Chemical Variation among Protostellar Cores: Dependence on Prestellar Core Conditions

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Abstract

Hot corino chemistry and warm carbon chain chemistry (WCCC) are driven by gas–grain interactions in star-forming cores: radical–radical recombination reactions to form complex organic molecules (COMs) in the ice mantle, sublimation of CH4 and COMs, and their subsequent gas-phase reactions. These chemical features are expected to depend on the composition of the ice mantle, which is set in the prestellar phase. We calculated the gas–grain chemical reaction network considering a layered ice mantle structure in star-forming cores to investigate how the hot corino chemistry and WCCC depend on the physical condition of the static phase before the onset of gravitational collapse. We found that WCCC becomes more active if the temperature is lower, or the visual extinction is lower in the static phase, or the static phase is longer. The dependence of hot corino chemistry on the static-phase condition is more complex. While CH3OH is less abundant in the models with a warmer static phase, some COMs are formed efficiently in those warm models because there are various formation paths of COMs. If the visual extinction is lower, photolysis makes COMs less abundant in the static phase. Once the collapse starts and visual extinction increases, however, COMs can be formed efficiently. The duration of the static phase does not largely affect COM abundances. The chemical diversity between prototypical hot corinos and hybrid sources, in which both COMs and carbon chains are abundantly formed, can be explained by the variation of prestellar conditions. Deficiency of gaseous COMs in prototypical WCCC sources is, however, hard to reproduce within our models.

Unified Astronomy Thesaurus concepts: Star formation (1569); Astrochemistry (75)

1. Introduction

Various molecular emission lines have been detected in the central regions of low-mass protostellar cores. Emission lines of complex organic molecules (COMs), which are defined as organic molecules with six atoms or more, are detected in the hot (≥100 K) central (∼100 au) region in several protostellar cores, for example, IRAS 16293-2422B and NGC 1333-IRAS4A (e.g., van Dishoeck et al. 1995; Cazaux et al. 2003; Bottinelli et al. 2004a, 2004b; Ceccarelli et al. 2007; Caux et al. 2011; Taquet et al. 2015; Jørgensen et al. 2016; Oya et al. 2016; López-Sepulcre et al. 2017). Toward IRAS 04368+2557 in L1527 and IRAS 15398-3359, on the other hand, unsaturated carbon chains (e.g., C2H and C3H) are abundantly detected in the vicinity of a protostar (Sakai et al. 2008, 2009a). In this work, we reserve the term carbon chains for such significantly unsaturated carbon chains to discriminate them from hydrocarbons, which are molecules made of C and H in general.

In theoretical models, the formation of both carbon chains and COMs is explained, at least qualitatively, by the gas–grain chemistry in the sequence of star formation. In cold (∼10 K) prestellar cores, molecules with heavy elements such as CO are frozen onto grains. Hydrogen atoms can thermally migrate and hydrogenate CO and other adsorbed atoms and molecules on grain surfaces. While the successive hydrogenation of CO produces CH2OH, the intermediate radicals such as HCO can also react with each other, if they are in neighboring adsorption sites, to form more COMs. Eventually, star formation starts and the dust temperature gradually rises, which enhances the thermal diffusion of adsorbed species and reactions among them to produce various COMs. Icy molecules are sublimated according to their volatility, and reactions proceed in the gas phase as well. When the dust temperature exceeds ∼100 K, the dominant constituent of ice, H2O, sublimes together with COMs (Rodgers & Charnley 2003; Garrod & Herbst 2006; Aikawa et al. 2008; Herbst & van Dishoeck 2009; Aikawa et al. 2012; Garrod & Widicus Weaver 2013; Taquet et al. 2014; Chuang et al. 2016; Cuppen et al. 2018; Lu et al. 2018). The low-mass protostars with bright emission of COMs at the central hot region (R ≤ 100) are called hot corinos. The unsaturated carbon chains, on the other hand, are formed by the gas-phase reactions triggered by the sublimation of CH4 at ∼25–30 K; this is called warm carbon chain chemistry (WCCC; Aikawa et al. 2008; Hassel et al. 2008; Sakai et al. 2008; Sakai & Yamamoto 2013). Protostars are called WCCC sources if the emission lines of unsaturated carbon chains become bright inward of about a few 102 au, suggesting their abundance jump.

In theory, both WCCC and COM formation proceed in a star-forming core. Indeed, both carbon chains and COMs have been recently detected in B335 and L483 (Imai et al. 2016; Oya et al. 2017), which are called hybrids (of hot corinos and WCCC). The emission of carbon chains is more extended (r of about a few 100–102 au) than that of COMs (r ≲ 100 au), which supports the theoretical model. It should be noted, however, that the prototypical hot corino sources are deficient in carbon chains, while COMs are deficient in the first two WCCC sources. The column density ratio of C2H/CH3OH is
~0.1 in prototypical hot corinos such as IRAS 16293 and NGC 1333 IRAS 4A, while it is ~4 in L1527 (Higuchi et al. 2018; Bouvier et al. 2020, and references therein). Higuchi et al. (2018) observed multiple lines of C2H, c-C3H2, and CH3OH toward 36 Class 0/I protostars in the Perseus molecular cloud complex using the IRAM 30 m and NRO 45 m telescopes to derive the chemical composition averaged over the 1000 au scale. The column density ratio of C2H/CH3OH varies by two orders of magnitude among sources. One caution in such single-dish observations is a possible contamination of the emission of a parental molecular cloud (Bouvier et al. 2020). Follow-up observations are necessary to disentangle the molecular cloud and protostellar core and to confirm the abundance jump of COMs and unsaturated carbon chains, which characterizes the hot corino and WCCC. In the ALMA observation of IRAS 16293 B, for example, C2H emission is detected, but its spatial distribution is different from that of C3H2 (Murillo et al. 2018). It is indeed unexpected in WCCC and thus suggests the chemistry in IRAS 162293 B would be different from that of prototypical WCCC.

What is the origin of such chemical variation among protostellar cores? Since the sublimation temperatures of COMs are higher than that of CH4, WCCC cores could be deficient in COMs if the central protostar is not bright enough. But it cannot explain the deficiency of carbon chains (or lack of WCCC) around hot corinos. Higuchi et al. (2018) showed that the column density ratio of C2H/CH3OH in protostellar cores does not correlate with the evolutionary indicator, such as bolometric temperature, or with luminosity. Alternatively, the chemical composition of protostellar cores could reflect the ice composition set in the prestellar phase. Graninger et al. (2016) observed C2H and CH3OH toward 16 deeply embedded, low-mass protostars using the IRAM 30 m telescope, and they found that the gaseous C2H/CH3OH abundance ratio tentatively correlates with the CH3OH/CH3/OH ice abundance ratio determined by the Spitzer c2d survey (Boogert et al. 2008; Öberg et al. 2008). The ice composition, in turn, would be determined by the physical conditions. For example, if a core is located near the periphery of a molecular cloud, the penetrating UV radiation keeps carbon atoms abundant, which activates the formation of hydrocarbons. Then the ratio of CH3OH/CH3/OH in the ice mantle could be relatively high compared with that in cores in the high visual extinction. While the correlation of ice abundances with UV radiation is hard to investigate observationally, the correlation between gaseous molecules with the UV radiation field is found in low-mass star-forming cores. Lindberg et al. (2015) showed that in the protostellar core R CrA IRS7B COMs are underabundant, while CN emission is strong, which is an indicator of photon dominated region (PDR) chemistry. Higuchi et al. (2018) found that the protostars located near cloud edges or in isolated clouds tend to have a high C2H/CH3OH ratio. In a prototypical prestellar core, L1544, Spezzano et al. (2016) found that c-C3H2 emission peaks close to the southern part of the core, where the surrounding molecular cloud has a sharp edge, while CH3OH mainly traces the northern part of the core. The gas in the north and south would eventually fall to the central region to set the chemistry in the protostellar phase. Since a protoplanetary disk is being formed in the central region of a protostellar core, the chemical composition of a core might be inherited by a forming disk and eventually by a planetary system.

Several theoretical works investigated the dependence of molecular abundances on core models. Garrod & Herbst (2006) showed that grain surface reactions become more important for COM formation in models with slower warm-up, while the peak abundance of each molecular species shows a complex dependence on the warm-up timescale. Aikawa et al. (2012) showed that for WCCC to be active, the gas density around the CH4 sublimation zone should be low enough for C+ to be abundant. Sakai & Yamamoto (2013) pointed out that CH4 should be more abundant than 10−7 relative to hydrogen to be the major reactant with C+ (competing against C+ + OH) to trigger WCCC. But there are a few theoretical works that investigate both WCCC and hot corino chemistry systematically. In this paper, we study the dependence of COMs and warm carbon-chain abundances in protostellar cores on the physical conditions in the prestellar phase via numerical calculations. Specifically, we vary the temperature, visual extinction of the ambient clouds, and duration of the static phase before gravitational collapse.

