Methylacetylene (CH$_3$CCH) and propene (C$_3$H$_6$) formation in cold dense clouds: a case of dust grain chemistry.

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We present an extensive review of gas phase reactions producing methylacetylene and propene showing that these relatively abundant unsaturated hydrocarbons cannot be synthesized through gas-phase reactions. We explain the formation of propene and methylacetylene through surface hydrogenation of C$_3$ depleted onto interstellar ices, C$_3$ being a very abundant species in the gas phase.

1. INTRODUCTION

The formation of Complex Organic Molecules (COMs) in the interstellar medium is a challenging issue, specifically with respect to their observation in dense molecular clouds. This is particularly true for propene (CH$_3$-CH=CH$_2$, hereafter named C$_3$H$_6$) and methylacetylene (CH$_3$-CCH), their formation in dense molecular clouds is not well understood. Gas phase formation routes for these compounds have been extensively investigated but fail to reproduce the observed abundances of these species in dense molecular clouds (Lin et al. 2013, Öberg et al. 2013, Vastel et al. 2014) suggesting that important formation pathways could be missing at low temperature.

Methylacetylene was first detected in TMC-1 35 years ago (Irvine et al. 1981) with an abundance of around $6.10^{-9}$ relative to H$_2$. Askne et al (1983) and Kuiper et al (1984) detected methylacetylene in various interstellar media (DR21(OH), TMC-1, W3(OH), W51, Orion A, Sgr B2, ..) with a variable abundance around a few $10^{-9}$ relative to H$_2$. The authors of both of
these papers proposed that methylacetylene could be used as a probe of the kinetic temperature of interstellar clouds. Methylacetylene has also been detected in small translucent clouds (Turner et al. 2000, Turner et al. 1999) and in star forming regions (Miettinen et al. 2006), with a positive correlation between the fractional CH$_3$CCH abundance and $T_{\text{kin}}$, suggesting a possible desorption scenario with grain surface production.

The first positive detection of propene was much more recent, firstly in TMC-1 (Marcelino et al. 2007) and then in four additional cold dense clouds Lupus-1A, L1495B, L1521F and Serpens South (Agúndez et al. 2015) with an average abundance around $2 \cdot 10^{-9}$ relative to H$_2$.

In this study, we review the reactions producing methylacetylene and propene. Firstly, we review the reactions present in the usual astrochemical databases (KIDA (Wakelam et al. 2015) and UMIST (McElroy et al. 2012)). Then we perform an extensive search for new gas phase reactions leading to these unsaturated hydrocarbons. In the end, to explain the observation of propene and methylacetylene we propose efficient surface synthesis followed by a release into the gas phase through chemical desorption mechanisms (Vasyunin & Herbst 2013, Garrod et al. 2007). We also focus on the critical role of the O + C$_3$ reaction.

2. The chemical model

To calculate the methylacetylene and propene abundances we use the chemical model Nautilus (Hersant et al. 2009, Semenov et al. 2010). The Nautilus code computes the gas-phase and grain surface composition as a function of time taking into account reactions in the gas-phase, physisorption onto and desorption from grain surfaces and reactions at the surface. The surface reactions are based on the Langmuir-Hinshelwood mechanism with the formalism of Hasegawa et al. (1992) and includes the low temperature Eley-Rideal and complexation mechanisms considered by Ruaud et al (2015). For desorption, we consider thermal desorption as well as desorption induced by cosmic-rays (Hasegawa & Herbst 1993) and chemical reactions (the exothermicity of surface chemical reactions allows for the species to be desorbed after their formation) (Garrod et al. 2007). We consider in the nominal model that 1% of the newly formed species desorb and 99% remain on the grain surfaces.

The gas-phase network is based on kida.uva.2014 (http://kida.obs.ubordeaux1.fr/models (Wakelam et al. 2015)), with the modifications described in section 3. The surface network and parameters are the same as in (Ruaud et al. 2015). Following (Hincelin et al. 2015), the encounter desorption mechanism is included in the code. This mechanism
accounts for the fact that the $H_2$ binding energy on itself is much smaller than on water ices and prevents the formation of several $H_2$ monolayers on grain surfaces.

The chemical composition of the gas-phase and the grain surfaces is computed as a function of time. The gas and dust temperatures are equal to 10 K, the total H density is equal to $2 \cdot 10^4$ cm$^{-3}$ for molecular clouds. The cosmic-ray ionization rate is equal to $1.3 \cdot 10^{-17}$ s$^{-1}$ and the visual extinction is equal to 30. All elements are assumed to be initially in atomic form, except for hydrogen, which is entirely molecular. The initial abundances are similar to those of Table 1 of Hincelin et al. (2011), the C/O elemental ratio being equal to 0.7 in this study. We also considered larger C/O elemental ratios up to 1.0 but found that the $C_3H_4$ and $C_3H_6$ abundances are not sensitive to this parameter (propene reacts relatively quickly with oxygen atoms but also with carbon atoms. On the other hand, the high carbon abundance favours hydrocarbon formation). The grains are considered to be spherical with a 0.1 $\mu$m radius, a 3 g.cm$^{-3}$ density and about $10^6$ surface sites, all chemically active. The dust to gas mass ratio is set to 0.01 and the barrier to diffusion for all species is assumed to be half of their binding energies.

3. Review of the gas phase reactions

We performed an extensive review of potential gas phase chemical schemes leading to methylacetylene and propene. A large part, but not all, of these reactions were already included in current networks, but for all of them we checked the cited references leading to various changes in the rate constants and branching ratios. The important reactions for methylacetylene and propene production and loss in the conditions of cold interstellar clouds are listed in Table I including an extensive bibliography presented in the supplementary information.

