Is There Any Linkage between Interstellar Aldehyde and Alcohol?

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Abstract

It is speculated that there might be some linkage between interstellar aldehydes and their corresponding alcohols. Here an observational study and astrochemical modeling are coupled together to illustrate the connection between them. The ALMA cycle 4 data of a hot molecular core, G10.47+0.03, are utilized for this study. Various aldehydes (acetaldehyde, propanal, and glycolaldehyde), alcohols (methanol and ethylene glycol), and a ketone (acetone) are identified in this source. The excitation temperatures and column densities of these species were derived via the rotation diagram method assuming local thermodynamic equilibrium conditions. An extensive investigation is carried out to understand the formation of these species. Six pairs of aldehyde–alcohol are considered for this study: (i) methanal and methanol, (ii) ethanal and ethanol, (iii) propanal and 1-propanol, (iv) propenal and allyl alcohol, (v) propynal and propargyl alcohol, and (vi) glycolaldehyde and ethylene glycol. One pair of ketone–alcohol (acetone and isopropanol) and ketene–alcohol (ethenone and vinyl alcohol) are also considered. Two successive hydrogenation reactions in the ice phase are examined to form these alcohols from aldehydes, ketone, and ketene, respectively. Quantum chemical methods are extensively executed to review the ice-phase formation route and the kinetics of these species. Based on the obtained kinetic data, astrochemical modeling is employed to derive the abundances of these aldehydes, alcohols, ketone, and ketene in this source. It is seen that our model could successfully explain the observed abundances of various species in this hot molecular core.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Chemical abundances (224); Interstellar molecules (849); Observational astronomy (1145); Spectral line identification (2073)

1. Introduction

More than 200 molecular species have been identified in the interstellar medium (ISM) and circumstellar shells (McGuire 2018, https://cdms.astro.uni-koeln.de/classic/molecules), which resolved the unexplained mystery of the molecular universe. Interstellar grains accelerate the formation of complex organic molecules (COMs; molecules with >six atoms) in space. During the warm-up stage of a star-forming core, radicals or simple molecules on the grain surface become mobile and could produce various COMs (Chakrabarti et al. 2006a, 2006b; Garrod & Herbst 2006; Das et al. 2008a, 2010, 2016; Garrod et al. 2008; Das & Chakrabarti 2011; Sil et al. 2018). These ice-phase species may transfer to the gas phase by various desorption mechanisms.

Alcohols and aldehydes were identified in various parts of the ISM. Methanal (formaldehyde, H₂CO) is the simplest form of aldehyde, which was first observed in space by Snyder et al. (1969). It is an intermediary of the large COMs, which can help constrain physical conditions in the star-forming regions (Persson et al. 2018). Methanol (methyl alcohol, CH₃OH) is the simplest alcohol and one of the most abundant interstellar molecules. It was widely observed toward various sources (Allamandola et al. 1992; Pontoppidan et al. 2003) and is used as a reliable tracer of high-density environments (Menten et al. 1988). A large number of studies reported the chemical origin of methanol starting from formaldehyde (Watanabe & Kouchi 2002; Fuchs et al. 2009; Goumans 2011; Song & Kästner 2017). Methanol is ubiquitous in star-forming regions (Weaver et al. 2018) and mainly formed on the interstellar dust via successive hydrogen addition reactions with carbon monoxide (Fedoseev et al. 2015; Chuang et al. 2016; Butscher et al. 2017).

Woon (2002a) carried out a theoretical study of the formation of H₂CO and CH₃OH. Quantum chemical calculations were carried out to determine the activation barrier for the hydrogen addition reactions (H + CO and H + H₂CO) in gas, with water clusters (H₂O)n (n ≤ 3) and in ice phases. He included explicit water molecules to show the catalytic effect on the activation barrier by surrounding water molecules. Das et al. (2008b) and Rimola et al. (2014) studied methanol formation by successive hydrogen addition with CO in water ice. They compared their simulated abundance with observations. Recently, Song & Kästner (2017) derived the tunneling rate constant of the H₂CO + H reaction on amorphous solid water (ASW) for various product channels: CH₂OH, CH₃O, and H₂ + HCO. They also provided the activation barrier of these three product channels and rate coefficients.

Identification of ethanol (acetaldehyde, CH₂CHO) was first reported by Gottlieb & Snyder (1973) toward Sgr B2 and Sgr A. They reported an emission at 1065 MHz, which was
assigned to the $1_{01} \rightarrow 1_{11}$ transition of CH$_3$CHO. This assignment was based on the agreement in radial velocity with other molecules, which were observed in the galactic center region. Then Fourikis et al. (1974) observed it toward Sgr B2 with the Parkes 64 m telescope. Its successor, ethanol (ethyl alcohol, C$_2$H$_5$OH), is among the earliest complex molecules and was identified toward Sgr B2 (Zuckerman et al. 1975).

Propanal (propionaldehyde, CH$_3$CH$_2$CHO) is identified in Sgr B2(N) (Hollis et al. 2004), where it coexists with propynal (HC$_3$CHO) and propenal (CH$_3$CH$_2$CHO). The detection of these three aldehydes toward the same source suggests that successive hydrogen additions might be an efficient process to establish the chemical linkage between propynal, propenal, and propanal (Hollis et al. 2004). Propenal (also known as acrolein) is the simplest unsaturated aldehyde. It is the second most stable isomer of the C$_3$H$_4$O isomeric group (Etim et al. 2018). Allyl alcohol (CH$_2$CHCH$_2$OH) is an isomer of propanal and the corresponding alcohol of propanal (Zaverkin et al. 2018). Acetaldehyde is supposed to be a potential ancestor of carbohydrates and propenal (also known as acrolein; Pizzarelli & Weber 2004; Córdova et al. 2005).

The corresponding alcohol of propanal is 1-propanol (CH$_3$CH$_2$CH$_2$OH), which is yet to be observed in space. However, trans-ethyl methyl ether (CH$_2$CH$_2$OCH$_3$), which is one of the isomers of the same isomeric group, was tentatively detected toward Orion KL (Tercero et al. 2015). Zaverkin et al. (2018) reported that the propanal to 1-propanol production by the hydrogenation reaction might be inefficient due to the efficient hydrogen abstraction reaction.