The rest of the paper is organized as follows. Our chemical and physical models are described in Section 2. The results of model calculations are presented in Section 3. We compare our results with previous work and observations in Section 4. Our conclusions are summarized in Section 5.

2. Model

2.1. Model of a Star-forming Core

The structure and evolution of molecular clouds are summarized as follows (André et al. 2014, and references therein). Molecular clouds consist of filaments. Herschel observations revealed that gravitationally bound prestellar cores and protostars are primarily found in filaments with H2 column densities of \( \gtrsim 7 \times 10^{21} \) cm\(^{-2} \). The radial density profiles of the filaments show a flat plateau with FWHM \( \sim 0.1 \) pc. The mean gas density in the star-forming filaments is thus \( n(H_2) \gtrsim 2 \times 10^3 \) cm\(^{-3} \). Statistical observations of cloud cores suggest the lifetime of a core with \( n(H_2) \sim 10^3 \) cm\(^{-3} \) to be 10\(^4\) yr, which coincides with the sound-crossing timescale of a filament. The typical column density of filaments with cores roughly coincides with the threshold value of gravitational instability, which indicates that the filaments fragment to form self-gravitating cores. Eventually the core collapses to form a protostar.

In the present work, we solve the rate equations of the gas–grain chemical reaction network in a fluid parcel that reaches the \( T \gtrsim 100 \) K region in a protostellar envelope. Considering the observational overview described above, we divide our model into two phases: the prestellar phase with density of \( \sim 10^3 \) cm\(^{-3} \) and the collapse phase (Figure 1).

For the latter phase, we adopt the 1D (spherical) radiation hydrodynamic model of low-mass star formation by Masunaga et al. (1998) and Masunaga & Inutsuka (2000). We assume a spherical collapse, although a flattened structure will form in the vicinity of the protostars (e.g., Terebey et al. 1984). The total mass and initial radius of the core are 3.852 \( M_\odot \) and \( R = 4 \times 10^4 \) au, respectively. The initial number density of hydrogen nuclei is \( \sim 6 \times 10^5 \) cm\(^{-3} \) (i.e., \( n(H_2) \sim 3 \times 10^4 \) cm\(^{-3} \)) at the core center. After the onset of gravitational collapse, the central density increases with time, and the protostar is formed in 2.5 \( \times 10^5 \) yr. After the birth of the protostar, the model further follows the evolution for 9.3 \( \times 10^4 \) yr, during which the protostar...
grows by mass accretion from the envelope. At each evolutionary stage, the model gives the total luminosity of the core and the radial distributions of density, temperature, and infall velocity self-consistently. At the final time step, the total luminosity of the core is $24 L_\odot$ and the temperature is higher than 100 K inside $R \sim 100$ au. While the temperatures of the gas and multiple components of dust material are calculated separately in the original model of Masunaga et al. (1998) and Masunaga & Inutsuka (2000), we assume that the dust temperature is equal to the gas temperature, for simplicity. A more detailed description of our core model can be found in Masunaga et al. (1998), Masunaga & Inutsuka (2000), and Aikawa et al. (2008, 2012).

In our previous work (Aikawa et al. 2008, 2012), we solved the rate equations in multiple infalling fluid parcels to derive the radial distributions of molecular abundances. In the present work, on the other hand, we follow the temporal variation of molecular abundances in one infalling fluid parcel that is initially located at $R = 1.01 \times 10^4$ au and reaches $R = 30.6$ au at the final time step, and we plot the abundances as a function of the temporal radial position of the fluid parcel. The green line in Figure 2(b) shows the time after the onset of collapse as a function of the location of the infalling fluid parcel. The figure also depicts the density, temperature, and visual extinction of the fluid parcel. As we will show in Section 3, the $R$-abundance plot is reasonably similar to the true radial distribution of molecules around WCCC and hot corino regions at the final time step. If we were to calculate the chemistry in multiple fluid parcels to derive the radial distributions with a similar spatial resolution as the $R$-abundance plot, we would need $\sim 100$ fluid parcels for each model, which is computationally expensive. We decided to use the $R$-abundance plot as a proxy for the radial distribution, considering the similarity between them.

For the prestellar phase, we assume that the initial core stays static for $t_{sta} = 1 \times 10^6$ yr. We thus call this phase the static phase in the following. This notation, static phase versus collapse phase, is clearer, since a protostar is not formed immediately after the onset of collapse; that is, the early

Figure 1. Schematic view of our core model (see text). The radial size is not to scale.

Figure 2. (a) Physical parameters (gas number density in black, temperature in red, and visual extinction in blue) in the static phase of our fiducial model. While they are plotted as a function of time, the values are constant in the static phase. (b) Physical parameters in the infalling fluid parcel in the collapse phase as a function of the radial location of the fluid parcel (see text) in our fiducial model. The time after the onset of collapse is depicted by the green line. The red dotted line depicts the temperature in the model with $T_{min} = 10$ K.
Table 1

| Fixed Parameters |
|------------------|
| Total mass of the core | 3.852 ($M_\odot$) |
| Core radius | $4 \times 10^3$ (au) |
| Initial position of the infalling fluid parcel | $1.01 \times 10^4$ (au) |
| Final position of the infalling fluid parcel | 30.6 (au) |

| Varied Parameters$^a$ |
|-----------------------|
| Temperature in the static phase | $T_{\text{init}}$, 10, 15, 20, 25 (K) |
| Minimum temperature | $T_{\text{min}}$, 10, 15, 20, 25 (K) |
| Visual extinction of the ambient gas | $A_{\text{amb}}$, 1, 3, 5 (mag) |
| Duration of static phase | $t_{\text{sta}}$, $3 \times 10^2$, $1 \times 10^5$, $3 \times 10^6$ (yr) |

Note.
$^a$ The fiducial values are in bold font.

collapse phase is actually a prestellar phase. In the fluid parcel we follow, which is located at $R = 1.01 \times 10^3$ au, the density and temperature are $n_H = 2.28 \times 10^3$ cm$^{-3}$ and $T_{\text{init}} = 10$ K (Figure 1 and Figure 2(a)). The gas column density from the core outer boundary ($R = 4 \times 10^5$ au) to the location of the fluid parcel corresponds to the visual extinction of $A_v = 1.51$ mag. Outside the core, we assume an ambient gas of $A_{\text{amb}} = 3$ mag. The interstellar UV radiation field is thus attenuated by the total visual extinction of 4.51 mag (Figure 2(a)). These parameters are chosen to be consistent with the physical conditions in the filaments and to make the transition to the infalling stage simple and smooth. Ideally, we need to also consider the formation of a filament and its fragmentation to form prestellar cores. We will include the filament formation in our model in Section 3.5.

In order to investigate the dependence of WCCC and COM formation on the physical parameters of the static phase, we vary the initial temperature ($T_{\text{init}} = 10$, 15, 20, or 25 K), the visual extinction of the ambient gas ($A_{\text{amb}} = 1$, 3, or 5 mag), and the duration of the static core phase ($t_{\text{sta}} = 3 \times 10^2$, $1 \times 10^5$, or $3 \times 10^6$ yr) (Table 1). In the collapse phase of these models, the temporal variation of the temperature is assumed to be the same as the fiducial model, while the visual extinction is modified in accordance with $A_{\text{amb}}$. Namely, even in the model with high $T_{\text{init}}$, the temperature of the fluid parcel decreases below 10 K in the early phase of collapse, shielded from the interstellar radiation field. As we will see in Section 3, the ice composition is significantly changed during this period, which dilutes the effect of the warm static phase in the models with $T_{\text{init}} > 10$ K. In order to further investigate the effect of thermal history, we also calculated models in which the minimum temperature is set to be $T_{\text{min}} = 10$, 15, 20, or 25 K; the temperature of the fluid parcel is fixed at $T_{\text{min}}$ in the static phase and early collapse phase, and it starts rising when it exceeds $T_{\text{min}}$ in the original model. The dotted line in Figure 2(b), for example, depicts the temporal temperature variation in the model of $T_{\text{min}} = 10$ K. Warm temperatures in the static and early collapse phases would be possible if the core is in, for example, cluster-forming regions.