The main gas phase source of $CH_2CCH$ is thought to be ionic reactions producing $C_3H_5^+$ followed by dissociative recombination (DR) with minor contributions from neutral reactions, mainly $CH + C_2H_4 \rightarrow CH_2CCH + H$ (the branching ratio of this reaction toward methylacetylene and/or allene production is subject to discussion (Goulay et al. 2009, Zhang et al. 2012)). The most efficient source of methylacetylene through $C_2H_5^+$ production was thought to be the $C_2H_5^+ + H_2 \rightarrow C_3H_5^+ + h\nu$ (1) radiative association reaction. Herbst et al (2010) performed theoretical calculations leading to a high rate constant for this process, in disagreement with earlier experimental results on the analogous three-body association process measured by (McEwan et al. 1999) which was found to be very slow. Some of these authors revisited reaction (1) some years later (Lin et al. 2013) through a coupled experimental and
theoretical study showing that, no matter which of the isomers of C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} are considered, the radiative association leading to protonated methylacetylene has sufficiently high barriers that these reactions are unimportant in the cold interstellar medium and cannot be an efficient way to form methylacetylene in molecular clouds. Other gas phase reactions can produce C\textsubscript{3}H\textsubscript{5}\textsuperscript{+}, and then methylacetylene through DR, the most efficient being C\textsubscript{2}H\textsubscript{3}\textsuperscript{+} + CH\textsubscript{4} \rightarrow C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} + H\textsubscript{2} (Anicich 2003) with secondary contributions from C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} + CH\textsubscript{4}, CH\textsubscript{3}\textsuperscript{+} + C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}\textsuperscript{+} + C\textsubscript{2}H\textsubscript{4} as well as C\textsuperscript{+} + C\textsubscript{3}H\textsubscript{6} (Anicich 2003). Nevertheless, all of these ionic reactions involve fluxes that are too small to produce the observed methylacetylene abundances. It should be noted that the protonation reactions of methylacetylene (CH\textsubscript{3}CCH + H\textsuperscript{+}, HCO\textsuperscript{+} ... ) lead to C\textsubscript{3}H\textsubscript{5}\textsuperscript{+}, but these processes act as destruction mechanisms for CH\textsubscript{3}CCH as the dissociative recombination (DR) of C\textsubscript{3}H\textsubscript{5}\textsuperscript{+} does not lead back to CH\textsubscript{3}CCH with 100% efficiency. With regard to neutral reactions, the CH + C\textsubscript{2}H\textsubscript{4} \rightarrow CH\textsubscript{3}CCH + H reaction produces directly some methylacetylene with a large rate constant at low temperature but this process involves small fluxes. The C + C\textsubscript{2}H\textsubscript{5} \rightarrow CH\textsubscript{3}CCH + H and H + C\textsubscript{3}H\textsubscript{5} \rightarrow CH\textsubscript{3}CCH + H\textsubscript{2} reactions also involve small fluxes considering only gas-phase networks as C\textsubscript{2}H\textsubscript{5} and C\textsubscript{3}H\textsubscript{5} are essentially formed on grains, or through the protonation of C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{6} (both essentially formed on grains) followed by DR of C\textsubscript{3}H\textsubscript{7}\textsuperscript{+} and C\textsubscript{3}H\textsubscript{7}\textsuperscript{+}. Then the gas phase abundances of C\textsubscript{2}H\textsubscript{5} and C\textsubscript{3}H\textsubscript{5} are strongly related to grain chemistry so that gas phase reactions alone do not produce large amounts of C\textsubscript{2}H\textsubscript{5} and C\textsubscript{3}H\textsubscript{5}. These gas phase reactions alone are not sufficient to reproduce the observations of methylacetylene in dense molecular clouds. As shown in Fig. 1 (continuous line), the gas phase formation of CH\textsubscript{3}CCH leads to abundances three orders of magnitude below the observations even with the reaction review listed in Table I.
Table I: Summary of reaction review.

\[ k = \alpha(T/300)^\beta \exp(-\gamma/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} , \text{ T range is 10-300K} \]

except for :

Ionpol1: \[ k = \alpha \beta (0.62+0.4767\gamma(300/T)^{0.5}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \], (Wakelam et al. 2012, Wakelam et al. 2010)

Ionpol2: \[ k = \alpha \beta (1+0.0967\gamma(300/T)^{0.5}+\gamma^2/10.526) (300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ F_0 = \exp(\Delta k/k_0) \text{ and } F(T)=F_0\exp(g|1/T_0-1/T|) \]