The simplest form of sugar, glycolaldehyde (HOCH$_2$CHO), plays an essential role in forming amino acids and complex sugars (Collins et al. 1995; Weber 1998). Glycolaldehyde was also detected outside of the Galactic center toward the hot core G31.41+0.31 (hereafter G31; Beltrán et al. 2009). Ethylene glycol (HOCH$_2$CH$_2$OH) is the corresponding alcohol of glycolaldehyde. It was detected in a wide variety of sources, such as the Galactic center (Hollis et al. 2002; Belloche et al. 2013), NGC 1333–IRAS 2A (Maury et al. 2014), and the Orion bar (Brouillet et al. 2015), as well as comets C/1995 O1 (Hale–Bopp) (Crovisier et al. 2004), C/2012 F6 (Lemmon), and C/2013 R1 (Lovejoy) (Biver et al. 2014). It was also identified in the Murchinson and Murray meteorites (Cooper et al. 2001). The abundance ratio of glycolaldehyde and ethylene glycol in star-forming regions and comets can help in understanding the possible preservation of COMs (Coutens et al. 2018). Methyl formate (CH$_3$OCHO) and acetic acid (CH$_3$COOH) are two isomers of glycolaldehyde. The linkage between methyl formate, acetic acid, and glycolaldehyde can constrain the understanding of the chemical and physical conditions of the star-forming core (Woods et al. 2013). Acetone (CH$_3$COCH$_3$) is one of the most important molecules in organic chemistry, and it was the first species containing 10 atoms identified in the ISM (Combes et al. 1987). Acetone was also found to be present in comet 67P/Churyumov–Gerasimenko (Altwegg et al. 2017). Etheneone (ketene, CH$_2$CO) was identified for the first time toward Sgr B2(OH) by Turner (1977) through microwave measurements. Recently, Turner et al. (2020) performed an experiment combined with high-level quantum chemical calculations and provided compelling evidence of ketene formation in the processed mixture of water and carbon monoxide ices explaining the observed ketene detection in deep space. The simplest enol compound, vinyl alcohol (ethenol, CH$_2$CHOH), was identified in an interstellar cloud of dust and gas near the center of the Milky Way toward Sgr B2(N) utilizing its millimeter-wave rotational transitions (Turner & Apponi 2001). In the dark cloud, the nonenergetic process plays an active role in processing the ice constituents. In contrast, in the latter stages of star and planet formation, various energetic procedures play a crucial role (Fedoseev et al. 2017). Laboratory experiments of methanol dissociation studied through various energetic processes, such as photons, electrons, vacuum ultraviolet photons, X-rays, etc., LM could lead to the synthesis of various COMs. Öberg et al. (2009) found that the ratio between ethylene glycol to ethanol and methyl formate to ethanol varies with the ice temperature and irradiation.

In this work, Atacama Large Millimeter/submillimeter Array (ALMA) archival data of a hot molecular core, G10.47+0.03 (hereafter G10), which is located at a distance of 8.6 kpc, is analyzed (Sanna et al. 2014). This is a young cluster (Cesaroni et al. 1998; Rolfis et al. 2011) whose luminosity is $\sim5 \times 10^5 L_{\odot}$ (Cesaroni et al. 2010). Many simple species, complex organics, and molecules with a higher upper energy state (such as HC$_3$N and HCN) were observed in this source, suggesting an active site for chemical enrichment (Wyrowski et al. 1999; Ikeda et al. 2001; Gibb et al. 2004; Rolfis et al. 2011; Gorai et al. 2020).

Recently, Qasim et al. (2019) showed that the aldehyde and primary alcohol may be linked via successive hydrogen addition reactions. A similar connection is also observed between ketones and secondary alcohols; i.e., isopropanol (CH$_3$CHOHCH$_3$) can be synthesized via two successive hydrogen additions with acetone (Hiraoka et al. 1998). Here several aldehydes and alcohols are identified. Obtained column densities, rotation temperatures, and spatial distributions of these molecules are discussed to understand the morphological correlation between these aldehydes and alcohols. The astrochemical model is implemented to compare with the observational finding. This work demonstrates that consecutive hydrogen addition could contribute to forming some complex interstellar molecules. Here the kinetics of the consecutive hydrogen addition reactions of alcohol production from aldehyde, ketone, and ketene are examined. Binding energies (BEs) of a species with a grain substrate are essential for constructing a chemical model. Most COMs are primarily produced on the dust surface and further desorbed back to the gas phase (Requena-Torres et al. 2006). Most of the time, the BE of these species is estimated, which may induce uncertainties in the results. Our estimated BE values with the water-ice surface are included in our chemical model to see their impact. The proton affinity (PA) is not directly included in our model. But it is computed to check the reactivity of these species with H$. The role of the PA of various species and their intermediate steps is also discussed to synthesize new COMs. Some of our obtained kinetic parameters are directly included in our chemical model to compare between the observation and modeling yields.

The remainder of this paper is organized as follows. In Section 2, the observational results are presented. The computational details adopted to explain the chemical linkage between aldehyde and alcohol are given in Section 3. Astrochemical modeling and its implication are discussed in Section 4, and finally, in Section 5, we conclude.
2. Observations of a Hot Molecular Core, G10

2.1. Observations and Data Analysis

This paper uses the ALMA cycle 4 archival data (12 m array data) of the observations (#2016.1.00929.S) of G10. The pointing center of the G10 observations is located at $\alpha$ (J2000) = 18\h 08\m 38\s 24.2, $\delta$ (J2000) = -19\d 51\arcmin 50\arcsec 4. This observation was performed with band 4 having four spectral bands covering the sky frequencies of 129.50–131.44, 147.50–149.43, 153.00–154.93, and 158.49–160.43 GHz, and the corresponding angular resolution at four different frequencies is 1\farcs 47 (12.642 au), 1\farcs 72 (14.792 au), 1\farcs 66 (14.276 au), and 1\farcs 76 (15.136 au), respectively. The spectral resolution of the data is 976 kHz. The number of antennas used for the corresponding four spectral windows is 39, 40, 41, and 39, respectively. The flux, phase, and bandpass calibrators of this observation are J1733–1304, J1832–2039, and J1924–2914. The systemic velocity of the source is 68 km s$^{-1}$ (Rolffs et al. 2011). A detailed description of the observations was presented in Gorai et al. (2020). Here all of the analyses (spectral and line analysis) are carried out using CASA 4.7.2 software (McMullin et al. 2007). Since G10 is a line-rich source, the corrected sigma-clipping method of the STATCONT package (Sánchez-Monge et al. 2018) is used to determine the continuum level in the data cube. Further, the spectral window of the data cube is divided into two data cubes (continuum and line emission) using the “uvcontsub” command in the CASA program. Line identification is performed with CASSIS (Vastel et al. 2015). This software has been developed by IRAP-UPS/CNRS (http://cassis.irap.omp.eu), which uses the Cologne Database for Molecular Spectroscopy (CDMS; Müller et al. 2001, 2005; Endres et al. 2016) and Jet Propulsion Laboratory (JPL; Pickett et al. 1998) databases. Various physical parameters ($V_{\text{LSR}}$, line blending, upper-state energy, Einstein coefficient, and 3$\sigma$ significance level) are considered. Local thermodynamic equilibrium (LTE) synthetic spectra are generated with the best-fit parameters to compare the observed spectral feature and line identification. We have also used https://splatologue.online for the additional confirmation of our choices.