2.2. Chemistry

Our reaction network model is based on Garrod (2013) and includes the following updates. The gas-phase reaction of H$_2$CO + OH has two production paths: HCOOH + H and H$_2$O + HCO. In our previous model (Aikawa et al. 2012), the former was one of the major formation paths of HCOOH in the gas phase. According to quantum calculations and laboratory experiments (D’Anna et al. 2003; Sivakumaran et al. 2003; Xu et al. 2006), however, the former branch has an activation barrier of $\sim$2500 K and is thus negligible compared with the latter branch, which is barrierless. We thus deleted the former path in the present work, while the rate coefficient of the latter path is set to be $1.0 \times 10^{-11} (T/300.0$ K)$^{-0.6}$ cm$^3$ s$^{-1}$ (see also Raouf et al. 2015). While HCOOH consists of five atoms, we consider it as a COM in the present work, since it is often observed in hot coronas (e.g., Remijan & Hollis 2006; Imai et al. 2016). The gas-phase reaction rate coefficient of NH$_2$ + H$_2$CO → NH$_2$CHO + H is set to be $2.6 \times 10^{-12} (T/300.0$ K)$^{-2.1} \exp(-26.9$ K/T) cm$^3$ s$^{-1}$ following Barone et al. (2015). On grain surfaces, the reaction of H + NH$_2$CO results in hydrogen abstraction (H + HNCO) rather than hydrogenation (NH$_2$CHO; Noble et al. 2015). The grain surface reaction of HCO + CH$_3$ has three possible production paths: CH$_4$ + CO, CH$_3$CHO, and CH$_3$OH. We neglected the latter two paths following Enrique-Romero et al. (2016), who showed that only the first path is plausible considering the orientation of the reactants on amorphous water ice (see Section 4.2 for further discussions). We also added the gas-phase reactions of H$_2$ with C$_2$H, C$_3$H, and C$_3$H$_2$, which result in a hydrogen addition to the carbon chains (i.e., C$_n$H$_m$ + H$\rightarrow$ C$_n$H$_{m+1}$ + H); the barrier is set to be 998 K, 950 K, and 1740 K, respectively, by referring to the KIDA database for astrochemistry (kida.obs.u-bordeaux1.fr).

The simplest model of gas–grain chemistry consists of two phases, gas phase and ice phase, and thus is called a two-phase model (Hasegawa et al. 1992). While the ice mantle consists of $\sim$10$^4$ monolayers of molecules and atoms in cold, dense prestellar cores, such a layered structure is not considered in the two-phase model. For example, all CO molecules in the ice mantle have an equal probability of reaction and an equal probability of desorption. This is obviously a simplification. Hasegawa & Herbst (1993) then proposed the three-phase model that consists of a gas phase, ice surface phase, and ice mantle phase. In the original three-phase model, the ice mantle phase is assumed to be chemically inert, while chemical reactions are considered in the ice surface phase. In more recent three-phase models, chemical reactions are often considered in the ice mantle phase as well, but with slower rates than in the ice surface phase. The basic assumption of the three-phase model is that the ice mantle phase has a uniform chemical composition, which is not true. Infrared absorption bands of interstellar ices suggest that the ice mantle is made of a polar (water-rich) component and an apolar (CO- and CO$_2$-rich) component (e.g., Gibb et al. 2004). In order to take into account such inhomogeneity in the ice mantle, we adopt a seven-phase model that consists of the gas phase, the ice surface phase, and five phases of ice mantle. We assume that the top four monolayers are the ice surface phase (Vasyunin & Herbst 2013), while each mantle phase consists of a few tens of monolayers at a maximum. Since the term phase is used to discriminate between gas and ice, that is, the gas phase
versus ice phase, and also to specify the evolutionary stage of a star-forming core, that is, the static phase and infalling phase. In the present work, we will use the term layer to specify different phases of ice. In summary, ices in our model consist of six layers: the ice surface layer and five mantle layers.

We assume the Langmuir–Hinshelwood mechanism for reactions in the ice surface layer and mantle layers; species can diffuse by thermal hopping and react with each other when they meet. No quantum tunneling is assumed in the migration, reactions in the ice surface layer and mantle layers; species versus ice phase, and also to specify the evolutionary stage of a

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depending on gas density, which is reached when the fluid parcel is at \( R = 2000–3000 \) au. Since the ice mantle is multilayered and made of a mixture of ices in our model, only a fraction of CO and CH\(_4\) is sublimated. The majority of icy molecules are trapped in water ice until water is sublimated at \( \sim 100 \) K. This entrapment is in agreement with laboratory experiments, at least qualitatively, while the actual fraction of trapped volatiles depends on the ice thickness and the mixture ratio in experiments and the parameterization of diffusion and swapping efficiency in numerical simulations (Collings et al. 2004; Fayolle et al. 2011).

Figures 3(c) and (g) show the abundances of several icy radical species in the static phase and collapse phase, respectively. Radicals are efficiently formed, trapped, and stored in ice in the cold phase (Lu et al. 2018). Compared with the two-phase model, various radicals are abundant in the multilayered ice mantle model for the following reasons. First, icy species, including radicals, are trapped beneath the surface layer and are not directly subject to desorption to the gas phase. Radicals beneath the surface layer do not react with newly adsorbed atoms and molecules from the gas phase, either. In the two-phase model, on the other hand, all icy radicals can react with newly adsorbed species, such as H atoms, to form saturated molecules. Lastly, the thermal diffusion and thus the reactions (e.g., radical–radical reactions) are slower in ice mantle layers than in the surface layer. When the temperature rises, however, the stored radicals start to react with each other to form COMs. CH\(_3\)OCH\(_3\), for example, is mainly formed in the ice mantle via the reaction of CH\(_4\) + CH\(_2\)O when the temperature of the fluid parcel is \( \sim 20 \) K (Figure 3(f)). The CH\(_3\)OCH\(_3\) abundance in the final time step in the present model (9.7 \times 10\(^{-9}\)) is much higher than that in the two-phase model of Aikawa et al. (2012; 1.2 \times 10\(^{-10}\)) adopting the same collapse model. The gas-phase reactions of sublimated molecules also contribute to the formation of COMs, for example, C\(_2\)H\(_5\) + O \rightarrow CH\(_3\)CHO + H and NH\(_2\) + H\(_2\)CO \rightarrow NH\(_3\)CHO + H at \( R \sim 90 \) au.

When the fluid parcel reaches \( R \sim 2000 \) au, the temperature rises to \( \sim 25 \) K, which is the sublimation temperature of CH\(_2\). Sublimation of CH\(_2\) triggers the WCCC; for example, CH\(_4\) reacts with C\(^+\) to produce C\(_2\)H\(_3\), which then recombines to form C\(_2\)H. The carbon chain also extends via the reactions with C atoms (e.g., C + CH\(_3\)\(_\rightarrow\)C\(_2\)H\(_2\) + H). It should be noted that CH\(_2\) does not fully sublimate at its own sublimation temperature (\( \sim 25 \) K), which suppresses the WCCC compared with the two-phase model of Aikawa et al. (2008). Closely looking at Figures 3(f) and (h), we also note that WCCC enhances the abundance of some COMs, as well. For example, the NH\(_2\)CHO abundance increases around the WCCC region (\( R \sim 1900 \) au); CH\(_3\) reacts with O atoms in the gas phase to form H\(_2\)CO, which then reacts with NH\(_2\) to form NH\(_3\)CHO. Later, the temperature rises to the sublimation temperature of H\(_2\)CO (\( \sim 40 \) K) when the fluid parcel reaches \( \sim 750 \) au. Then the gas-phase reactions initiated by the sublimation of H\(_2\)CO further enhance the abundance of NH\(_2\)CHO.

The crosses in Figures 3(e), (f), and (h) depict the radial distribution of gaseous molecular abundances at the final time step; we calculated the gas–grain chemistry in the fluid parcels that reach the radius of 62.4 au, 125 au, 250 au, 500 au, 1000 au, 2000 au, 4000 au, and 8000 au. The \( R \)-abundance plot of the infalling fluid parcel (i.e., solid lines) is quite similar to this true radial distribution inside the radius of \( \sim 10^3 \) au. This is reasonable, because the infall timescale inside \( 10^3 \) au is

3. Results

3.1. Fiducial Model

Figures 3(a)–(d) shows the temporal variation of molecular abundances in the static prestellar core phase. The solid lines depict the molecular abundances of gaseous molecules relative to hydrogen nuclei, while the dashed lines show those of icy molecules, that is, the sum of ices in the surface layer and mantle layers. As we start with atoms and ions, C\(^+\) is gradually converted to atomic carbon and then to CO in the gas phase, while oxygen is hydrogenated to form water on grain surfaces (Figure 3(a)). After 10\(^7\) yr, the ice abundances of CO, CO\(_2\), and CH\(_2\)OH relative to water are in reasonable agreement with observation toward low-mass protostars and background stars (i.e., CO/H\(_2\)O ~ 0.3, CO\(_2\)/H\(_2\)O ~ 0.3–0.4, and CH\(_2\)OH/H\(_2\)O about a few 10\(^{-2}\); Öberg et al. 2011). Hydrocarbons, including carbon chains, are efficiently formed from C\(^+\) and atomic C both in the gas phase and ice before carbon is fully converted to CO (Figure 3(d)). Hydrocarbons and carbon chains also react with N atoms and O atoms to form CH\(_3\)CN and CH\(_2\)CHO in the gas phase (Figure 3(b)). CH\(_3\)CHO, for example, is mainly formed via O+CH\(_3\)H\(_3\) at \( t \sim 10^4 \) yr in our model.

