2}$  in order to avoid macroscopic heating of the target. Infrared transmittance spectra of the samples were obtained before and after each step of irradiation by a Fourier Transform Infrared (FTIR) spectrometer ( $4400\text{--}400 cm^{-1} = 2.27\text{--}25 \mu m$ ). More details on the experimental procedure can be found in Palumbo, Ferini & Baratta (2004) and in Modica & Palumbo (2010).

Pure  $CH_3OH$  and a  $CO:CH_3OH$  mixture were irradiated at 16 K with 200-keV  $H^+$  ions. In both cases, after irradiation, the IR spectra show several absorption bands which testify for the formation of new molecules not present in the original sample. Among these, two bands due to  $CH_4$  appear at  $3010$  and  $1304 cm^{-1}$  (Palumbo, Castorina & Strazzulla 1999);  $CO_2$  bands appear at  $2344$  and  $660 cm^{-1}$  ( $^{12}CO_2$ ) and  $2278 cm^{-1}$  ( $^{13}CO_2$ );  $H_2CO$  is detected at  $1720 cm^{-1}$  (Hudson & Moore 2000);  $C_2H_4(OH)_2$  (ethylene glycol) is observed at  $1090 cm^{-1}$  (Hudson & Moore 2000). Moreover, a band is observed near  $1160 cm^{-1}$  and is attributed to methyl formate ( $HCOOCH_3$ ), and a band near  $1067 cm^{-1}$  is assigned to glycolaldehyde ( $HCOCH_2OH$ ) (Modica & Palumbo 2010).

Fig. 1 shows the ratio between the column density of methyl formate and methanol,  $N(HCOOCH_3)/N(CH_3OH)$ , as a function of ion fluence (ions  $cm^{-2}$ ), measured after each step of irradiation. The experimental data have been fitted with an exponential curve:

$$N(HCOOCH_3)/N(CH_3OH) = A(1 - e^{-\sigma\Phi}),$$



**Figure 1.** The ratio between the column density of methyl formate and methanol,  $N(HCOOCH_3)/N(CH_3OH)$ , as a function of ion fluence after irradiation of a  $CO:CH_3OH$  mixture at 16 K.

where  $A$  is the asymptotic value,  $\sigma$  is the cross-section ( $cm^2$ ) and  $\Phi$  is the ion fluence (ions  $cm^{-2}$ ).

The fitting procedure gives  $A = 0.0042$  and  $\sigma = 8.6 \times 10^{-15} cm^2$ .

To apply the laboratory results to the interstellar medium (ISM) conditions, we assume a standard ionization rate ( $\zeta = 3 \times 10^{-17} s^{-1}$ ) and derive the flux  $F_{ISM} = 0.5$  ions  $cm^{-2} s^{-1}$  of cosmic ions in the approximation of effective monoenergetic 1-MeV protons (see Mennella et al. 2003).  $F_{ISM}$  must be regarded as an effective quantity. It represents the equivalent flux of 1-MeV protons, which gives rise to the ionization rate produced by the cosmic ray spectrum if 1-MeV protons were the only source for ionization. Furthermore, we assume that the cross-section scales with the stopping power ( $S$ , energy loss per unit path-length) of impinging ions. According to SRIM code (Ziegler, Biersack & Ziegler 2008), in the case of protons impinging on a  $CO:CH_3OH$  mixture ( $S(200\text{-keV protons}) = 2.9 \times S(1\text{-MeV protons})$ ).

We defined  $\sigma_{ISM} = A \times \sigma/2.9 cm^2$ , where the product  $A \times \sigma$  is the initial slope of equation (1). The formation rate of methyl formate is given by

$$R(s^{-1}) = \sigma_{ISM}(cm^2) \times F_{ISM}(cm^{-2} s^{-1}).$$

Using  $\sigma_{ISM}$  and  $F_{ISM}$  as estimated above, we obtain  $R = 6.2 \times 10^{-18} s^{-1}$ .