| Reaction | $\alpha$ | $\beta$ | $\gamma$ | $F_0$ | $g$ | ref |
|----------|---------|---------|---------|-------|-----|-----|
| 1. $\text{H} + \text{C}_3\text{H}_5 \rightarrow \text{H}_2\text{C}-\text{CCH} +$ $\rightarrow \text{C}_3\text{H}_6 + \text{hv}$ | 1.5e-11 | 0 | -1.5 | 0 | 3 | 0 | (Hanning-Lee & Pilling 1992, Harding et al. 2007, Hébrard et al. 2013). H abstraction may be very low at 10K. |
| 2. $\text{C}^+ + \text{C}_3\text{H}_4$ $\rightarrow \text{C}_3\text{H}_4^+ + \text{H}_2$ $\rightarrow \text{C}_3\text{H}_4^+ + \text{C}$ $\rightarrow \text{C}_3\text{H}_4^+ + \text{CH}$ $\rightarrow \text{C}_3\text{H}_4^+ + \text{C}_2\text{H}_2$ $\rightarrow \text{C}_2\text{H}_3^+ + \text{C}_2\text{H}$ | 5.7e-10 | -0.5 | 0 | 1.6 | 0 | (Bohme et al. 1982) considering the dipole of $\text{C}_3\text{H}_4$ |
| 3. $\text{C}^+ + \text{C}_3\text{H}_6$ $\rightarrow \text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_3$ $\rightarrow \text{C}_3\text{H}_4^+ + \text{CH}$ $\rightarrow \text{C}_3\text{H}_4^+ + \text{CH}_3$ $\rightarrow \text{C}_2\text{H}_3^+ + \text{C}_2\text{H}_4$ $\rightarrow \text{C}_2\text{H}_5^+ + \text{C}$ $\rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 + \text{H}$ | 6.0e-10 | -0.5 | 0 | 1.6 | 0 | (Bohme et al. 1982) considering the dipole of $\text{C}_3\text{H}_4$ |
| 4. $\text{C}^+ + \text{C}_3\text{H}_8$ $\rightarrow \text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_3$ $\rightarrow \text{C}_3\text{H}_5^+ + \text{C}_2\text{H}_3$ $\rightarrow \text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_6$ | 7.0e-10 | 0 | 0 | 1.6 | 0 | (Bohme et al. 1982) |
|   | Reaction                                                                 | Rate Constant | Branching Ratio | Comments                                                                                       |
|---|--------------------------------------------------------------------------|---------------|-----------------|------------------------------------------------------------------------------------------------|
| 5. | $\text{C} + \text{C}_2\text{H}_5 + \text{H} \rightarrow \text{CH}_2\text{CCH} + \text{C}_2\text{H}_2$ | 1.0e-10, 1.0e-10 | 0               | 0 3 0 0 0 KIDA, close to capture rate.                                                         |
| 6. | $\text{C} + \text{C}_2\text{H}_5 \rightarrow \text{H} + \text{CH}_2\text{CH}_2\text{H}$ | 2.0e-10       | 0               | 0 4 0 0 Rate constant from capture rate theory and branching ratio deduced from theoretical study of the isomeric $\text{CH} + \text{C}_2\text{H}_4$ reaction (Goulay et al. 2009, Loison & Bergeat 2009). |
| 7. | $\text{C} + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4$ | 2.0e-10, 1.0e-10 | 0               | 0 1.6 0 0 (Chastaing et al. 1999, Loison & Bergeat 2004, Chin et al. 2013)                     |
| 8. | $\text{C} + \text{C}_2\text{H}_7 \rightarrow \text{H} + \text{CH}_2\text{CHCHCH}_2$ | 1.6e-10, 4.0e-11 | 0               | 0 4 4 0 Rate constant from capture rate theory and branching ratio deduced from theoretical study of the isomeric $\text{CH} + \text{C}_2\text{H}_6$ (Trevitt et al. 2013, Loison & Bergeat 2009). |
| 9. | $\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{CCCH}_2 + \text{H}$ | 2.4e-10, 1.0e-10 | -0.546          | 29.6 1.6 7 (Butler et al. 1981, Berman et al. 1982, Thiesemann et al. 1997, Thiesemann et al. 2001, Canosa et al. 1997, McKee et al. 2003, Goulay et al. 2009, Gosavi et al. 1985, Wang & Huang 1998, Davis et al. 1999, Stranges et al. 2008, Zhang et al. 2012, Loison & Bergeat 2009) |
| 10. | $\text{CH} + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4$ | 2.8e-11, 5.0e-12 | -0.648          | 43.6 1.6 7 (Butler et al. 1980, Butler et al. 1981, Berman & Lin 1983, Canosa et al. 1997, McKee et al. 2003, Galland et al. 2003) |
| 11. | $\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{H} + \text{CH}_2\text{CHC}_2\text{H}$ | 4.2e-10        | 0               | 0 1.4 14 (Fleming et al. 1980, Butler et al. 1981, Daugey et al. 2005, Goulay et al. 2009, Loison & Bergeat 2009) |