Molecular evolution in the collapse phase is shown as a function of the radial position of the infalling fluid parcel in Figures 3(e)–(h). The sublimation temperatures of the most volatile C-bearing molecules, CO and CH\(_4\), are \( \sim 20–30 \) K, depending on gas density, which is reached when the fluid parcel is at \( R = 2000–3000 \) au. Since the ice mantle is multilayered and made of a mixture of ices in our model, only a fraction of CO and CH\(_4\) is sublimated. The majority of icy molecules are trapped in water ice until water is sublimated at \( \sim 100 \) K. This entrapment is in agreement with laboratory experiments, at least qualitatively, while the actual fraction of trapped volatiles depends on the ice thickness and the mixture ratio in experiments and the parameterization of diffusion and swapping efficiency in numerical simulations (Collings et al. 2004; Fayolle et al. 2011).
Figure 3. Left column: molecular abundances relative to hydrogen nuclei as a function of time in the static phase in our fiducial model. The solid lines show the gas-phase abundances, while the dashed lines depict the ice abundances. Right column: molecular abundances in the infalling fluid parcel in the collapse phase as a function of the radial location of the fluid parcel (see text) in our fiducial model. The arrows in panel (e) depict the radius where the thermal desorption timescale is equal to the adsorption timescale for CO (black), CH$_3$ (orange), and CH$_3$OH (green). The crosses in the panels show the radial distributions of gaseous molecules at the final time step in our model.
CH₃O and subsequent minimum temperatures of 10, 15, 20, and 25 K is higher than the current temperature and thus is reasonable agreement with the radial distribution. This can be used the R-abundance plot to investigate the hot corino chemistry and WCCC.

3.2. Dependence of COM Abundances on T_init and T_min

We calculate the molecular evolution in the fluid parcels with the temperature in the static phase T_init of 15, 20, and 25 K. The gaseous abundances of COMs in the final time step (i.e., R = 30.6 au) are shown in Figure 4(a) as a function of T_init. A naive expectation is that the higher T_init makes the freeze-out and grain surface hydrogenation less efficient, resulting in lower abundances of icy molecules and COMs. Indeed, the abundances of CH₃OH and CH₃CHO are lower in the model with T_init = 25 K than in the fiducial model (i.e., T_init = 10 K), but the abundances of some COMs, such as CH₂CN, CH₃OCH₃, and HCOOH, are higher with T_init = 25 K than in the fiducial model.

In order to investigate the chemistry with high T_init, we plot the temporal variation of molecular abundances in the model with T_init = 25 K; Figures 5(a), (b) show the temporal variation in the static phase, while Figures 5(c), (d) show the R-abundance plot in the infalling phase. In the static phase, the abundances of H₂O ice and CO ice are indeed lower than in our fiducial model; at the end of the static phase (t = 10⁶ yr), their abundances are 1 × 10⁻³ (H₂O) and 3 × 10⁻⁶ (CO). CO₂ ice, on the other hand, is abundantly formed via CO + OH on grain surfaces; for example, its abundance reaches ~7 × 10⁻⁵ at t = 10⁶ yr. The warm temperature makes the CO freeze-out less efficient but enhances the thermal diffusion of species with moderately high binding energy. In numerical models of gas–grain chemistry, molecules tend to be converted to and accumulate as stable icy species whose sublimation temperature is higher than the current temperature (e.g., Aikawa et al. 1997; Furuya & Aikawa 2014). Icy abundances of COMs in the static phase are also higher than those in our fiducial model. While CH₃OH is mainly formed via hydrogenation of CO in our fiducial model (T_init = 10 K), it is formed via the grain surface association of CH₃ + O → CH₃O and subsequent hydrogenation in the T_init = 25 K model. CH₃ and O atoms, in turn, are formed via photodissociation of larger hydrocarbons and CO₂, respectively. The grain surface reaction of CH₃ with CH₃O forms CH₃OCH₂. In other words, formation of COMs starts from carbon chains and hydrocarbons, which are abundantly formed in both the gas and ice phases before carbon is fully converted to CO. Once CO becomes the dominant carbon reservoir (t ~ 10⁵ yr), COM abundances temporally decline, as the destruction (e.g., photodissociation) dominates over the formation.

The model results are in line with recent laboratory experiments showing that CH₃OH can be formed in a CH₄ ice mixture. Qasim et al. (2018) performed temperature programmed desorption (TPD) from the mixed ice of CH₄, O₂, and H atoms to find that CH₃OH is produced. The analysis of the experimental data with different ice mixtures indicates that CH₃OH is formed via CH₄ + OH → CH₃ + H₂O and CH₃ + OH → CH₃OH. The latter reaction is one of the main formation paths of CH₃OH in the collapse phase of the T_init = 25 K model. In the static phase of our model with T_init = 25 K, CH₄ ice abundance is not high, since T_init coincides with its sublimation temperature. CH₃ is thus formed from larger hydrocarbons, and then quickly reacts with atoms and radicals in the ice mantle.

Figure 5(c), (d) is the R-abundance plot in the infalling phase of the model with T_init = 25 K. It should be noted that the temperature of the fluid parcel falls to ≤10 K at the onset of collapse, and the low temperature ≤20 K continues for ~3.1 × 10⁵ yr (Section 2.1). During this period, CH₃OH ice is abundantly formed via CO ice hydrogenation, while the thermal diffusion of species with heavy elements and thus radical–radical reactions are quenched. In Figure 4(a), we can compare the abundances of gaseous CH₃OH at the final time step (i.e., R = 30.6 au; solid cyan line) and CH₃OH ice at the end of the static phase (dashed–dotted cyan line); the former is much higher than the latter at T_init ≥ 15 K mainly due to the
CH$_3$OH formation during this temporal cold phase. Radicals are also abundantly stored in the ice mantle then. This makes the dependence of the final COM abundances on $T_{\text{init}}$ less significant than that on $T_{\text{min}}$ (see below). Yet, the chemical signature of warm $T_{\text{init}}$ remains in some layers in the ice mantle. For example, CH$_3$CHO is less abundant in the model with $T_{\text{init}} = 25$ K, since its precursor CH$_3$ in the ice mantle is less abundant. On the other hand, HCOOH is abundantly formed via OH + HCO in the upper layers of the bulk ice mantle at $R \sim 1 \times 10^3$ au in the model of $T_{\text{init}} = 25$ K. CO ice is not abundant in those layers, and HCO is formed via reaction of OH + H$_2$CO, while H$_2$CO is formed via photodissociation or H abstraction of CH$_3$OH. At the same radius in the fiducial model, OH reacts with CO, which is relatively abundant in all of the ice mantle layers.

While it is reasonable that the core temperature decreases as the gas density increases in the early collapse phase, we also calculated models with a fixed minimum temperature. The model with $T_{\text{min}} = 25$ K, for example, is similar to the model with $T_{\text{init}} = 25$ K, but the temperature is kept at 25 K even in the early collapse phase (i.e., $t = 1 \times 10^6$ to $1.33 \times 10^7$ yr). Figure 4(b) shows the abundances of gaseous COMs at the final time step, and Figures 5(c), (d) show the $R$-abundance plots of radicals and COMs in the collapse phase of the $T_{\text{min}} = 25$ K model. Note that their abundances in the static phase are the same as in Figures 5(a), (b). Although the icy abundances of CH$_3$OH and some radicals increase temporally after the onset of collapse, the increment is smaller than in the model with $T_{\text{init}} = 25$ K (Figures 5(c), (d)). COM abundances depend more sensitively on $T_{\text{min}}$ than on $T_{\text{init}}$; for example, CH$_3$OCH$_3$, which is formed via CH$_3$O + CH$_3$ in the ice mantle, is least abundant with $T_{\text{min}} = 20$ K, and it becomes more abundant with $T_{\text{min}} = 25$ K. The reactant CH$_3$O is mainly formed via photodissociation of CH$_3$OH in the low-$T_{\text{min}}$ model ($<20$ K), while it is formed from hydrocarbon (CH$_3$ + O) in the model of $T_{\text{min}} = 25$ K. Either path is not efficient in the $T_{\text{min}} = 20$ K model.