## 3 CHEMICAL MODEL

The chemical model is UCL\_CHEM, developed by Viti & Williams (1999) and Viti et al. (2004b). UCL\_CHEM is a time- and depth-dependent gas–grain chemical model which estimates the fractional abundances (with respect to the total number of hydrogen nuclei) of gas and surface species in every environment where molecules are present. For this purpose, it was adapted to model low- and high-mass star-forming regions. The model performs a two-step calculation: Phase I starts from a fairly diffuse medium in atomic form and undergoes a free-fall collapse until densities typical of the gas that will form hot cores and hot corinos are reached ( $10^7$  and  $10^8 cm^{-3}$ , respectively). During this time, atoms and molecules are depleted on to grain surfaces, and they hydrogenate when possible. The depletion efficiency is determined by the fraction of the gas-phase material that is frozen on to the grains. This approach allows a derivation of the ice composition by a time-dependent computation of the chemical evolution of the gas–dust interaction process. The initial elemental abundances of the main species (such as H, He, C, O, N, Si and Mg) are the main input for the chemistry. In our model, surface reactions only occur during this phase. Phase II is the warming-up phase and follows the chemical evolution of the remnant core when the hot core itself is formed. It simulates the effect of the presence of an infrared source in the centre of the core or in its vicinity by subjecting the core to an increase in the gas and dust temperature. We derived the temperature of the gas as a function of the luminosity (and therefore the age) of the protostar. The treatment of the evaporation of the code is either time-dependent in which mantle species desorb in various temperature bands according to the experimental results by Collings et al. (2004) or instantaneous in that all species will desorb off grain surfaces in the first time-step. The temperature profile is another input parameter. For this study, the model does not take into consideration the desorption of molecules due to UV photons and cosmic rays.

Most of the gas-phase reactions that occur in the ISM are collected from the UMIST data base (<http://www.udfa.net>, Woodall et al. 2007). Because of the failure of gas-phase chemistry to reproduce abundances of particular molecules, in this paper, a

**Table 1.** Gas-phase and solid-state routes of methyl formate destruction and formation. The top panel shows the gas-phase reactions involving methyl formate, whose rate coefficients are taken from the KIDA data base. The bottom panel contains the new experimental path of methyl formate formation on grain surface as investigated by Modica & Palumbo (2010).

R1	R2	P1	P2	P3	$\alpha$	$\beta$	$\gamma$
HCOOCH <sub>3</sub>	H <sub>3</sub> <sup>+</sup>	H <sub>2</sub>	H <sub>5</sub> C <sub>2</sub> O <sub>2</sub> <sup>+</sup>		4.05E−09	−0.5	0
HCOOCH <sub>3</sub>	He <sup>+</sup>	He	CH <sub>3</sub>	HCO <sub>2</sub> <sup>+</sup>	3.54E−09	−0.5	0
HCOOCH <sub>3</sub>	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	H <sub>5</sub> C <sub>2</sub> O <sub>2</sub> <sup>+</sup>		1.81E−09	−0.5	0
HCOOCH <sub>3</sub>	HCO <sup>+</sup>	CO	H <sub>5</sub> C <sub>2</sub> O <sub>2</sub> <sup>+</sup>		1.55E−09	−0.5	0
HCOOCH <sub>3</sub>	C <sup>+</sup>	COOCH <sub>4</sub> <sup>+</sup>	C		2.17E−09	−0.5	0
HCOOCH <sub>3</sub>	H <sup>+</sup>	COOCH <sub>4</sub> <sup>+</sup>	H		6.9E−09	−0.5	0
H <sub>5</sub> C <sub>2</sub> O <sub>2</sub> <sup>+</sup>	e <sup>−</sup>	HCOOCH <sub>3</sub>	H		1.5E−07	−0.5	0
mCH <sub>3</sub> OH	mCO	mHCOOCH <sub>3</sub>			6.20E−18	0	0