2.2. Synthesized Images

Continuum maps at 1.88, 1.94, 2.02, and 2.30 mm were presented in Gorai et al. (2020). They obtained the corresponding synthesized beam and position angle 2\farcs 38 $\times$ 1\farcs 39 and 77\arcsec4, 2\farcs03 $\times$ 1\farcs47 and 73\farcs50, 1\farcs98 $\times$ 1\farcs57 and 64\farcs28, and 2\farcs44 $\times$ 1\farcs64 and 63\farcs16, respectively. Other parameters of continuum images, such as frequency, peak flux, integrated flux, and deconvolved beam size (FWHM), were presented in Table 2 of Gorai et al. (2020). The synthesized beam size of this data cube was not sufficient to resolve the continuum emission. The hydrogen column density and dust optical depth of each continuum map were presented in Table 4 of Gorai et al. (2020). The average value of the hydrogen column density is $\sim$1.35 $\times$ 10$^{25}$ cm$^{-2}$, and the dust optical depth is 0.136, which implies that the source is optically thin (Gorai et al. 2020).

2.3. Line Analysis

The observed spectra obtained within the circular region having a diameter of 2\farcs0 ($\sim$17.200 au) centered at R.A. (J2000) = (18\h 08\m 38\s 232), decl. (J2000) = (-19\d 51\arcmin 50\arcsec 4) are continuum-subtracted for the analysis. The line width ($\Delta V$), local standard of rest velocity ($V_{\text{LSR}}$), and integrated intensity ($\int T_{\text{mb}}dV$) of each transition that is obtained after Gaussian fitting to the observed transition is noted. All of the line parameters corresponding to an observed transition, such as associated quantum numbers $J'_{K_{\text{A}}K_{\text{C}}} - J''_{K_{\text{A}}K_{\text{C}}}$, rest frequency ($\nu_0$), $\Delta V$, $\int T_{\text{mb}}dV$, upper-state energy ($E_u$), and $V_{\text{LSR}}$, are presented in Table 1. Multiple transitions of methanol (CH$_3$OH), acetaldehyde (CH$_3$CHO), ethylene glycol [CH$_2$OH$_2$], glycolaldehyde (HOCH$_2$CHO), propanal (CH$_3$CH$_2$CHO), acetone (CH$_3$COCH$_3$), methyl formate (CH$_3$COH), and dimethyl ether (CH$_3$OCH$_3$) are identified. This is the first time ethylene glycol and propanal are identified in G10. Only two lines of glycolaldehyde are identified. Therefore, it is considered a tentative detection in this source. The observed spectra of these species and the fitted spectra are shown in Appendix B (see Figure B1). The integrated intensity for the methanol, ethylene glycol, and glycolaldehyde is obtained by simple Gaussian fitting to each transition. In the case of acetaldehyde, propanal, acetone, methyl formate, and dimethyl ether, torsional substates due to the internal rotation of the methyl group are noticed. For acetone and dimethyl ether, these substates are AA, EE, EA, and AE. In the case of acetaldehyde, propanal, and methyl formate, A and E substates are noticed. But these transitions are found to be blended with different substates. These transitions were not resolved due to the low spectral resolution of the present spectra. The integrated intensity is obtained with the Gaussian fitting and then divided according to the $S/V^2$ values (obtained from https://www.cv.nrao.edu/php/splat). The transition with maximum intensity between the torsional substates was considered in the rotation diagram analysis to calculate the rotation temperature and column density.

2.4. Spatial Distribution of Aldehydes and Alcohols

The integrated intensity distribution of CH$_3$OH, CH$_3$CHO, CH$_3$OH$_2$, HOCH$_2$CHO, CH$_3$CH$_2$CHO, CH$_3$COCH$_3$, CH$_2$OH, and CH$_3$OCH$_3$ are shown in Appendix (see Figures C1–C4). The source sizes are determined by using two-dimensional Gaussian fitting of the images. The deconvolved beam size of the emitting region is estimated as $\theta = \sqrt{\theta_{50}^2 - \theta_{\text{beam}}^2}$, where $\theta_{50} = 2\sqrt{A/\pi}$ is the diameter of the circle whose area ($A$) encloses a 50% line peak, and $\theta_{\text{beam}}$ is the half-power width of the synthesized beam (Rivilla et al. 2017). It is noticed that all of the lines have their peak around the position of the continuum. The emitting diameter of the observed species is summarized in Table A1. It is noticed that the emitting diameters of different observed transitions are smaller than the beam size. So all of these transitions are not well spatially resolved or, at best, marginally resolved to an extent. In the case of methanol, the emitting region varies from 1\farcs23 to 1\farcs81, and it is noticed that the emitting regions of methanol decrease with an increase of upper-state energy. Therefore, methanol could trace the temperature distribution of the source. However, our data cannot provide much insight into the source’s temperature distributions due to the low angular resolution. All transitions of acetaldehyde having upper-state energy <100 K are detected from the 1\farcs33 to 1\farcs53 region. The

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11 https://cdms.astro.uni-koeln.de
12 https://spec.jpl.nasa.gov
emitting region of dimethyl ether and methyl formate transitions having upper-state energy < 100 K varies between 18°83−1°795 and 1°66−1°95, respectively. So, dimethyl ether and methyl formate transitions are found from roughly a similar region as acetaldehyde. But the transitions of propional, glycolaldehyde, acetone, and ethylene glycol are detected from different positions. It is observed that the transitions of propional, glycolaldehyde, and ethylene glycol emissions are very compact toward the dust continuum, except for some transitions. These suggest the grain surface origin of these species. Emissions of dimethyl ether and methyl formate are found to be comparatively extended compared to the other species. The emitting region of ethylene glycol is small compared to the emission of all other COMs identified in this work. The emitting region of dimethyl ether is found to be more extensive compared to all other species. The emitting region of ethylene glycol is small compared to the emission of all other COMs identified in this work. The emitting region of dimethyl ether is found to be more extensive compared to all other species.