### 3.3. Dependence of WCCC on $T_{\text{init}}$ and $T_{\text{min}}$

In Figures 6(a) and (b), we plot the minimum and maximum abundances of CH$_4$, C$_2$H, C$_3$H$_2$, and C$_4$H around the CH$_4$ sublimation region, which we set at $R = 1455$–2850 au, in models with $T_{\text{init}} = 10, 15, 20, 25$ K (panel (a)) and $T_{\text{min}} = 10, 15, 20, 25$ K (panel (b)). The minimum and maximum values are connected by a vertical solid line if the abundance increases with decreasing radius in the CH$_4$ sublimation region, which indicates that WCCC is active. A dotted vertical line, on the other hand, is used if the abundance decreases inward. We can see that the CH$_4$ abundance decreases with increasing $T_{\text{init}}$ and $T_{\text{min}}$; this is natural because both the grain surface formation and freeze-out of CH$_4$ become less efficient at warmer temperatures. The carbon-chain abundances also decrease with $T_{\text{init}}$ and $T_{\text{min}}$, and the abundances of C$_3$H and C$_3$H$_2$ do not increase inward when
$T_{\text{init}} \geq 20$ K and $T_{\text{min}} \geq 20$ K. As an example, an R-abundance plot of CH4 and carbon chains in the model with $T_{\text{init}} = 20$ K is depicted in Figure 6(c).

Sakai & Yamamoto (2013) argued that the CH4 abundance relative to H2 should be higher than several $10^{-7}$ for the WCCC to be active, that is, for CH4 to be the major reactant for C+ competing with OH and other molecules. In the sublimation region of CH4 in our fiducial model, the reaction $C^+ + CH_4 \rightarrow C_2H_2 + H$ competes with $C^+ + H_2 \rightarrow CH_2$ and $C^+ + NH_3 \rightarrow H_2CN^+ + H$, although the rates are higher for the latter two. The reaction $C + CH_3 \rightarrow C_2H_2 + H$ also contributes to the WCCC, where a fraction of CH4 contributes to form C atoms and CH3, as well. While the model details are different between the present work and Sakai & Yamamoto (2013), we can see in Figure 6 that the gaseous CH4 abundance of $10^{-7}$ would roughly be a condition for WCCC. The abundances of C2H, C2H, and C2H2 correlate with the sublimated abundance of CH4.

In Figures 6(a) and (b), the dashed–dotted orange lines depict the CH4 ice abundance at the end of the static phase, while the (nonvertical) solid orange lines depict the gaseous CH4 abundance at the final time step ($R = 30.6$ au). Except for the models with $T_{\text{init}} > 20$ K, the solid line overlaps the dashed–dotted line, which means that the total abundance of CH4 is mostly determined by the CH4 ice abundance in the static phase. In the models with $T_{\text{init}} = 25$ K, the CH4 abundance increases on the grain surfaces in the early collapse phase. We also note that the (nonvertical) solid lines are well above the upper values of the orange vertical solid lines, which means that only a fraction of icy CH4 sublimates in the WCCC region, except in the model with $T_{\text{init}} \geq 20$ K. The trapping and layering of molecules in ice determine what fraction of CH4 can sublimate at $T \sim 25$ K and contribute to the WCCC.

3.4. Dependence on UV Extinction by Ambient Clouds

In the fiducial model, we assumed that the initial prestellar core is embedded in ambient gas, which attenuates the interstellar UV radiation field by $A_\nu^{\text{amb}} = 3$ mag (Figure 1). We calculated two additional models with $A_\nu^{\text{amb}} = 1$ mag and 5 mag; that is, the visual extinction in the static phase is 2.51 mag, and it is 6.51 mag in the fluid parcel. Figure 7 shows the gaseous COM abundances at the final time step (panel (a)) and the minimum and maximum abundances of CH4, C2H, C2H2, and C2H3 around the CH4 sublimation region (panel (b)) as a function of $A_\nu^{\text{amb}}$. A naive expectation is that in the prestellar core with lower $A_\nu^{\text{amb}}$, CH3OH would be less abundant, while CH4 would be more abundant, which results in less abundant COMs and more active WCCC in the protostellar phase. While CH4 abundance is indeed high and WCCC is more active in the models with lower $A_\nu^{\text{amb}}$ (Figure 7(b)), the dependence of COM abundances on $A_\nu^{\text{amb}}$ is not so simple.

Figures 7(c)–(e) show the R-abundance plot of the infalling fluid parcel in the model with $A_\nu^{\text{amb}} = 1$ mag. In the static phase, photolysis makes CH3OH and other COMs less abundant both in the gas phase and the ice mantle in the model with $A_\nu^{\text{amb}} = 1$ mag than in the fiducial model. Their abundances, however, become as high as in the fiducial model once the visual extinction gets high enough in the collapse phase. Even though CO ice abundance is lower than in the fiducial model, CH3OH can be formed via CH3 + OH.

In the model with $A_\nu^{\text{amb}} = 5$ mag, HCOOH is less abundant, while HCOOCH3 is more abundant than in the fiducial model. In the fiducial model, HCOOH is formed around $R \sim 3 \times 10^3$ au in the ice mantle via CO + OH → COOH and COOH + H → HCOOH. The abundance of OH radicals in the ice mantle is lower in the model with $A_\nu^{\text{amb}} = 5$ mag. HCOOCH3 is formed via HCO + CH3O in the ice mantle at $R \sim 1 \times 10^3$ au in the model with $A_\nu^{\text{amb}} = 5$ mag. Both of the reactants are formed in the reaction network of CH3OH (i.e., photodissociation of CH3OH and CH3O + H2CO → CH3OH + HCO), which is more abundant in the ice mantle with $A_\nu^{\text{amb}} = 5$ mag than in the fiducial model.

3.5. Dependence on the Duration of the Static Phase

In the classical pseudo-time-dependent models of molecular clouds, carbon is initially in the form of C+, which is converted to C atoms and then to CO. Carbon chains and CH4 are formed from C atoms and thus reach the maximum abundance in the gas phase before carbon is fully converted to CO (e.g., Suzuki et al. 1992). Then one would naively expect that if the star formation sets in earlier, the ice abundance ratios of CO/CH4...
and thus CH$_3$OH/CH$_4$ would be lower, which is favorable for WCCC rather than hot corinos.

In order to test this expectation, we run models with various $t_{\text{sta}}$; Figure 8 shows the gaseous COM abundances at the final time step (panel (a)) and the minimum and maximum abundances of CH$_4$, C$_2$H, C$_3$H$_2$, and C$_4$H around the CH$_4$ sublimation region (panel (b)). While the dependence of COM abundances on $t_{\text{sta}}$ is rather weak, the abundance jump of carbon chains around the CH$_4$ sublimation region is larger (i.e., WCCC is more active) in models with longer $t_{\text{sta}}$. This counterintuitive dependence is caused by the stability of CH$_4$ in the ice. Referring to Figure 3, we note that after the conversion of C atoms to CO and CO ice, the CH$_4$ ice abundance does not decrease, while gaseous CH$_4$ (and carbon chains in the gas phase) does decrease. Actually, at $t \gtrsim 10^9$ yr in the static phase, CO is gradually converted to CH$_4$ via CO + He$^+ \rightarrow$ C$^+$ + O + He and subsequent reactions with H$_2$. The conversion of CO to CH$_4$ is also found in previous work, for example, Hassel et al. (2008), and is also responsible for the slight decrease of CH$_3$OH with $t_{\text{sta}}$. We also note that in the models with $t_{\text{sta}} = 3 \times 10^7$ yr, the abundances of C$_2$H$_2$ and C$_3$H decrease inward around the CH$_4$ sublimation radius. Their abundances at the outermost radius ($\sim 10^4$ au) are higher than those in our fiducial model by about one order of magnitude. In other words, the remnant carbon chains from the prestellar phase dominate over production via WCCC.