| 12. | $\text{CH} + \text{C}_2\text{H}_6 \rightarrow \text{H} + \text{CH}_2\text{CHCHCH}_2$ | 3.3e-10, 9.0e-11 | 0               | 0 1.4 7 (Daugey et al. 2005, Trevitt et al. 2013, Loison & Bergeat 2009)                         |
| 13. | $\text{CH}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4^+ + \text{CH}_4$ | 4.9e-10, 4.0e-11, 5.4e-10 | 0               | 0 1.2 0 (Anicich 2003)                                                                            |
| 14. | $\text{CH}_3^+ + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5^+ + \text{CH}_4$ | 1.5e-9, 1.1e-10, 8.0e-11 | 0               | 0 1.6 0 (Anicich 2003)                                                                            |
| 15. | $\text{CH}_3^+ + \text{C}_2\text{H}_8 \rightarrow \text{C}_3\text{H}_7^+ + \text{CH}_4$ | 1.0e-9           | 0               | 0 1.6 0 (Anicich 2003) and by comparison with $\text{CH}_3^+ + \text{C}_2\text{H}_6$               |
| 16. | $\text{CH}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_3\text{H}_5 + \text{H}$ | 1.0e-10, 3.3e-11 | 0               | 0 1.4 0 At low pressure (Fahr et al. 1999, Stoliarov et al. 2000, Hébrard et al. 2013, Thorn et al. 2000) |
| Reaction | Rate Constant | Branching Ratio | Notes |
|----------|---------------|-----------------|-------|
| $\text{C}_2\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5 + \text{H}_2$ | 2.1e-10 | 0 | (Carty et al. 2001) |
| $\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_5 + \text{H}_3$ | 2.0e-10 | 0 | (Chastain et al. 1998, Vakhtin et al. 2001, Woon & Park 2009) |
| $\text{C}_2\text{H}_2^+ + \text{CH}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2$ | 1.9e-10 | 0 | (Anicich 2003) |
| $\text{C}_2\text{H}_3^+ + \text{CH}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_3$ | 7.0e-10 | 0 | (Anicich 2003) |
| $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_3$ | 6.5e-10 | 0 | (Anicich 2003) |
| $\text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_3$ | 7.2e-10 | 0 | (Anicich 2003) |
| $\text{C}_2\text{H}_2^+ + \text{CH}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2$ | 7.1e-11 | 0 | (Anicich 2003) |
| $\text{C}_2\text{H}_3^+ + \text{CH}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2$ | 6.0e-13 | 0 | (Hiraoka & Kebarle 1975, Hiraoka & Kebarle 1976, Hiraoka et al. 1993, Collins & O'Malley 1994) |
| $\text{O} + \text{C}_3\text{H}_5 \rightarrow \text{C}_2\text{H}_3\text{CHO} + \text{H}$ | 9.0e-11 | 0 | (Hoyermann et al. 2009) |
| $\text{O} + \text{C}_3\text{H}_6 \rightarrow \text{C}_2\text{H}_3\text{CHO} + \text{H}$ | 3.6e-12 | 0 | Rate constant in the 10-50K deduced from (Sabbah et al. 2007), branching ratio mainly from (Savee et al. 2012) (see also (Knyazev et al. 1992, Cavallotti et al. 2014, Leonori et al. 2015)) |
| $\text{O} + \text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_3\text{CHO} + \text{H}$ | 6.0e-11 | 0 | (Tsang & Hampson 1986) with branching ratio from (Hoyermann & Sievert 1979) considering similar amounts of i-C$_3$H$_7$ and n-C$_3$H$_7$. |
|  | \( \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 \) | \( \rightarrow \text{C}_2\text{H}_3\text{CN} + \text{H}_2 \) | \( \rightarrow \text{C}_2\text{H}_4 + \text{HCN} \) | \( \rightarrow \text{NH} + \text{C}_2\text{H}_4 \) | By comparison with \( \text{N} + \text{C}_2\text{H}_3 \). We consider that \( ^2\text{CH}_2-\text{CH}-\text{CHN} \) react with H atom on singlet surface leading to \( ^2\text{C}_2\text{H}_3\text{CN} + ^2\text{H}_2 \) and \(^1\text{C}_2\text{H}_4 + ^1\text{HCN} \). | \( \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{CN} \) | By comparison with \( \text{N} + \text{C}_2\text{H}_3 \) considering only n-\( \text{C}_2\text{H}_5 \). |
|---|---|---|---|---|---|---|---|
| 86. | \( \text{N} + \text{C}_3\text{H}_5 \) | \( \rightarrow \text{C}_2\text{H}_3\text{CN} + \text{H}_2 \) | \( \rightarrow \text{C}_2\text{H}_4 + \text{HCN} \) | \( \rightarrow \text{NH} + \text{C}_2\text{H}_4 \) | \( 3.2\times10^{-11} \) | \( 0.17 \) | \( 0 \) | \( 3 \) | \( 0 \) | \( \text{C} \) |
| 87. | \( \text{N} + \text{C}_3\text{H}_7 \) | \( \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{CN} \) | \( 1.0\times10^{-10} \) | \( 0 \) | \( 0 \) | \( 4 \) | \( 0 \) | \( \text{C} \)