2.5. Rotation Diagram Analysis

Here a rotation diagram analysis is performed by assuming the observed transitions are optically thin and in LTE. For optically thin lines, the column density can be expressed as

### Table 1

| Species            | $J'_{K'K''}/J''_{K''K''}$ | Frequency (GHz) | $E_u$ (K)  | $\Delta V$ (km s$^{-1}$) | $I_{\text{max}}$ (K) | $V_{\text{LSR}}$ (km s$^{-1}$) | $S$ (D$^2$) | $J'_{\text{rot}} dV$ (K km s$^{-1}$) |
|--------------------|--------------------------|----------------|-----------|--------------------------|---------------------|------------------|-----------|----------------------------------|
| Methanol (CH$_3$OH) | 21−0,21 = 21,12, E, $v_0 = 0$ | 129.720384 | 546.2     | 9.6 ± 0.2                | 30.1 ± 0.6          | 66.9 ± 0.1       | 19.8      | 308.7 ± 14.5                     |
| Ethylene glycol (CH$_2$OH) | 338,023 = 32,121, E, $v_0 = 0$ | 130.115657 | 323       | 7.7 ± 0.07               | 2.55 ± 0.01         | 67.8 ± 0.03      | 53        | 20.9 ± 0.3                       |
| Acetaldehyde (CH$_3$CHO) | 9,9 = 9,9, E, $v_0 = 0$ | 127.478806 | 39.6      | 12.1 ± 0.26              | 12.3 ± 0.8          | 69.9 ± 0.41      | 12.0      | 158.4 ± 0.5                      |
| Glycolaldehyde (HOCH$_2$CHO) | 20,0,13 = 20,14, E, $v_0 = 0$ | 159.768239 | 48.8      | 8.7 ± 0.25               | 9.32 ± 0.15         | 68.4 ± 0.08      | 62.8      | 86.6 ± 3.8                       |
| Dimethyl ether (CH$_2$OCH$_3$) | 6,1,6 = 7,0, E, $v_0 = 0$ | 146.005214 | 49.6      | 3.8 ± 0.12               | 3.6 ± 0.01          | 31.2 ± 0.23      | 24.0      | 66.7 ± 3.6                       |

Note. Optically thick.
(Goldsmith & Langer 1999)

\[
\frac{N^{\text{thin}}_{u}}{g_{u}} = \frac{3k_{B} \int T_{\text{mb}} dV}{8\pi^{2} \hbar^{2} S_{u} \mu^{2}},
\]

where \( g_{u} \) is the degeneracy of the upper state, \( k_{B} \) is the Boltzmann constant, \( \int T_{\text{mb}} dV \) is the integrated intensity, \( \nu \) is the rest frequency, \( \mu \) is the electric dipole moment, and \( S \) is the line strength. Under LTE conditions, the total column density would be written as

\[
\frac{N^{\text{thin}}_{u}}{g_{u}} = \frac{N_{\text{total}}}{Q(T_{\text{rot}})} \exp \left( \frac{E_{u}}{k_{B} T_{\text{rot}}} \right),
\]

where \( T_{\text{rot}} \) is the rotational temperature, \( E_{u} \) is the upper-state energy, and \( Q(T_{\text{rot}}) \) is the partition function at the rotational temperature. The above two equations can be rearranged as

\[
\ln \left( \frac{N^{\text{thin}}_{u}}{g_{u}} \right) = -\left( \frac{1}{T_{\text{rot}}} \right) \left( \frac{E_{u}}{k_{B}} \right) + \ln \left( \frac{N_{\text{total}}}{Q(T_{\text{rot}})} \right).
\]

The rotational temperature and total column density of a species are simultaneously determined from this expression. All of the spectroscopic parameters for this analysis are taken from the CDMS (https://cdms.astro.uni-koeln.de; Müller et al. 2001, 2005; Endres et al. 2016) or the JPL (http://spec.jpl.nasa.gov; Pickett et al. 1998) database. Rotation diagrams of methanol (CH\textsubscript{3}OH), acetaldehyde (CH\textsubscript{3}CHO), ethylene glycol ([CH\textsubscript{2}OH]\textsubscript{2}), glycolaldehyde (HOCH\textsubscript{2}CHO), propanal (CH\textsubscript{3}CH\textsubscript{2}CHO), acetone (CH\textsubscript{3}COCH\textsubscript{3}), methyl formate (CH\textsubscript{3}OCHO), and dimethyl ether (CH\textsubscript{3}OCH\textsubscript{3}) are shown in Figure 1. The derived rotational temperatures and column densities are summarized in Table 2. In Table 2, we have noted the errors. The relative percentage errors of the rotational temperature and column density are noted in the footnote of the table. The rotation diagram of glycolaldehyde is constructed with only two data points. Therefore, the rotational temperature has been assumed to some constant value. Methanol transitions with a wide range (166–664 K) of upper-state energies are observed. Some of these transitions are optically thick (i.e., 153.281 and 154.425 GHz). Therefore, it is challenging to construct the rotation diagram with all seven unblended methanol lines (noted in Table 1). Since two transitions are optically thick, these are excluded from the rotation diagram analysis. Furthermore, by considering the rest of the five transitions, considerable uncertainty in the estimated column density ((3.7 ± 3) \times 10^{18} \text{ cm}^{-2}) and rotational temperature (345 ± 198 K) is obtained. Comparatively, a better linear fit is possible if we exclude the 148.111 GHz transitions from the rotation diagram (by choosing the transitions with upper-state energy >300 K). It yields a column density and rotational temperature of methanol of (4.3 ± 3.4) \times 10^{18} \text{ cm}^{-2} and 206 ± 66 K, respectively.