So far, we have assumed that species are in the form of atoms or atomic ions, except for hydrogen, which is in H$_2$, at the start of the static phase with $n_{\text{H}} \sim 2 \times 10^4$ cm$^{-3}$ and $A_{\nu} \gtrsim 2$ mag. Such an initial abundance is often assumed, for example, in pseudo-time-dependent models and collapsing core models, because H$_2$ is self-shielded to be first formed, which is essential for the gas-phase two-body reactions to proceed. But this is obviously a simplified initial condition. Observations indicate that molecular formation both in the gas and ice phases starts in lower densities (e.g., Snow & McCall 2006; Whittet et al. 2009). Theoretical work shows that molecular clouds are formed via converging flows of H$_2$ gas (e.g., Inoue & Inutsuka 2012), and the ice formation in the postshock gas of converging flow reproduces important features of interstellar ices: D/H ratio of water ice and inhomogeneous distribution of polar (i.e., water) and apolar species within the ice mantle (Furuya et al. 2015). Since we aim to investigate the effect of ice composition on protostellar chemistry, we calculated another set of models, in which the initial molecular abundance of the static phase is set by solving the gas–grain chemistry in the converging flow. We solve the molecular evolution in the postshock gas in the same 1D steady-state shock model as Furuya et al. (2015) (Berger et al. 2004; Hassel et al. 2010), and we adopt the molecular abundance when $A_{\nu}$ reaches 1.2 mag.

This choice of visual extinction is rather arbitrary, but it roughly corresponds to the time when both gas-phase CO and water ice abundances reach the abundance of $10^{-4}$; CO abundance starts to decline with the conversion to CH$_4$ at larger $A_{\nu}$. The gas and ice are then put in the prestellar core, which is kept static for $t_{\text{sta}} = 3 \times 10^7$ yr, $1 \times 10^8$ yr, or $3 \times 10^8$ yr.

Figure 7. (a) Gas-phase abundances of COMs at the final time step in models with the visual extinction by ambient gas of $A_{\nu}^{\text{amb}} = 1$, 3, and 5 mag. The dashed–dotted cyan lines depict the CH$_3$OH ice abundance at the end of the static phase. (b) Maximum and minimum abundances of gaseous CH$_4$ (orange), C$_2$H (magenta), C$_3$H (green), and C$_4$H (cyan) around the CH$_4$ sublimation region ($R = 1455–2850$ au) as a function of $A_{\nu}^{\text{amb}}$. The upper solid orange line depicts the CH$_4$ gas abundance at the final time step (i.e., $R = 30.6$ au), while the dashed–dotted orange line (which overlaps the solid line) depicts the CH$_4$ ice abundance at the end of the static phase. (c)–(e) $R$-abundance plots in the collapse phase in the model with $A_{\nu}^{\text{amb}} = 1$ mag.
Figures 8(c), (d) show the gaseous COM abundances and the minimum and maximum abundances of CH₄ and carbon chains as in Figures 8(a), (b), but with the initial abundance set in the converging flow. We can see that the COM abundances, activity of WCCC, and their dependence on $t_{\text{sta}}$ are similar to those in panels (a) and (b). We note that the abundance of CH₃OCH₃ is higher in the model with a converging flow. It is most abundantly formed in the innermost layer of the ice mantle, the molecular abundance of which reflects the early evolution. A major characteristic of ice mantle composition set by the converging flow is that the innermost layer is CO-poor, which results in a relatively high abundance of OH. In our fiducial model, CO ice is more uniformly distributed in bulk ice layers and reacts with OH to form CO₂, when the thermal diffusion becomes efficient. CH₃OCH₃ is formed via CH₃ + CH₂O. In the OH-rich ice layer, CH₃ reacts with OH to re-form CH₂OH, which is photodissociated to CH₂O. In the fiducial model, on the other hand, CH₃ reacts mainly with NH₂ to form CH₃NH₂. Thus, CH₃CN is more abundant in our fiducial model, while CH₃OCH₃ is more abundant with the ice mantle set by the converging flow.

3.6. A Grid of Models

So far we have varied one of the parameters of temperature, the visual extinction of ambient gas ($A_{\text{amb}}$), or the duration of the static phase ($t_{\text{sta}}$). COM abundances and WCCC activity in the protostellar phase are found to be most sensitive to the minimum temperature among these parameters. In this subsection, we investigate how this sensitivity depends on $A_{\text{amb}}$ and $t_{\text{sta}}$.

Figure 9 shows the COM abundances as a function of $T_{\text{min}}$ in models with $A_{\text{amb}} = 1$ mag, 3 mag, and 5 mag and $t_{\text{sta}} = 3 \times 10^5$ yr, $1 \times 10^6$ yr, and $3 \times 10^6$ yr. We can see that the dependence of COM abundances on $T_{\text{min}}$ is more significant in models with lower $A_{\text{amb}}$. In these models, the photodissociation of molecules, including COMs, is more effective. While the photodissociation produces radicals, which can recombine to reform COMs, the rates of their diffusion in the ice mantle and sublimation (i.e., loss to the gas phase) are very sensitive to the temperature. Photodissociation thus enhances the dependence of COM abundances on temperature. The dependence of some COM abundances on $T_{\text{min}}$ is also stronger in models with a longer static phase. In the middle row.
(Av = 3 mag) in Figure 9, for example, the CH$_3$CN abundance varies more than two orders of magnitude in the models with $t_{\text{sta}} = 3 \times 10^5$ yr, while the variation is within an order of magnitude in the models with $t_{\text{sta}} = 3 \times 10^5$ yr. When a gas–grain reaction network is kept at a constant temperature, specific molecules and radicals accumulate in ices, for example, species that can freeze out or species produced by the recombination of radicals that can thermally diffuse. If the duration of the constant temperature is longer, the accumulation of those specific species becomes more significant, which results in the higher dependence of protostellar core chemistry on $T_{\text{min}}$. Comparing the solid and dashed–dotted cyan lines, we note that a significant amount of CH$_3$OH is formed after the onset of collapse in models with low $A_{\text{amb}}$ ($\leq$3 mag). The abundance ratio of COMs to gaseous CH$_3$OH, as well as that to CH$_3$OH ice at the end of the static phase, varies significantly with $T_{\text{min}}$.

The WCCC activity in the same set of models is shown in Figure 10. The WCCC is activated when the sublimated CH$_4$ abundance around the WCCC region (i.e., $T \sim 25$ K) is, however, higher in models with larger $t_{\text{sta}}$. Since the conversion of CO to CH$_4$ becomes efficient later in the static phase, the CH$_4$ ice in the surface layer, which is subject to immediate sublimation at $\sim$25 K, is more abundant in models with larger $t_{\text{sta}}$. WCCC is thus more active in models with longer $t_{\text{sta}}$. In the models with $A_{\text{amb}} = 1$ mag and $T_{\text{min}} \gtrsim 20$ K, CH$_4$ ice abundance is very low at the end of the static phase, and thus WCCC is not active. In these models, a large fraction of CH$_4$ is formed after the onset of collapse by the gas-phase reactions starting from C$^+$ + H$_2$ → CH$_3$$. WCCC is activated in models with $T_{\text{min}} \lesssim 15$ K, even if the ambient visual extinction is low (i.e., $A_{\text{amb}} = 1$ mag).

4. Discussion

4.1. Comparison with Previous Work

The abundances of carbon chains and COMs in our fiducial model are different from those in our previous work.
(Aikawa et al. 2008, 2012) because we adopt the multilayered ice mantle model, rather than the two-phase model as described in Section 3.1. Entrapment of CH$_4$ suppresses the WCCC, while the entrapment of radicals enhances the formation of COMs (Lu et al. 2018).

Acharyya & Herbst (2018) investigated the hot corino chemistry in the Large Magellanic Cloud and Small Magellanic Cloud by calculating the two-phase model of gas–grain chemistry in the cold collapse stage and warm-up stage. The dependence of peak molecular abundances on the temperature in the collapse stage is investigated, as well. The peak abundances of COMs are basically lower in models with higher temperature in the collapse phase, which is qualitatively consistent with our results on $T_{\text{min}}$ (Section 3.2). The COM abundances in our model with $A_{\text{v,amb}} = 25$ K, however, tend to be much higher than those in Acharyya & Herbst (2018). This would be mostly due to the effect of the multilayered ice mantle model, which can keep various radicals even at warm temperatures. Our grid of models also suggests that the COM abundances depend more sensitively on $T_{\text{min}}$ when $A_{\text{v,amb}}$ is lower. This is in line with recent observations that show large abundance variations of COMs among cores in the LMC and SMC (Shimonishi et al. 2016; Sewilo et al. 2018; Shimonishi et al. 2018, 2020), since the visual extinction is lower in those low-metallicity galaxies compared with that in our Galaxy.