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| 88. | \( \text{C}_3\text{H}_4^+ + e^- \) | \( \rightarrow \text{H} + \text{C}_3\text{H}_3 \) | \( 3.0\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | Rate constant from (Florescu-Mitchell & Mitchell 2006), 89.7 % de \( \text{C}_3\text{H}_4 \) (supposed to be \( \text{C}_3\text{H}_4^* \)) and 10.3% of \( \text{CH}_3 + \text{C}_2\text{H}_4 \) (Angelova et al. 2004a). We supposed than \( \text{C}_3\text{H}_4^* \) leads mainly to \( \text{C}_3\text{H}_3 \) by comparison with \( \text{C}_3\text{H}_3 \) photodissociation (Deyerl et al. 1999). |
|  | \( \rightarrow \text{H} + \text{H} + \text{C}_2\text{H} \) | \( 1.0\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{H} + \text{C}_2\text{H} \) | \( 1.0\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{H} + \text{C}_2\text{H} \) | \( 1.0\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{H} + \text{t}\text{-C}_2\text{H} \) | \( 1.0\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{CH}_3 + \text{C}_2\text{H} \) |  |  |  |  |  |  | |

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| 89. | \( \text{C}_3\text{H}_4^+ + e^- \) | \( \rightarrow \text{H} + \text{CH}_3\text{CCH} \) | \( 7.0\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | 86.7 % de \( \text{C}_3\text{H}_4 \) (supposed to be \( \text{C}_3\text{H}_4^* \)) and 13.3% of \( \text{CH}_3 + \text{C}_2\text{H}_4 \) (Angelova et al. 2004a, Angelova et al. 2004b). We supposed than \( \text{C}_3\text{H}_4^* \) leads mainly to \( \text{C}_3\text{H}_3 \) by comparison with \( \text{C}_3\text{H}_4 \) photodissociation (Seki & Okabe 1992, Ni et al. 1999, Harich et al. 2000a, Harich et al. 2000b). |
|  | \( \rightarrow \text{H} + \text{C}_2\text{H}_4 \) | \( 4.2\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{C}_2\text{H}_4 \) | \( 1.1\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{C}_2\text{H}_4 \) | \( 5.0\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{C}_2\text{H}_4 \) | \( 5.0\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{t}\text{-C}_2\text{H}_4 \) | \( 4.7\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{t}\text{-C}_2\text{H}_4 \) | \( 4.7\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{CH}_3 + \text{C}_2\text{H}_2 \) |  |  |  |  |  |  | |
|  | \( \rightarrow \text{H} + \text{CH}_3\text{CCH} + \text{t}\text{-C}_2\text{H}_4 \) |  |  |  |  |  |  | |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 90. | \( \text{C}_3\text{H}_4^+ + e^- \) | \( \rightarrow \text{H} + \text{C}_3\text{H}_4 \) | \( 3.4\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | \( k = 8.8e-7(T/300)^{0.7} \) (Florescu-Mitchell & Mitchell 2006), branching ratio deduced from (Janev & Reiter 2004, Reiter & Janev 2010, Angelova et al. 2004b) |
|  | \( \rightarrow \text{H} + \text{H} + \text{C}_2\text{H}_2 \) | \( 8.8\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{H} + \text{C}_2\text{H}_2 \) | \( 3.6\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{H} + \text{C}_2\text{H}_2 \) | \( 3.6\times10^{-8} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
|  | \( \rightarrow \text{H} + \text{H} + \text{C}_2\text{H}_2 \) | \( 1.52\times10^{-7} \) | \( -0.7 \) | \( 0 \) | \( 2 \) | \( 0 \) | |
| Reactions                                                                 | ΔH (kcal/mol) | ΔS (cal/mol K) | ΔE (kcal/mol) | Ref.                          |
|--------------------------------------------------------------------------|---------------|----------------|---------------|-------------------------------|
| CH₃CCH → H + H₂ +                                                       | 3.2e-8        | -0.7           | 0             |                               |
| CH₂CCH₂ → H + H₂ +                                                      | 8.8e-8        | -0.7           | 0             |                               |
| C₂H₁₆ → H + CH₃ +                                                       |               | -0.7           | 0             |                               |
| C₂H₃ → CH₃ + C₂H₄                                                        |               | -0.7           | 0             |                               |
| + H₂ → CH₃ + C₂H₄                                                        |               | -0.7           | 0             |                               |
| C₃H₉⁺ + e⁻ → H + C₃H₆                                                  | 2.0e-7        | -0.7           | 0             |                               |
| C₃H₇ → H + H₂ +                                                        | 2.0e-7        | -0.7           | 0             |                               |
| C₃H₆ → H + H₂ +                                                        | 1.0e-7        | -0.7           | 0             |                               |
| + H₂ → CH₃ + C₂H₆                                                       | 1.0e-7        | -0.7           | 0             |                               |
| + H₂ → CH₃ + C₂H₄                                                       |               | -0.7           | 0             |                               |
| s-H + s-C₁ → s-l-C₃H                                                    | 0.5           | 0              | 0             | (Mebel & Kaiser 2002)         |
| → s-c-C₃H                                                             | 0.5           | 0              | 0             |                               |
| s-H + s-l-C₃H → s-l-C₃H₂                                                | 0.5           | 0              | 0             | (Mebel et al. 1998)          |
| → s-c-C₃H₂                                                             | 0.5           | 0              | 0             |                               |
| s-H + s-c-C₃H → s-l-C₃H₂                                                | 0.5           | 0              | 0             | (Mebel et al. 1998)          |
| → s-c-C₃H₂                                                             | 0.5           | 0              | 0             |                               |
| s-H + s-l,c-C₃H₂ → s-C₃H₁ (s-CH₂CCH)                                    | 1.0           | 0              | 0             | (Nguyen et al. 2001)         |
| s-H + s-C₃H₁ → s-CH₂CCH                                                | 1.0           | 0              | 0             | (Miller & Klippenstein 2003) |
| → s-C₃H₅                                                              | 1.0           | 2013           | 1000          | (Faravelli et al. 2000, Miller et al. 2008) |
| s-H + s-C₃H₅ → s-C₃H₇                                                   | 1.0           | 0              | 0             | (Qu et al. 2009)             |
| s-H + s-C₃H₆ → s-C₃H₇                                                   | 1.0           | 1600           | 1000          | (Tsang 1991, Seakins et al. 1993, Galland et al. 2003) |
| s-H + s-C₃H₈ → s-C₃H₈                                                    | 1.0           | 0              | 0             | (Harding et al. 2005)        |
| s-H + s-C₃H₆ + s-H₂ → s-C₃H₇ + s-H₂                                     | 1.0           | 4000           | 1000          | NIST                         |
| s-H₂ + s-C₁ → s-l-C₃H + s-H                                               | 0             | 0              | 0             | Widely endothermic            |
| → s-c-C₃H₂ + s-H                                                       | 0             | 0              | 0             | Widely endothermic            |
| s-H₂ + s-l-C₃H → s-l-C₃H₂ + s-H                                         | 0             | 0              | 0             | Widely endothermic            |
| → s-c-C₃H₂ + s-H                                                       | 0             | 0              | 0             | Large barrier (this work)    |
|   | Reaction                  |   |   |   |
|---|--------------------------|---|---|---|
| 54. | s-H₂ + s-c-C₃H₂ → s-H₂ + s-c-C₃H₂ + s-H | 1.0 | 3600 | M06-2X/cc-pVTZ/TST calculations (this work) |
| 55. | s-H₂ + s-l-C₃H₂ → s-C₃H₃ + s-H | 0 |   | endothermic |
| 56. | s-H₂ + s-c-C₃H₂ → s-C₃H₃ + s-H | 0 |   | endothermic |
Abundances of methylacetylene (continuous line) and propene (dashed line) as a function of time predicted by our models with $n(H_2) = 2 \cdot 10^4 \text{ cm}^{-3}$ using a model with gas phase reactions only. The horizontal lines represent the abundances observed by Markwick et al. (2002) and Marcelino et al (2007) in TMC-1 (CP): $9 \cdot 10^{-9}$ for CH$_3$CCH and $4 \cdot 10^{-9}$ for C$_3$H$_6$.

It should be noted that Occhiogrosso et al. recently published an astrochemical model for hydrocarbons, including CH$_3$CCH, in star-forming regions (Occhiogrosso et al. 2013). In their study, they used the UMIST 2006 network with some reactions from the online KIDA database and provide in the paper a list of reactions and rate coefficients to be used (in their Table 4). We want to emphasize that many of these values should not be used under astrochemical conditions either because the data are wrong or they cannot be extrapolated to low temperatures and/or densities. We give more explanations below for some systems.
- $\text{C}_2\text{H}_5 + \text{CH}_3\text{CHCH}_2 \rightarrow \text{C}_3\text{H}_5 + \text{C}_2\text{H}_6$ : in their work Occhiogrosso et al. do not consider any barrier but this reaction has in fact a (high) barrier (Tsang 1991),