For the sample of considered molecules, our estimated rotation temperature varies from 72 to 234 K. A low rotation temperature of \( \sim 72 ± 11 \text{ K} \) for acetaldehyde is obtained, which is in agreement with the rotation temperature of acetaldehyde obtained by Ikeda et al. (2001). Olmi et al. (1996) derived a temperature of 160 K for CH\textsubscript{3}CN. Rolffs et al. (2011) considered a temperature of 200 K to give an optimum fit to the data for line identification purposes. The average rotational temperature obtained from the species observed here is 177 K, which is in close agreement with Olmi et al. (1996) and Rolffs et al. (2011). There could be a possibility of beam dilution on the derived column densities and excitation temperatures. If the beam dilution effect is included in the rotation diagram, it is noticed that, on average, our column densities and temperatures increase by a factor of 3.2 and 1.4, respectively. Derived column density and rotational temperature are further used in the LTE module of CASSIS to produce synthetic LTE spectra and compare with our observations (see Figure B1). The average FWHM of each species from Table 1 is used for this computation. A source size of 2\textsuperscript{″} with the ALMA telescope is considered. Figure B1 shows a good agreement with the observed feature, except for the three transitions of methanol and all of the transitions of dimethyl ether. The intensity of the three methanol transitions is overproduced. Among them, the 153.281 and 154.425 GHz transitions are optically thick. All of the transitions of dimethyl ether are underproduced. During the line analysis, it is noticed that these transitions consist of multiple substates. The strongest transition is only considered based on their S\mu\nu\nu\nu\nn value. Thus, the obtained FWHMs are possibly overestimated during the Gaussian fitting, which can under-produce the intensity of these transitions in Figure B1.

3. Kinetics of the Aldehydes, Alcohols, Ketone, and Ketene Observed in G10

Here an extensive theoretical investigation is carried out to understand the formation mechanism of some aldehydes, alcohols, ketene, and ketone, which are observed in G10. All the quantum chemical results presented in this paper are carried out using the Gaussian 09 suite of programs (Frisch et al. 2013). The density functional theory (DFT) method with a B3LYP functional (Becke 1993) and 6-31+G(d,p) basis set is used in computing the activation barrier and enthalpy of the reactions. Both the activation and reaction energies are calculated including the harmonic zero-point vibrational energy (ZPVE) and considering a temperature of 298.15 K and 1 atmosphere pressure. A fully optimized ground-state structure is verified to be a stationary point (having a nonimaginary frequency) by harmonic vibrational frequency analysis. For the transition state (TS) calculation, the QST2 method of the Gaussian 09 program is used. All of the TSs are verified using the internal reaction coordinate analysis, which connects reactants and products through the minimum energy path of the potential energy surface (PES). Further, the higher-order method is employed to examine the effect on the activation barrier calculation. The single-point energy calculation of the TS structure and the optimized structure of the reactants at the CCSD(T)/aug-cc-pVTZ level is carried out. The ice mixture is considered embedded within a continuum solvation field to include the passive impact of bulk ice on the activation barrier and enthalpy of reaction. To mimic the ice-phase feature, water is used as the solvent. A self-consistent reaction field (SCRF) is routinely applied in the electronic structure calculations to study the spectroscopy and thermochemistry parameters of any species in the ice phase. Explicit water molecules can also generate a more realistic (inhomogeneous) field. Since the typical size of the interstellar water cluster (number of water molecules required) is not known with certainty, it is preferred to use the SCRF method (Woon 2002b). The polarizable continuum model (PCM) with different integral equation formalism (IEFFPCM) variants as a default SCRF method is used for this purpose (Cancès et al. 1997; Tomasi et al. 2005). A similar level of theory and basis set is used for the gas-phase calculations. This method creates a
solute cavity by overlapping spheres (Pascual-Ahuir et al. 1987; Tomasi & Persico 1994). The implicit solvation model places the molecule of interest inside a cavity in a continuous homogeneous dielectric medium (in this case, water) that represents the solvent. This method is proven to produce convincing results for ices. The PCM is used to consider the reaction field of bulk ice. Here the cluster is treated explicitly to avoid spurious boundary effects. In this framework, the reaction fields issuing from a dielectric constant of 78 for water or about 100 for ice (Aragones et al. 2011) are essentially identical. Hence, the solid-phase calculations and the thermochemistry parameters reported here are close to those in ice. The BE and PA of the aldehydes, ketone, ketene, and corresponding alcohols are also calculated quantum chemically discussed in Section 3.2.

3.1. Rate Constants

A crossover temperature, $T_c$, is defined as the maximum temperature below which a tunneling reaction dominates and above which a thermal activation reaction takes over. The $T_c$ is calculated by the following relation:

$$ T_c = \frac{\hbar \omega}{4 \pi^2 k_B}, $$

Figure 1. Rotation diagram of observed molecules. The best-fit rotational temperature and column density are given in each panel. Filled purple squares are the data points, and purple lines represent the error bars.
where \( h \) is Planck’s constant, \( k_B \) is the Boltzmann constant, and \( \omega \) is the absolute value of the imaginary frequency at the TS. For all gas-phase reactions, the TS theory (TST) is applied. The gas-phase rate constant can be calculated by the following expression:

\[
K = \left( \frac{k_B T}{\hbar \omega} \right) \exp(-\Delta G^\ddagger/RT),
\]

where \( \Delta G^\ddagger \) is the Gibbs free energy of activation, \( c^0 \) is the concentration (~1), \( R \) is the ideal gas constant, and \( T \) is the temperature.

High-level quantum chemical calculations of six aldehyde–alcohol pairs with one ketone–alcohol and one ketene–alcohol pair are presented and discussed in detail. Aldehyde-to-alcohol, ketone-to-alcohol, and ketene-to-alcohol formation may occur through successive hydrogen addition reactions in two steps. The first step is aldehyde/ketone/ketene + H \( \rightarrow \) radical-1, and the second step is radical-1 + H \( \rightarrow \) alcohol. The first step of all these reactions is a neutral–radical reaction, whereas the second step is a radical–radical reaction. The first step of all these reactions thus has an activation barrier, whereas the second step is barrierless, as both reactants have free electrons, which makes them very reactive. Our calculations show that six aldehydes (methanal, ethanol, propanal, propenal, propynal, and glycolaldehyde), one ketone (acetone), and one ketene (ethenone) are forming alcohols (methanol, ethanol, 1-propanol, allyl alcohol, propargyl alcohol, ethylene glycol, isopropanol, and vinyl alcohol, respectively) via two successive hydrogen addition reactions. In terms of stability, the observed alcohols are thermodynamically favorable compared to their isomers. The formation of complex molecules on the grain surface through successive hydrogen additions is found to be dominant. The formation pathways of these molecules are discussed below, and a graphical representation of the PESs of their formation mechanism considering the IEPPCM and DFT-B3LYP/6-31G+(d,p) level of theory is shown in Figure 2.