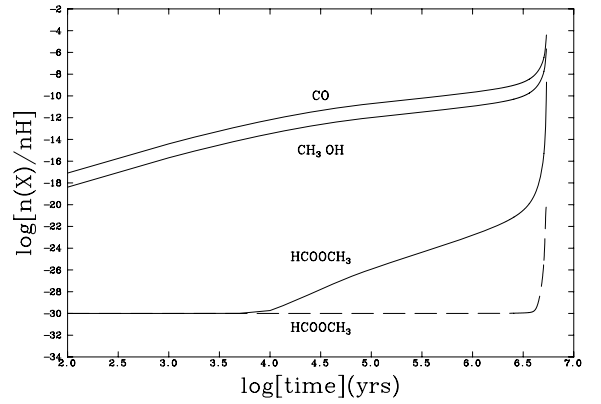
gas–grain network reaction is also taken into account, and particularly, we focused on methyl formate reactions. Table 1 shows on the top the updated gas-phase reaction rate coefficients as listed in the most recent Kinetics Database for Astrochemistry (KIDA) (<http://kida.obs.u-bordeaux1.fr>, Wakelam 2009). At the bottom, we report solid-state paths of formation of methyl formate, taking into account the new experimental rate coefficient for this reaction. Methyl formate is both one of the reactants (*R*) and product (*P*);  $\alpha$ ,  $\beta$  and  $\gamma$  are the rate coefficients. The first six are bimolecular reactions, where an exothermic proton transfer occurs between an ion and a neutral species. The last one is an electronic recombination, in which the recombination of a positive ion and an electron results in the dissociation of the molecule. In both cases, a Kooij formula (a modified version of the Arrhenius equation) is adopted to evaluate the reaction rate:

$$k(T) = \alpha \left( \frac{T}{300} \right)^\beta e^{-\gamma/T}, \quad (1)$$

where  $T$  is the gas temperature,  $\alpha$  is the cosmic ion rate,  $\beta$  contains the dipole effect and  $\gamma$  represents the probability per cosmic ray ionization, which for the updated methyl formate reactions is always zero.  $\beta$  includes the enhancement of ion-neutral rate coefficients for cases in which the neutral has a large, permanent electric dipole moment. This effect results in a rate coefficient that has a  $T^{1/2}$  dependence at low temperature (10–50 K) as observed by Herbst & Leung (1986). In the bottom panel of Table 1, the surface path of formation of methyl formate is summarized. One of the most abundant species in the ISM is carbon monoxide, which undergoes successive hydrogenations in the presence of a large amount of hydrogen (Watanabe et al. 2007; Fuchs et al. 2009). Consequently, methanol can be formed. After cosmic ion irradiation, CO reacts with CH<sub>3</sub>OH to produce methyl formate (see Modica & Palumbo 2010). The *m* before the molecular formulae has been inserted to underline the role of the surface chemistry that acts as a catalyst for the reactions with large energy barriers. The new experimental rate coefficient for this reaction is  $6.2 \times 10^{-18} \text{ s}^{-1}$ , as shown.

## 4 RESULTS

Fig. 2 shows the fractional abundances of selected species (from Table 1) as a function of time during Phase I. The solid lines represent the abundances of methanol, carbon monoxide and methyl formate when the new solid-state route is included in the model. The dashed line is methyl formate obtained from the model computed with the same chemistry as in the original code (Viti et al. 2004b). In the latter case, the reactant trends are the same as those shown



**Figure 2.** Fractional abundances (with respect to the total number of hydrogen nuclei) of selected species as a function of time.