- $\text{C}_2\text{H} + \text{CH}_3\text{CHCH}_2 \rightarrow \text{C}_3\text{H}_5 + \text{C}_2\text{H}_2$ : the rate constant used in Occhiogrosso et al. is coherent with Chataing et al (1998) and Vaktin et al (2001) but the main products are in fact $\text{C}_4\text{H}_4 + \text{CH}_3$ (Woon & Park 2009) and not $\text{C}_3\text{H}_5 + \text{C}_2\text{H}_2$ which have been estimated to be equal to 1% (Tsang 1991),

- $\text{C}_2\text{H}_6 + \text{CH}_2\text{CCH} \rightarrow \text{C}_3\text{H}_5 + \text{C}_2\text{H}_6$ : this reaction appears four times in Table 4 of Occhiogrosso et al., twice with a low “reasonable” estimate of the rate constant value although no studies exist, and twice with a negative barrier leading to $k(10\text{K}) = 1.2\text{e}^{-9} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ which is clearly incorrect considering the low reactivity of propargyl with closed shell molecules in general and alkanes specifically,

- $\text{C}_2\text{H}_3 + \text{C}_3\text{H}_5 \rightarrow \text{CH}_3\text{CCH} + \text{C}_2\text{H}_4$ : Occhiogrosso et al. use only one very minor channel of the Tsang (1991) estimation neglecting the main channel,

- $\text{CH}_3 + \text{C}_3\text{H}_5 \rightarrow \text{CH}_3\text{CCH} + \text{CH}_4$ : in this case Occhiogrosso et al. again used only one very minor channel of the Tsang (1991) estimation neglecting the main channel,

- $\text{C}_2\text{H} + \text{CH}_3\text{CHCH}_2 \rightarrow \text{CH}_3\text{CCH} + \text{C}_2\text{H}_3$ : as above, this is a very minor channel originating from the estimation of Tsang (1991) neglecting the much more recent results of Bouwman et al (2012) leading mainly to the formation of vinylacetylene and methyl and not to methylacetylene,

- $\text{OH} + \text{C}_3\text{H}_5 \rightarrow \text{CH}_3\text{CCH} + \text{H}_2\text{O}$ : this is also a minor reaction channel (Tsang 1991) while neglecting the main channel,

- $\text{H} + \text{C}_3\text{H}_5 \rightarrow \text{CH}_3\text{CCH} + \text{H}_2$ and $\text{CH}_2\text{CCH}_2 + \text{H}_2$ : Occhiogrosso et al. used in both cases the high pressure limiting rate constant leading to a large overestimation (Hanning-Lee & Pilling 1992). Moreover, this reaction is supposed to lead only to minor $\text{CH}_2\text{CCH} + \text{H}_2$ production while $\text{CH}_2\text{CCH}_2 + \text{H}_2$ are not produced (Harding et al. 2007)).

The gas phase synthesis of propene is much less efficient than that of methylacetylene. Ionic reactions producing $\text{C}_3\text{H}_7^+$ involve small fluxes so that the amount of $\text{C}_3\text{H}_7^+$ generated is too low to efficiently produce $\text{C}_3\text{H}_6$ through the DR reaction of $\text{C}_3\text{H}_7^+$. Herbst et al (2010) proposed that $\text{C}_3\text{H}_7^+$ could be efficiently synthesized through radiative associations: $\text{C}_3\text{H}_5^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_7^+ + \text{h} \nu$ (2). They performed theoretical calculations leading to a high rate constant
for this reaction, in disagreement with (McEwan et al. 1999). Lin et al (2013) also showed that the radiative association leading to protonated propene was slow, whichever C3H5+ isomer was considered, so that this process in unimportant in the cold interstellar medium. In a similar manner to methylacetylene, the protonation acts as an overall loss of C3H6 as the DR of C3H7+ does not lead back to C3H6 with 100% efficiency. Alternative pathways could have been the CH5+ + C2H4 or the C2H5+ + CH4 reactions. However the CH5+ + C2H4 reaction leads to C2H5+ + CH4, and not to C3H7+ + H2 (Anicich 2003), and the C2H5+ + CH4 → C3H7+ + H2 reaction shows a barrier (Hiraoka & Kebbarle 1975, Hiraoka & Kebarle 1976, Hiraoka et al. 1993, Collins & O'Malley 1994). As a result, these two reactions are not efficient at the low temperature of dense interstellar clouds. The only known reactions producing C3H7+ are C+ + C3H8, CH3+ + C2H6, CH3+ + C3H8, C2H4+ + C2H6, C2H5+ + C2H6 (Anicich 2003) which all involve small fluxes under dense cloud conditions by pure gas phase models, as C2H6 and C3H8 are not produced efficiently by gas phase reactions. With regard to neutral reactions, the CH + C2H6 reaction produces some propene but it involves small fluxes and the radiative association H + C3H5 → C3H6 + hv has a low flux as C3H5 is essentially formed on interstellar grains. The gas phase formation of propene is so inefficient in our network that the calculated abundance remains below 10^-15 as shown in Fig. 1 (dashed line).

It should be noted that the udfa network (http://udfa.ajmarkwick.net/) (McElroy et al. 2012) considers the older (and probably incorrect, as explained above) rate constant values for reactions (1) and (2) taken from (Herbst et al. 2010) which are expected to overestimate the pure gas phase production of both methylacetylene and propene.