### 3.1.1. Methanal and Methanol

Here the activation barrier of the reaction H+H\(_2\)CO is computed for the production of CH\(_3\)OH or CH\(_3\)O (reactions 1a and 2a of Table 3). It is noticed that the hydrogen addition to the carbon atom of H\(_2\)CO (i.e., the formation of CH\(_3\)O, methoxy radical) is more favorable than that of its addition to the O atom of H\(_2\)CO (i.e., the formation of CH\(_3\)OH) in both the gas and ice phases considering both the DFT-B3LYP/6-31+G(d,p) and CCSD(T)/aug-cc-pVTZ levels of theory. This is consistent with earlier experimental and theoretical results (Chuang et al. 2016; Song & Kästner 2017). Song & Kästner (2017) studied the TS of reactions 1a and 2a both in the gas phase and on five different binding sites of the ASW surface and calculated the corresponding activation energies. We compare our activation energy values with their gas and ice phases for binding site ASW 5 in Table 3, which shows a good agreement when we consider a CCSD(T)/aug-cc-pVTZ level of theory. Woon (2002a) predicted the barrier height of reaction 2a as 5.04 kcal mol\(^{-1}\) for the gas phase, and it decreases to 4.81 kcal mol\(^{-1}\) when the reaction is embedded with the isodensity surface polarized continuum model (IPCM) field. In our case, we also found a similar decreasing trend from the gas phase to the ice phase considering both levels of theory. Song & Kästner (2017) also computed the BE of H\(_2\)CO for different sites on the ASW surface and found that the BE values vary between 1000 and 9370 K. This uncertainty in the BE value may lead to a very different abundance of CH\(_3\)OH under different astrophysical environments. The hydrogen abstraction reaction of methanol also plays an essential role in controlling the abundance of COMs. The methanol abstraction reaction barrier and the rate constant are taken from Song & Kästner (2017).

### 3.1.2. Ethanal and Ethanol

Here the formation of C\(_2\)H\(_5\)OH via two successive hydrogen addition reactions with CH\(_3\)CHO is considered. The kinetic information (i.e., activation barrier and reaction enthalpy) of these two reactions is noted in Table 3. Looking at the activation barriers reported in Table 3, it is clear that, similar to methanol formation, here the hydrogen addition at the carbon atom position of CH\(_3\)CHO (i.e., the formation of CH\(_3\)CH\(_2\)OH; reaction 4a) is more efficient compared to the hydrogen addition at the O atom position (i.e., the formation of CH\(_3\)CHOH; reaction 3a). The relative abundances between the acetaldehyde and ethyl alcohol seem to depend upon the evolution time, availability of the hydrogen atoms, ice thickness, and ice morphology (Bisschop et al. 2007, 2008). Only the hydrogenation reactions are not enough in explaining the observed abundances of ethanol. It is necessary to consider the ice-phase reaction between CH\(_3\) and CH\(_3\)OH for the formation of ethanol in the ice phase.

### 3.1.3. Propanal and 1-propanol

The coexistence of propanal, propynal, and propenal in Sgr B2(N) (Hollis et al. 2004) could be explained by the following successive hydrogenation sequence: H\(_2\)C\(_2\)CHO (propenal) \( \rightarrow \) CH\(_3\)CH\(_2\)CHO (propenal) \( \rightarrow \) CH\(_3\)CH\(_2\)CHO (propanal). Recently, Qasim et al. (2019) studied propanal formation by the radical–radical reaction between HCO and H\(_2\)C\(_2\)H. They used the sequential hydrogenation of propanal to form 1-propanol. The first step of the reaction has a high activation barrier. But this reaction can change the saturated bond to the unsaturated radicals, which may again undergo some radical–radical recombination reactions. Qasim et al. (2019) obtained a significant production of 1-propanol with this pathway. Our
TST calculation for the successive hydrogenation pathways is shown in Table 3. It is noticed that the hydrogen addition at the carbon atom position of propanal (CH₃CH₂CHO formation; reaction 6a of Table 3) is favorable compared to the oxygen atom position of propanal (CH₃CH₂CH₂OH formation; reaction 5a). The gas-phase activation and reaction energies (including ZPVE) of Zaverkin et al. (2018) are compared with ours in Table 3, which is in good agreement with our values calculated using a higher level of theory. In addition to the successive hydrogenation reactions, following ice-phase reactions, are also considered for the formation of propynal, propenal, and propanal:

\[
\begin{align*}
\text{C}_2\text{H}_2 + \text{H}_2\text{O} & \rightarrow \text{propynal} + \text{H}, \\
\text{O} + \text{C}_3\text{H}_2 & \rightarrow \text{propenal} + \text{H}, \\
\text{HCO} + \text{C}_3\text{H}_3 & \rightarrow \text{propenal} + \text{H}, \\
\text{HCO} + \text{H}_2\text{CCH}_2 & \rightarrow \text{propanal} + \text{H}.
\end{align*}
\]

3.1.5. Propenal and Propargyl Alcohol

Propenal is also a product of the two successive hydrogenation reactions with propynal:

\[
\text{propynal} + 2\text{H} \rightarrow \text{propenal} (\text{CH}_2\text{CHCHO}).
\]

Here the other product channel of this reaction is studied. First, the hydrogenation reaction of propynal would form propenal. In the second step, propenal could undergo another hydrogenation reaction to form allyl alcohol. The TS calculation of the first step found an activation barrier of 2.60 kcal mol⁻¹ in the gas phase and 2.57 kcal mol⁻¹ in the ice phase, considering a lower level of theory (see Figure 2). Table 3 shows the activation barriers for the hydrogen addition at the propenal’s carbon and oxygen atom position. It is noted that, unlike the other cases, here the hydrogen addition at the oxygen atom of propenal (CH₂CHCHOH formation; reaction 7a) seems to be more favorable than it is with the carbon atom position (CH₂CHCH₂O formation; reaction 8a) considering a lower level of theory. But when considering a higher level of theory, the opposite trend is found, which agrees well with the values calculated by Zaverkin et al. (2018), shown in Table 3 for comparison.