Vidal et al. (2019) calculated the three-phase model in 110 models of the star-forming core of Vaytet & Haugbolle (2017). They statistically analyzed the correlation of molecular abundances and physical model parameters and found that CH$_3$CN abundance correlates positively with the initial core temperature. Since they plot the final molecular abundance in all of the fluid parcels of 110 models as a function of the initial temperature, CH$_3$CN abundance is scattered over one order of magnitude or more at each initial temperature bin. The dependence of the CH$_3$CN abundance (i.e., the maximum or mean value) on the initial temperature is similar to the dependence of CH$_3$CN on $T_{\text{init}}$ in our model (Figure 4); the dependence is weak at $T_{\text{init}} = 10$–20 K, while the abundance is about one order of magnitude higher at $T_{\text{init}} = 25$ K. They concluded that the positive correlation is caused by enhanced

Figure 10. Gas-phase abundances of CH$_4$ and carbon chains around the CH$_4$ sublimation region as a function of $T_{\text{min}}$ in the grid of models. The upper solid orange lines depict the CH$_4$ gas abundance at the final time step (i.e., $R = 30.6$ au), while the dashed–dotted orange line depict the CH$_4$ ice abundance at the end of the static phase.
diffusion of CN and CH$_3$ in the ice mantle. We speculate that this explanation is too simplified; other COM abundances would show a positive correlation with the initial core temperature if the diffusion rate is the key. As we discussed in Section 3, the formation paths of COMs vary with the initial temperature; new formation paths open in the model with $T_{\text{min}} = 25$ K.

We adopted the chemical reaction network of Garrod (2013), who investigated the formation of COMs, especially glycine, in warm-up models mimicking the star-forming core. Their model consists of the cold collapse phase and the warm-up phase. In the former, the initial gas density increases from $n_{\text{HI}} = 3 \times 10^4$ cm$^{-3}$ to $1 \times 10^4$ cm$^{-3}$ in $\sim 10^4$ yr. The dust temperature and visual extinction $A_v$ are initially 16 K and 2 mag, respectively. The temperature decreases as $A_v$ increases, reaching the minimum value of 8 K. In the warm-up phase, the temperature increases from 8 to 100 K, while the density is kept constant ($1 \times 10^4$ cm$^{-3}$). Three models are calculated with the warm-up timescale of 7.12 $\times$ 10$^4$ yr (fast), 2.85 $\times$ 10$^5$ yr (medium), and 1.43 $\times$ 10$^6$ yr (slow). Comparing the timescale of temperature rise from 20 K to 100 K, our model is similar to the fast or medium model of Garrod (2013), in which the peak abundances of gaseous CH$_3$OCH$_3$, CH$_3$CN, and CH$_3$CHO are (3–5) $\times$ 10$^{-8}$, (2–5) $\times$ 10$^{-9}$, and (3–9) $\times$ 10$^{-9}$, respectively. Despite the differences in the physical model and chemical model (the three-phase model with swapping versus the multilayered ice mantle model without swapping), these COM abundances are similar to our results. Our abundances of NH$_2$CHO and HCOOH at the final time step are smaller than those in Garrod (2013) by more than an order of magnitude, since we deleted some reactions relevant for their formation (Section 2.2; see also Section 4.2).

4.2. Uncertainties in the Reaction Network of COMs

Besides the treatment of grain surface chemistry (e.g., two-phase, three-phase, and multiphase model) and the physical model of core formation and evolution, there are uncertainties in the chemical reaction network. One of the major uncertainties in the hot corino chemistry is the branching ratio of radical reactions in the ice, as it is difficult to directly measure in laboratory experiments. Quantum chemical calculations have been useful for estimating such branching ratios, but they are often not straightforward, since the interaction with the grain surface and neighboring icy species needs to be included (e.g., Kayanuma et al. 2019). While the main aim of the present work is to investigate how the WCCC and hot corino chemistry as a whole depend on the physical conditions in the prestellar phase, rather than the dependence of each COM species, it is useful to check the effect of uncertainties in the reaction network on our model results.

Specifically, we modified the branching ratio of two grain surface reactions: NH$_2$ + H$_2$CO and HCO + CH$_3$. In the gas phase, Barone et al. (2015) found that the activation barrier of NH$_2$ + H$_2$CO $\rightarrow$ NH$_2$CHO + H is very low (26.9 K), which we adopt in our fiducial model. For the reaction of NH$_2$ + H$_2$CO in ice, on the other hand, we assumed the products to be NH$_3$ + HCO with the activation barrier of 2360 K, as assumed in the original network of Garrod (2013), to be conservative (see also discussions in Fedoseev et al. 2016). In order to check the effect of the uncertainty of this reaction, here we assume that NH$_2$CHO and H are formed without an activation barrier in ice. As for the icy reaction of HCO + CH$_3$, we assume the products to be CH$_4$ + CO in our fiducial model, referring to

Enrique-Romero et al. (2016). Recently, Enrique-Romero et al. (2020) reinvestigated this reaction with the broken-symmetry approach to find that the formation of CH$_3$CHO proceeds without a barrier, while the direct H transfer to form CO + CH$_4$ can be a competitive channel. We thus assume a 1:1 branching ratio for the product channels of CH$_3$CHO and CO + CH$_4$.

Figure 11 shows the COM abundances at the final time step ($R = 30.6$ au) in models with the minimum temperature of 10, 15, 20, and 25 K with the modified branching ratios of NH$_2$ + H$_2$CO and HCO + CH$_3$. The dashed-dotted cyan lines depict the CH$_3$OH ice abundance at the end of the static phase.

4.3. Comparison with Observations

We found that WCCC, that is, the formation of carbon chains around the CH$_4$ sublimation region, is more active and their abundances are higher in models with lower $T_{\text{init}}$ and $T_{\text{min}}$ lower $A_v^{\text{amb}}$, and longer $t_{\text{sta}}$. The abundance of C$_4$H in L1527 and IRAS 15398, which are prototypical WCCC sources, is $\geq 10^{-9}$, while it is $\sim 10^{-11}$ in the prototypical hot corino IRAS 16293 (Sakai et al. 2009a). This range of C$_4$H abundance is covered by the models in the present work. The molecular D/H ratio could be a key to discriminating which parameter, $T_{\text{init}}$ ($T_{\text{min}}$), $A_v^{\text{amb}}$, or $t_{\text{sta}}$ is responsible for the variation of carbon-chain abundances in protostellar cores; low $T_{\text{init}}$ and long $t_{\text{sta}}$ would enhance the D/H ratio, while a low D/H ratio is expected for low $A_v^{\text{amb}}$. In L1527, the column density ratio of c-C$_3$HD/c-C$_2$H$_3$ is 4.4% (Yoshida et al. 2019; see also Sakai et al. 2009b), while the ratio is observed to be 14% toward
IRAS 16293 (Majumdar et al. 2017), which may suggest that the variation is caused by the visual extinction.

The dependence of COM abundances on the static-phase conditions is more complex because there are various formation paths of COMs, and because their efficiency depends on the composition of each layer of ice mantle. Among the parameters investigated, \( T_{\text{min}} \) is the most effective. While \( \text{CH}_3\text{OH} \) basically decreases with \( T_{\text{min}} \), for example, is least abundant in the model with \( T_{\text{min}} = 20 \) K and is more abundant in the model with \( T_{\text{min}} = 25 \) K, in which COMs can be formed from large hydrocarbons. It should be noted that the observations often evaluate the COM abundances relative to \( \text{CH}_3\text{OH} \). In our models, the COM abundances relative to \( \text{CH}_3\text{OH} \) tend to increase with \( T_{\text{min}} \) and \( T_{\text{init}} \) as \( \text{CH}_3\text{OH} \) decreases, although either \( \text{CH}_3\text{OH} \) or other COMs would not be detected if their abundances are too low. Recently, Oya et al. (2019) observed Class I protostellar source Elias 29 to find both COMs and carbon chains are deficient; the abundances of \( \text{C}_2\text{H} \) and \( \text{c-C}_3\text{H}_2 \) are \( \lesssim 10^{-11} \), and those of \( \text{HCOOCH}_3 \) and \( \text{CH}_3\text{OCH}_3 \) are \( \lesssim 10^{-9} \). Considering the uncertainties of the upper limits, these abundances are consistent in our model with \( T_{\text{min}} = 20 \) K.