4. Surface reactions

As gas phase reactions cannot reproduce the observed abundances for methylacetylene and propene, we consider the possibility of surface reactions. Following the formalism of Hasegawa et al. (1992), we consider that species formed in the gas phase can stick on grains. At 10 K, only light species (H and H2) can move on the surface. As only H atoms are considered to be reactive, the main reactions are hydrogenation, apart from the specific Eley-Rideal processes introduced by (Ruaud et al. 2015). As a result, C3 (and also l,c-C3H and l,c-C3H2 but at lower levels) is efficiently formed in the gas phase in our model, and can stick on the surface, undergo successive hydrogenations to form closed shell s-C3H4 molecules (s-C3H4 represents C3H4 residing on the grain surface). As, by comparison with the gas phase, these hydrogenation reactions are considered to be barrierless (or with very low barriers) up to s-C3H4 (Mebel et al.
1998, Nguyen et al. 2001, Mebel & Kaiser 2002, Miller & Klippenstein 2003, Hébrard et al. 2013), this is an efficient route for s-C$_3$H$_4$ synthesis (both methylacetylene and allene, but only the methylacetylene isomer is considered in this work). Also by comparison with the gas phase, the subsequent hydrogenation step to s-C$_3$H$_5$ shows a small barrier (Whytock et al. 1976, Faravelli et al. 2000, Miller et al. 2008, Vuitton et al. 2012) which can be overcome through tunneling. The hydrogenation of s-C$_3$H$_6$ to s-C$_3$H$_7$ is similarly affected by a small barrier in the gas phase (Tsang 1991, Seakins et al. 1993). In contrast, the radical hydrogenation steps s-C$_3$H$_5$ + H and s-C$_3$H$_7$ + H are barrierless in the gas phase (Hanning-Lee & Pilling 1992, Harding et al. 2007, Hébrard et al. 2013). In this study we neglect most of the H atom abstraction reactions. Indeed, for gas phase H + radical (or carbynes such as c-C$_3$H$_2$) reactions (H + c,l-t-C$_3$H, c,l,t-C$_3$H$_2$, C$_3$H$_3$, C$_3$H$_5$, C$_3$H$_7$), the strength of all C-H bonds prevent H atom abstraction to be competitive with H atom addition as there is without doubt a notable barrier for H atom abstraction whereas H atom addition is barrierless. For the H + C$_3$H$_4$ reactions there are various theoretical and experimental studies (Wang et al. 2000, Miller et al. 2008) showing that indeed tunneling is efficient but H atom addition is strongly favoured at low temperature and high pressure (the high pressure limiting rate is expected to be close to the surface reaction one as the energized intermediate can be quickly relaxed through surface interaction). This is also the case for the H + propene reaction (Miller & Klippenstein 2013). Moreover, the H atom abstraction leading to H$_2$ results in radical formation (C$_3$H$_3$ and C$_3$H$_5$) which will lead back to C$_3$H$_4$ and C$_3$H$_6$ through subsequent H atom addition (H is the only species moving quickly on the surface at 10 K) which is unlikely to change the result of the model.

The binding energies of methylacetylene on icy surfaces have been measured equal to 2500 K (Kimber et al. 2014) and the one for propene should be relatively close.

5. Modeling results

The relative abundances with respect to H$_2$ of the various s-C$_3$H$_x$ compounds (with x = 0 to 8) computed by our chemical model (with the reactions listed in Table I) are shown Fig. 2. The cyclic and linear C$_3$H and C$_3$H$_2$ species have the same predicted abundances on the surfaces.
Abundances of $C_3$ in the gas phase and $s$-$C_3H_{x=0-8}$ surface species as a function of time, predicted by our model.

The formation of $s$-$C_3H_4$ in a few $10^4$ yr is explained by the depletion onto ices of $C_3$ produced in the gas phase followed by the quick transformation of $s$-$C_3$ into $s$-$C_3H_4$ through barrierless H atom addition. $s$-$C_3H_4$ is then more slowly converted into $s$-$C_3H_6$ and $s$-$C_3H_6$ into $s$-$C_3H_8$ in a few $10^5$ yr (time scale comparable to dense cloud ages). The smaller peak abundance of $s$-$C_3H_6$ relative to $s$-$C_3H_4$ is due to the fact that $s$-$C_3H_6$ is more easily hydrogenated than $s$-$C_3H_4$. At $10^6$ yr a large part (20%) of the $C_3$ produced in the gas phase is transformed into $s$-$C_3H_8$ which represents 1 % of the initial carbon, the main reservoir of carbon atoms being CO and $s$-CO. As $C_3H_8$ is relatively non reactive on ices at 10 K, further evolution is mainly driven by photodissociation processes which are almost unknown for species in ices. Then the composition of the ice given by the model is highly hypothetical for times greater than $10^6$ yr although the gas phase CH$_3$CCH and C$_3$H$_6$ abundances at times relevant to dense molecular clouds (around few $10^5$ years) are unaffected.

The gas phase C$_3H_4$ and C$_3H_6$ abundances (relative to H$_2$) are shown in Fig. 3 together with the observed abundances in cold cores.
Figure 3
Abundances of methylacetylene (continuous line) and propene (dashed line) species as a function of time predicted by our model. The horizontal lines represent the abundances observed by Markwick et al. (2002) and Marcelino et al (2007) in TMC-1 (CP): $9 \times 10^{-9}$ for CH$_3$CCH and $4 \times 10^{-9}$ for C$_3$H$_6$.

The agreement between observations and calculations is much better than with the model considering gas phase reactions only (see Fig. 3). The predicted abundances in the gas-phase are however still an order of magnitude smaller than the observational values in TMC-1 (CP) at typical cloud ages (around few $10^5$ years). Considering the large amount of s-C$_3$H$_4$ and s-C$_3$H$_6$ on the grains, more efficient non-thermal desorption, such as chemical desorption for instance, improves the agreement with the observations. With a higher chemical desorption efficiency, from 1% up to 10%, we obtain a much better agreement between calculations and observations for CH$_3$CCH and C$_3$H$_6$, but also for CH$_3$OH, H$_2$CO and NH species which are partly or mostly formed on grains (Ruaud et al. 2015). However, this results in less good agreement for NH$_3$ which becomes over-abundant. Chemical desorption is a complex
mechanism that very likely depends on the species involved. Very recent work by Minissale et al. (Minissale et al. 2016) proposes a semi empirical model to estimate the efficiency of chemical desorption for particular species. From this model, using the binding energy of methylacetylene on amorphous water? ice measured by (Kimber et al. 2014) (equal to 2500 K) for methylacetylene and propene, leads to about 1 % of chemical desorption. This efficiency is highly dependent on the binding energy as well as the semi-empirical parameter ε of (Minissale et al. 2016) which corresponds to the fraction of kinetic energy retained by the product colliding with the surface. It should be noted that other non-thermal desorption mechanisms, such as cosmic-ray explosive desorption (Ivlev et al. 2015) may play a role. More accurate predictions of species formed on interstellar grains can only be provided by more detailed models of these surfaces, as well as through precise measurements (or calculations) of the efficiency of the chemical desorption mechanism in interstellar ice analogs. In our nominal model we keep the fraction of desorption for the newly formed species on grains equal to 1% which seems a reasonable value considering the latest work from Minissale et al (2016).