3.1.6. Glycolaldehyde and Ethylene Glycol

Glycolaldehyde is the simplest form of the aldose family. Sugars like glucose, ribose, and erythrose belong to this family. Therefore, the presence of glycolaldehyde in space is an indication of the precursor of biologically relevant molecules. Identification of the numerous COMs in the Galactic center makes it an active area of research. Specifically, the study of the chemical evolution of the grain mantle, where various energetic processes (like UV radiation, X-rays, cosmic rays, etc.) may reprocess the mantle composition, is fascinating. The C and O addition to the formyl radical and then three successive hydrogen additions yield glycolaldehyde. The two subsequent hydrogen additions to the glycolaldehyde can produce ethylene glycol (Charnley 2001). Fedoseev et al. (2015) proposed that two HCO radicals can recombine to produce glyoxal (HC(O)CHO), which
Table 3
Calculated Gibbs Free Energy of the Activation, Activation Barrier, and Reaction Enthalpy of Alcohol Formation via Successive Hydrogen Addition with Aldehydes, Ketone, and Ketene by Using Lower [B3LYP/6-31+G(d,p)] and Higher [CCSD(T)/aug-cc-pVTZ] Levels of Theory Considering a 298.15 K Temperature and 1 Atmospheric Pressure

| Serial No. | Reaction Type | Reactions                  | Gibbs Free Energy of Activation (kcal mol⁻¹) | Activation Barrier (kcal mol⁻¹) | Enthalpy of Reaction (kcal mol⁻¹) |
|------------|---------------|----------------------------|-----------------------------------------------|--------------------------------|----------------------------------|
|            |               |                            | Gas Phase | Ice Phase | Gas Phase | Ice Phase | Gas Phase | Ice Phase |
| Methanal-Methanol |               | H₂CO + H → CH₂OH         | 10.57     | 11.32     | 5.59      | (9.35)[10.35] (i) | 6.49      | (10.02)[11.16] (i) | -32.31    | -32.39   |
|            |               | CH₂OH + H → CH₂OH       | 0.00     | 0.00     | 0.00      | (3.58)[4.29] (i) | 4.25      | (5.38)[4.78] (i) | -27.61    | -27.07   |
|            |               | CH₃O+H → CH₂OH          | 0.00     | 0.00     | 0.00      | -4.94    | -20.27   | -99.44    | -100.24  |
| Ethanal-Ethanol |               | CH₃CH₂CHO + H → CH₃CH₂CHO | 11.41     | 12.44     | 5.91 (9.38)a | 6.91 (10.24)a | -27.96    | -26.80   |
|            |               | CH₃CHOH + H → CH₃CHOH   | 0.00     | 0.00     | 0.00      | -9.62    | -93.21   | -99.07    | -99.74   |
|            |               | CH₃CHO + H → CH₃CHO      | 10.10     | 10.24     | 4.11 (5.36)a | 4.25 (5.38)a | -21.50    | -20.27   |
|            |               | CH₃CH₂CHO + H → CH₃CH₂CHO | 0.00     | 0.00     | 0.00      | -9.89    | -99.46   | -99.95    | -99.95   |
| Propenal-Allyl Alcohol |               | CH₃CHCHO + H → CH₃CHCHO | 9.56      | 10.48     | 4.00      | (6.30)[7.89] (ii) | 2.36 (10.47)a | -40.29    | -39.59   |
|            |               | CH₃CHCHOH + H → CH₃CHCHOH | 0.00     | 0.00     | 0.00      | -7.62    | -77.07   | -101.80   | -101.80  |
|            |               | CH₃CHCHO + H → CH₃CH₂O   | 10.32     | 10.24     | 4.43 (5.79)a | 4.38 (6.60)a | -18.00    | -16.72   |
|            |               | CH₃CH₂CHO + H → CH₃CH₂OH | 0.00     | 0.00     | 0.00      | -9.90    | -99.95   | -99.95    | -99.95   |
| Propynal-Propargyl Alcohol |               | HC₃CHO + H → HC₃CHOH | 8.86      | 9.65      | 3.41 [7.41] (ii) | 4.20 (8.28)a | -43.92    | -43.22   |
|            |               | HC₃CHOH + H → HC₃CHOH   | 0.00     | 0.00     | 0.00      | -79.53   | -80.44   | -92.44    | -92.44   |
|            |               | HC₃CHO + H → HC₃CHO      | 9.63      | 9.47      | 3.74 [5.78] (ii) | 3.59 (5.68)a | -22.42    | -22.20   |
|            |               | HC₃CH₂OH+H → HC₃CH₂OH    | 0.00     | 0.00     | 0.00      | -101.02  | -101.46  | -101.46   | -101.46  |
| Glycolaldehyde-Ethylene Glycol |               | HOCH₂CHO + H → HOCH₂CHOH | 11.42     | 12.31     | 5.50      | (8.75)[9.51] (iii) | 6.32 (9.29)a | -29.43    | -30.43   |
|            |               | HOCH₂CHOH + H → HOCH₂CHOH | 0.00     | 0.00     | 0.00      | -92.18   | -92.44   | -92.44    | -92.44   |
|            |               | HOCH₂CHO + H → HOCH₂CHO   | 9.43      | 9.67      | 3.34 (4.47) [4.97] (iii) | 3.38 (4.17)a | -22.38    | -22.61   |
|            |               | HOCH₂CH₂OH+H → HOCH₂CH₂OH | 0.00     | 0.00     | 0.00      | -99.22   | -100.25  | -100.25   | -100.25  |
can also subsequently convert to glycolaldehyde. Coutens et al. (2018) investigated the formation mechanism of these two species (glycolaldehyde and ethylene glycol) using a gas-grain chemical model. They studied the EG/GA ratio for various luminosities. Álvarez-Barcia et al. (2018) studied two successive hydrogen addition reactions with acetaldehyde that can produce ethylene glycol. They also studied the hydrogen abstraction reactions of GA and EG. Table 3 shows the kinetics involved in converting ethylene glycol from glycolaldehyde. Like the methanal–methanol, ethanal–ethanol, propanal–1–propanol, and ice-phase pathways of propynal–propargyl alcohol pairs, the favorable position of the hydrogen addition is noted to be the carbon atom (HOCH2CH2O formation; reaction 12a) instead of the oxygen atom (HOCH2CHO formation; reaction 11a) of glycolaldehyde.

### 3.1.7. Acetone and Isopropanol

Acetone (propanone, CH3COCH3) and isopropanol (isopropyl alcohol, 2-propanol, CH3CHOHCH3) might be chemically connected. Table 3 shows the two successive hydrogenations of acetone (reactions 13 and 14). We check the TST calculations for the hydrogen addition either with the oxygen atom (activation energy 5.56 kcal mol\(^{-1}\)) or with the carbon atom (activation energy 6.29 kcal mol\(^{-1}\)) position of acetone and find that the former one is more favorable than the latter in the gas phase considering a lower level of theory. In contrast, the opposite trend was noted in the ice phase. We could not find a proper TS using a higher level of theory for reaction 14a in the ice phase.