In our models with higher \( T_{\text{init}} \), higher \( A_{\text{v, am}} \), or shorter \( t_{\text{stat}} \), WCCC is less active, while COMs can be abundantly formed; these models can explain the deficiency of carbon chains in hot coronas. The deficiency of COMs in WCCC sources is, on the other hand, hard to reproduce by simply varying the static-phase conditions; COM abundances do not monotonically decrease with a specific parameter, and COMs are abundantly formed in models with active WCCC. While COM abundances are low in the model with \( T_{\text{min}} = 20 \) K, WCCC is not active, either. Alternatively, the deficiency of COM emissions could be due to temperature distributions in the WCCC sources. The sublimation temperature of COMs is typically 100 K. The size of the hot corino, that is, the radius of the COM sublimation region, is typically \( \lesssim 100 \) au. If the central protostar is less luminous, the sublimation region could be significantly smaller; the COM emission lines could be weakened by the beam dilution and high dust opacity, since the (column) density is higher at smaller radii. Indeed, the luminosity of the prototypical hot corino sources (e.g., 9.1 \( L_{\odot} \) in NGC 1333 IRAS4A and 22 \( L_{\odot} \) in IRAS 16293-2422) tends to be higher than that of WCCC sources, for example, 1.9 \( L_{\odot} \) and 1.8 \( L_{\odot} \) for L1527 and IRAS 15398, respectively (Froebrich 2005; Crimier et al. 2010; Kristensen et al. 2012; Jørgensen et al. 2013; Karska et al. 2013). One notable exception is B335; while its luminosity is as low as 0.72 \( L_{\odot} \), COMs emission is detected within a few tens of astronomical units at the core center, where the fractional abundances of COMs are comparable to those in the prototypical hot corino IRAS 16293 (Imai et al. 2016). A possible explanation would be that B335 experienced a temporal outburst, which sublimated COMs, but is currently back to its quiescent phase. COMs are still in the gas phase if the time after the outburst is less than the refreeze-out timescale, that is, \( \sim 10^3 \) (10 \( ^3 \) cm\(^{-3} \) yr\(^{-1} \)) yr.

We note that the kinetic structure inside a few hundred astronomical units is as relevant as temperature distributions. Once \( \text{CH}_3\text{OH} \) and other COMs are sublimated to the gas phase, they are destroyed by gas-phase reactions within several 10\(^4 \) yr (Charnley et al. 1992; Nomura et al. 2009; Taquet et al. 2016). The spatial extent of gaseous COMs is thus estimated to be the product of the destruction timescale and the radial velocity of the gas. When the \( T \sim 100 \) K region is located in the envelope, we can naively expect a constant gaseous abundance of COMs inside this region, since infall is faster than COM destruction in the gas phase (Figure 12(a)). If the \( T \sim 100 \) K region is inside the rotationally supported disk, the other hand, the spatial extent of gas-phase COMs would be very narrow, limited by the competition between gas-phase destruction of COMs and the slow radial migration of gas in the disk (Figure 12(b)). While the spatially resolved observation of a hot corino is challenging, Imai et al. (2019) recently resolved the COM emission in B335 and showed that the variations between velocity gradients of COM emissions are well explained by the model of infalling and rotating gas, rather than Keplerian motion. Observations with high spatial resolution (e.g., \( \sim 0''/1 \)) or in a lower frequency band, in which the dust opacity is lower, are desirable for investigating the physical structure, such as temperature and density distributions and the radius of the forming disk.

5. Summary

We investigated the dependence of WCCC and hot corino chemistry on the physical parameters in the static phase before the onset of collapse: the initial and minimum temperatures \( (T_{\text{init}} \) and \( T_{\text{min}} \)), visual extinction of ambient gas \( (A_{\text{v, am}}) \), and the duration of the static phase \( (t_{\text{stat}}) \). Our findings are as follows:

1. Among the parameters, \( T_{\text{min}} \) is the most effective for COM abundances. \( \text{CH}_3\text{OH} \) and some other COMs tend to decrease with increasing \( T_{\text{min}} \), since freeze-out of molecules and hydrogenation on grain surfaces are less efficient at warm temperatures. But molecules with higher sublimation temperatures can still be adsorbed onto grains, and there are various formation paths of COMs, some of which become efficient at warm temperatures. The abundance of \( \text{CH}_3\text{OCH}_3 \), for example, is higher in the model with \( T_{\text{min}} = 25 \) K than that with \( T_{\text{min}} = 20 \) K. The dependence of COM abundances on \( T_{\text{init}} \) is weaker, since various molecules, including CO, can be frozen and hydrogenated on grain surfaces during the cold phase right after the onset of collapse.

2. The gaseous \( \text{CH}_3\text{OH} \) abundance in the central hot region \( (\gtrsim 100 \) K) monotonically decreases with increasing \( T_{\text{init}} \) and \( T_{\text{min}} \), except for the models with low visual extinction \( (A_{\text{v, am}} = 1 \) mag). The dependence of other COM abundances on \( T_{\text{init}} \) and \( T_{\text{min}} \) is not monotonic, as described above. The relative abundance of COMs to \( \text{CH}_3\text{OH} \), which is often derived and discussed in the observational studies, could then be higher in cloud cores with higher \( T_{\text{init}} \) and \( T_{\text{min}} \).

3. WCCC is less active and carbon-chain species are less abundant in models with higher \( T_{\text{init}} \) or \( T_{\text{min}} \), since both the grain surface formation and freeze-out of \( \text{CH}_4 \) become less effective at warm temperatures. A warm temperature also enhances the conversion of CO to \( \text{CO}_2 \) on grain surfaces, which reduces gaseous CO and the production of \( \text{C}^+ \) via \( \text{CO} + \text{He} \rightarrow \text{C}^+ + \text{O} + \text{He} \).

4. While \( \text{CH}_4 \) and carbon chains are more abundant in the models with lower \( A_{\text{v, am}} \), the dependence of COM abundances on \( A_{\text{v, am}} \) is more complex. Even though photolysis makes \( \text{CH}_3\text{OH} \) and other COMs less abundant in the static phase of the lower \( A_{\text{v, am}} \) model, they can be formed via various reactions in the ice mantle, for
example, CH₃ + OH → CH₃OH, once the collapse starts and Aᵥ increases.

5. When the duration of the static phase tصحاب is varied from 3 × 10⁵ yr to 3 × 10⁶ yr, the COM abundances in the protostellar phase vary less than an order of magnitude. WCCC, on the other hand, is more active in the model with longer tصاحب, since CH₄ ice is stable and accumulates during the static phase. In the model with short tصاحب, the remnant of carbon chains from the prestellar phase dominates over those formed via WCCC.

6. We also calculated additional models in which the initial molecular abundances are set by considering the cloud formation via converging flow. The COM abundances and WCCC activities in the protostellar phase are basically similar to those in the fiducial model. A notable difference is that the ice mantle has a larger chemical gradient; for example, the innermost ice layer is deficient in CO ice. This enhances the abundances of OH radicals and CH₃OCH₃ in the ice mantle in the protostellar phase compared with the fiducial model.

7. We calculated a grid of models to investigate how the dependence of COMs and WCCC on T_{min} varies with A_v^{amb} and tصاحب. Variation of COM abundances with T_{min} is enhanced in models with low A_v^{amb}. The models with low A_v^{amb} could also be relevant to the recent observations of hot cores in the LMC and SMC, where significant variations are found in COM emission. The dependence of some COM abundances on T_{min} is also stronger in models with longer tصاحب. In the models with longer tصاحب, a larger fraction of CH₄ ice is in surface layers of the ice mantle, which sublimates and activates WCCC at T ~ 25 K.

8. Our models show that the variation of T_{init} (or T_{min}), A_v^{amb}, and tصاحب can explain the chemical diversity between prototypical hot corinos, in which carbon chains are deficient, and hybrid sources, toward which both COM and carbon chains are abundant. A relatively low D/H ratio of carbon chains observed in a prototypical WCCC source L1527 may indicate that A_v^{amb} is the key parameter. Deficiency of COMs in prototypical WCCC sources is, however, hard to reproduce within our models; that is, models with active WCCC have relatively abundant COMs. A possible explanation for the deficiency would be the small size of the COM sublimation region (i.e., ≳100 K) or the kinetic structure there. Brightness of the COM lines would be suppressed if the COM sublimation region is significantly smaller than the beam size or within the rotationally supported disk, in which the radial extent of gaseous COMs is limited by the competition between destruction in the gas phase and the slow radial accretion of gas. If the COM sublimation region is small, the emission lines could also be hidden by the high dust opacity. Observations with high spatial resolution are desirable for investigating the physical structure in the central regions of protostellar cores such as temperature and density distributions and the radius of the forming disk.

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Figure 12. Schematic view of CH₃OH gas distribution in (a) a hot corino source with the T ~ 100 K region located in the infalling envelope and (b) a protostellar core with the T ~ 100 K region located in the rotationally supported disk.