in the updated version of the code. While the reactants, CO and CH<sub>3</sub>OH, reach a fractional abundance of  $4 \times 10^{-5}$  and  $2 \times 10^{-6}$ , respectively, methyl formate is produced in a negligible quantity ( $< 10^{-21}$ ) on to the grains. By considering the solid-state path of methyl formate formation with the experimental rate coefficient of  $6.2 \times 10^{-18} \text{ s}^{-1}$  (as described in Sections 2 and 3), a value of  $1.8 \times 10^{-9}$  is reached for its fractional abundance (solid line). In order to compare our theoretical abundances with those from the observations, we also run Phase II for a typical hot core. In order to facilitate the calculation, we set an instantaneous evaporation instead of a time-dependent sublimation for molecules that sublimate from the grain into the gas phase. As a result, we obtained a detectable abundance of methyl formate with a value of  $1.7 \times 10^{-9}$ . An alternative route for the synthesis of methyl formate in a hot core was previously investigated by Garrod & Herbst (2006), which proposed both gas-phase and grain-surface processes to produce most species during the warm-up phase. They estimated that the gas-phase/accretion path, involving protonated methanol and formaldehyde, is responsible for the formation of 25 per cent of the total HCOOCH<sub>3</sub> present on the grain surface before sublimation. Indeed, during the warm-up phase, the surface reaction between CH<sub>3</sub>O and HCO radicals is allowed, and it is thought to be the dominant mechanism; when significant amount of H<sub>2</sub>CO begins to evaporate, the methyl formate formation on grains is inhibited and formaldehyde is protonated to produce methyl formate on gas phase. These reactions are more efficient in hot corinos than in hot cores. They found a trend where methyl formate reaches a fractional

abundance of about  $10^{-8}$  at  $10^6$  yr. Both mechanisms seem therefore to be viable.

In order to compare the theoretical abundance of methyl formate with the observational data, we model two high mass star-forming regions, the Orion hot core and G31.41+0.31, a low-mass source, NGC 1333–IRAS2, and the cold gas near the region B1-b in Perseus using our two-phase UCL\_CHEM. The physical and chemical parameters for each model are listed below. In Phase II of all models, we now assume a time-step sublimation instead of an instantaneous evaporation for molecules that sublime from the grains into the gas phase during the warm-up stage of star formation process, as described by Viti et al. (2004b).

### Orion KL hot core

The Orion Molecular Cloud 1 (OMC1) is a dense clump at 480 pc that contains several distinct infrared-emitting regions. Among these, the Kleinmann–Low (KL) region is composed of four different components: the hot core, the compact ridge, the plateau and the photodissociation region (PDR) surrounding the quiescent gas. While the hot core and the plateau are characterized by elevated temperatures, the ridge consists of an extended and cooler region with quiescent material. We focused on the Orion hot core as it is one of the richest known astronomical sources of molecular lines. The main heating mechanism in this location is radiative, and gas kinetic temperatures are close to 200 K. Using UCL\_CHEM, Lerate et al. (2008) computed different chemical models to simulate each component of the KL region. In the present work, we used the physical and chemical parameters for their best-fitting model.

A comparison between our model calculations and the observational column densities through the Orion hot core is shown in Table 2. Observational data are taken from Remijan et al. (2003), which have surveyed this source with the Berkeley–Illinois–Maryland (BIMA) with angular resolution of about 2–5 arcsec.

### G31.41+0.31

G31.41+0.31 is another example of a multiple massive star formation region located at 7.9 kpc. It is associated with an HMC of 0.048 pc in size, where the temperature is found to be about 300 K and the luminosity is about  $3 \times 10^5 L_{\odot}$  (Churchwell, Walmsley & Cesaroni 1990). It is in fact the region where the simplest sugar, glycolaldehyde (and also one of the methyl formate isomers) was first detected by Beltrán et al. (2009) through IRAM Plateau de Bure Interferometer (PdBI) observations. Beltrán et al. (2009) also used UCL\_CHEM to try to reproduce the abundance for glycolaldehyde. We adopted the physical and chemical input parameters from their study for our model.

We compared our theoretical results with those given by Cesaroni et al. (1994), which performed high-resolution observations by using IRAM PdBI.

### NGC 1333–IRAS2

Located in the cloud NGC 1333, belonging to the Perseus complex at 220 pc in distance, IRAS2 is a low-mass binary protostellar system, including IRAS2A and IRAS2B, separated by 30 arcsec. An infalling envelope, a circumstellar disc and multiple outflows seem to be associated with them. The advantage of observing such nearby objects is that these sources can be spatially resolved with millimetre interferometers. As a result, we adopted a multipoint model in order to reproduce the density profile of the hot corino associated with IRAS2, as reported in Maret et al. (2004). We also used the temperature profile for hot corino given in Awad et al. (2010).