5. The C₃ + O reaction

The chemistry of C₃H₄ and C₃H₆ on grains is triggered by the depletion of gas phase C₃H₈ species (where x can be zero). Then the amount of C₃Hₓ in the gas phase controls the grain production of C₃H₄ and C₃H₆ (and therefore the amount of C₃H₄ and C₃H₆ released back into the gas phase through reactive desorption). In our network, the most abundant C₃H₈ compound produced in the gas phase is C₃ (by far), reaching a maximum abundance of 10⁻⁵[H₂] at 10⁵ years so that efficient C₃H₄ and C₃H₆ production on grains is directly linked to the large gas phase C₃ abundance. C₃ is abundant in the gas phase as a result of various efficient neutral pathways producing C₃ (among them the C + C₂H and C + C₂H₂ reactions) with very few destruction mechanisms. Indeed, C₃ has a low reactivity with abundant species in molecular clouds such as O, H, N, CO, CH₄, C₂H₂ (Woon & Herbst 1996, Nelson et al. 1982, Nelson et al. 1981, Mebel et al. 2007, Guo et al. 2007, Li et al. 2005, Szczepanski et al. 2004). C₃ reacts without a barrier with C atoms leading to C₄ through radiative association (Wakelam et al. 2009), with highly reactive radicals such as CH and C₂H species (Hébrard et al. 2013) these reactions involving small fluxes, and with H₃⁺, HCO⁺ and HCNH⁺ through proton transfer. As C₄ leads mainly back to C₃ through reactions with C, O and N atoms (Wakelam et al. 2009), the only efficient reactions for C₃ loss are with H₃⁺, HCO⁺ and HCNH⁺ and through depletion onto grains. The low reactivity of C₃ allows it to reach high abundance levels, which is at the origin of the rich C₃Hₓ chemistry on grains. To estimate the importance of the O + C₃ reaction,
which has been studied only theoretically by (Woon & Herbst 1996) who found a small barrier in the entrance valley, we performed a run considering no barrier for this reaction and a rate constant equal to \(2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}\) (close to the capture rate constant). The results for the abundances of C\(_3\)H\(_4\) and C\(_3\)H\(_6\) in the gas phase are shown in Fig. 4.

![Abundance vs Time](image)

**Figure 4**

Abundances of gas phase methylacetylene (continuous line) and propene (dashed line) as a function of time predicted by our model considering no barrier for the O + C\(_3\) reaction. The horizontal lines represent the abundances observed by Markwick et al. (2002) and Marcelino et al (2007) in TMC-1 (CP): 9.10\(^{-9}\) for CH\(_3\)CCH and 4.10\(^{-9}\) for C\(_3\)H\(_6\).

It is clear that the simulated abundances cannot reproduce the observed ones for typical cloud ages of a few \(10^5\) years. The abundances of these species on the surfaces are also strongly decreased, yielding values below the gas-phase ones. It is worth noting that the absence of barrier for the O + C\(_3\) reaction affects various large species in the gas phase, namely C\(_3\)H\(_{x=0-6}\), C\(_3\)O, C\(_3\)S, C\(_3\)N, HC\(_3\)N and C\(_4\)H. For almost all these species, the absence of barrier for the O + C\(_3\) reaction leads to large disagreements between calculated abundances and observations in
the current state of the model. It appears likely that the calculations of Woon & Herbst (1996) for the \( \text{O} + \text{C}_3 \) reaction are reliable and should be used in chemical networks. We have also looked to the \( \text{C}_3 + \text{H} \rightarrow \text{C}_3\text{H} \) reaction which is calculated to be barrierless (Mebel & Kaiser 2002, Hébrard et al. 2013) but may show a small barrier considering the theoretical uncertainties. In the gas phase, even without a barrier, the radiative association rate is estimated to be below \( 10^{-14} \text{ cm}^3 \text{ s}^{-1} \) at 10 K (Hébrard et al. 2013) so this process has a negligible flux. For the surface reaction, \( \text{s-C}_3 + \text{s-H} \rightarrow \text{s-C}_3\text{H} \), the presence of a small barrier has very little effect on \( \text{s-CH}_3\text{CCH} \) and \( \text{s-C}_3\text{H}_6 \) abundances. So, in contrast to the \( \text{O} + \text{C}_3 \) reaction, the \( \text{H} + \text{C}_3 \) reaction is not a critical one in dense molecular clouds.

### 6. Conclusion

We have shown, using our gas-grain chemical model NAUTILUS, that surface reactions may explain the observed abundances of methylacetylene and propene in cold dense molecular clouds. Based on the recent calculations by Lin et al (2013) and the current review of gas-phase reactions, gas-phase reactions are unlikely to produce enough of these species. These results are in good agreement with the suggested scenario by Miettinen et al (2006) who found a gas-phase methylacetylene abundance which increases with the temperature in star forming regions, suggesting its formation on ice surfaces followed by thermal desorption. We also highlight the critical role of the \( \text{O} + \text{C}_3 \) reaction which is likely to possess a substantial barrier, in good agreement with the calculations of Woon & Herbst (1996) leading to a high \( \text{C}_3 \) abundance in dense molecular clouds.

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