We evaluated the total column density for the methyl formate as described in Viti et al. (2004a):

$$N(\text{HCOOCH}_3) = \sum (X \times A_v \times L) \times N(\text{H}_2), \quad (2)$$

where  $X$  is the methyl formate fractional abundances and  $A_v$  is the visual extinction at length  $L$  (pc).

### B1-b core

The protostar associated with the B1-b core is believed to be between a pre-stellar and Class 0 protostar evolutionary stage. Two sources are identified with the B1-b core, designed as B1-bN and B1-bS, separated by 20 arcsec in the north–south direction at about 350 pc in distance (Hirano et al. 1999). The physical parameters of two sources are very similar ( $T_{\text{dust}}$  18 K, mass of 1.6–1.8  $M_{\odot}$  and luminosity about 2.6–3.1  $L_{\odot}$ ). We qualitatively model the B1-b core running our two-phase model; for this core, during Phase II the temperature only rises up to 30 K; this implies that only the weakly bound species partly sublime due to thermal desorption (see Collings et al. 2004); hence, any methyl formate formed on the grains would remain in solid phase. However, non-thermal desorption processes are known to be efficient even at 10 K (see Boland & de Jong 1982; Hasegawa & Herbst 1993; Branga & Johnson 2004; Roberts et al. 2007). We have therefore ran Phase I including some non-thermal desorption mechanisms (as in Roberts et al. 2007). We compare our results for methyl formate with those reported in Öberg et al. (2010). Note that our computed methyl formate is a lower limit as our non-thermal desorption mechanisms did not include direct UV photodesorption.

Table 2 reports all our model results and compares the theoretical predicted column densities for methyl formate with those observed

**Table 2.** Observed and predicted column densities towards Orion KL hot core, G31.41+0.31, NGC 1333–IRAS2 and B1-b core.

Source	Type	Distance (pc)	$T_{\text{rot}}$ (K)	Observations ( $\text{cm}^{-2}$ )	Model ( $\text{cm}^{-2}$ )
Orion KL Hot Core	High mass	480	250	$6.9 \times 10^{16}{}^a$	$3.5 \times 10^{14}$
G31.41+0.31 HMC	High mass	7900	300	$6.8 \times 10^{18}{}^b$	$9.3 \times 10^{15}$
NGC 1333-IRAS2	Low mass	220	38	$5.8 \times 10^{14}{}^c$	$6.4 \times 10^{12}$
B1-b	Dark core	350	<30	$8.3 \times 10^{12}{}^d$	$1.2 \times 10^{12}$

<sup>a</sup> Remijan et al. (2003).

<sup>b</sup> Note that the total methyl formate abundance reported herein is twice the value of form-E given in Cesaroni et al. (1994).

<sup>c</sup> Note that the total methyl formate abundance reported herein is twice the value of form-A given in Bottinelli et al. (2007).

<sup>d</sup> Öberg et al. (2010).

in the sources described above. A relatively good agreement within a factor of 10 was found for the dark core associated with B1, but the theoretical values are too low for the cases of warmer star-forming regions. In fact, around protostars, the flux of ions due to stellar flares should also be considered. As discussed by Garozzo et al. (2011), the effects induced by cosmic rays on icy grain mantles during the collapse-phase era are comparable to the effects induced by stellar flare ions during the warm-up phase.

In summary, using the rate coefficient derived from laboratory experiments of ice irradiation, we investigated the viability of a cold solid-state path to form methyl formate during the evolution of protostellar cores when the temperatures are low (10 K). We find that we cannot reproduce the abundance of methyl formate found in hot cores and hot corinos without invoking gas- or solid-phase reactions which necessitate high temperatures (and that can therefore only occur during the warm-up phase once the star is formed), while we were able to reproduce the observed abundances in dark clouds. This paper supports the idea that cosmic ion irradiation of icy grain mantles may be able to contribute to the production of the methyl formate observed in dense molecular clouds, but that other routes of formation are also required.

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