### 3.1.8. Ethenone and Vinyl Alcohol

Vinyl alcohol is a planar molecule that has two conformations. The “syn” conformer is found to be more stable than the “anti” conformer (Turner & Apponi 2001). Here also, the “syn” conformer of vinyl alcohol is considered for the quantum chemical calculations. Here the TS of the two successive hydrogen addition reactions to ketene is examined for the formation of vinyl alcohol. The first step has an activation barrier, whereas the second step is a radical–radical reaction and assumed to be barrierless. Vinyl alcohol can also form from acetaldehyde via the isomerization process (Kästner et al. 2020). Table 3 indicates that the hydrogen addition at the carbon atom position is more favorable than the oxygen atom position of ethenone. Table 3 shows that the H addition to the O atom position of ketene (reaction 15a) requires a significantly higher activation barrier than the H addition to the O atom position of the other species (reactions 1a, 3a, 5a, 7a, 9a, 11a, and 13a) reported here. It could be due to the change of the hybridization of the C atom of ketene from sp\(^{2}\) to sp\(^{3}\) during the H addition reaction. On the other hand, there is no change of hybridization upon H addition to the other aldehyde, which requires only a small structural change; thus, the activation energy could be small.

Table 3 (Continued)

| Serial No. | Reaction Type | Reactions | Gibbs Free Energy of Activation (kcal mol\(^{-1}\)) | Activation Barrier (kcal mol\(^{-1}\)) | Enthalpy of Reaction (kcal mol\(^{-1}\)) |
|-----------|--------------|-----------|-----------------------------------------------|--------------------------------------|-------------------------------------|
|           |              |           | Gas Phase | Ice Phase | Gas Phase | Ice Phase | Gas Phase | Ice Phase |
| Acetone–Isopropanol |
| 13a | NR | CH3:COCH3 + H → CH3:COHCH3 | 11.27 | 12.44 | 11.80 | 12.49 | 17.52 | 18.22 |
| 13b | RR | CH3:COHCH3 + H → CH3:COHCH3 | ... | ... | 0.00 | 0.00 | 6.29 | 6.55 |
| 14a | NR | CH3:COCH3 + H → CH3:COCH3 | 12.97 | 12.97 | 6.29 | 6.55 | 10.04 | 9.92 |
| 14b | RR | CH3:COCH3 + H → CH3:COCH3 | ... | ... | 0.00 | 0.00 | 5.56 | 4.26 |
| Ethene–Vinyl Alcohol |
| 15a | NR | CH2:CO + H → CH2:COH | 17.52 | 18.22 | 11.80 | 12.49 | 17.59 | 18.14 |
| 15b | RR | CH3:COH + H → CH3:COH | ... | ... | 0.00 | 0.00 | 6.83 | 6.33 |
| 16a | NR | CH2:CO + H → CH2:CHO | 10.04 | 9.92 | 4.36 | 4.26 | 5.43 | 5.21 |
| 16b | RR | CH2:CHO + H → CH2:CHO | ... | ... | 0.00 | 0.00 | 5.43 | 5.21 |

Notes. Here NR refers to neutral–radical reactions and RR to radical–radical reactions.

a Bracketed values are calculated using the CCSD(T)/aug-cc-pVTZ level.
b We did not find true TSs. (i) Song & Kästner (2017), (ii) Zaverkin et al. (2018), (iii) Álvarez-Barcia et al. (2018).

3.2. BE and PA

A sizable portion (~60%–70% of the surface coverage) of the interstellar icy layers may contain water molecules. That is why the BE of the interstellar species is usually explored with the H2O surface. However, the rest (~30%–40%) of the grain mantle would comprise other impurities. Here CO2, CO, and CH3OH can occupy a sizable portion of the grain mantle in different lines of sight. Keane et al. (2001) summarized that the relative abundance of CO, CO2, and CH3OH relative to water ice could vary in the range of 0.4–15, 0.17–21, and 1.5–30, respectively, in different lines of sight. So, the BE with these surface species is also important in the various evolutionary stages. It is needed to construct a model that can consider the BE depending on the surface composition of the ice. Furuya & Persson (2018) reported a model in which the BE depends on the surface composition of ice mantles. However, showing the results of such a chemical model is outside the scope of this work.
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A realistic estimation of the BEs with various substrates is not available. In the absence of any experimental values, the quantum chemical method provides an educated estimate (Wakelam et al. 2017; Das et al. 2018). Here CO and CH$_3$OH molecules are considered a substrate for this purpose.

The Gaussian 09 suite of programs employed for the quantum chemical calculations is utilized to evaluate the BE values. To calculate the BE, the optimized energy for the complex system (where a species is placed at a suitable distance from the grain surface) is subtracted from the tomaul optimized energies of the grain surface and species. To find the optimized energy of all structures, a second-order Møller–Plesset (MP2) method with an aug-cc-pVDZ basis set (Dunning 1989) is used following Das et al. (2018). The ZPVE and basis set superposition error correction are not considered for BE calculations.

Obtained BE values are shown in Table 4. It is interesting to note that a higher BE for the alcohol is obtained in most cases than for the corresponding aldehyde, ketone, or ketene. Obtained values with CO and CH$_3$OH differ significantly from that of water. In terms of average values, the BE value with a water monomer is ~2.85 times higher than the CO monomer and 1.16 times lower in comparison to the CH$_3$OH monomer. Here, in our chemical model, the obtained BE values with CO and CH$_3$OH are not included because they are not available for the other species. However, BE values obtained with the c-tetramer water configuration are included in our model with the appropriate scaling factor suggested in Das et al. (2018). In Table 4, the ground-state spin multiplicity of the species used to calculate the BE is also noted. Separate calculations (job type “opt+freq” in the Gaussian 09 suite) with different spin multiplicities are used. The lowest-energy electronic state in between these is noted as the ground state.

The protonation reactions (i.e., X + H$^+$ → XH$^+$) and proton transfer reactions (i.e., X + YH$^+$ → XY$^+$ + Y) have a significant impact on the interstellar chemistry (Herbst & Leung 1986; Wakelam et al. 2010). The ab initio quantum chemical approaches provide a reliable value of the PA for small molecules, where the experimental determination of these parameters is a difficult task. A systematic study to calculate the adiabatic PA of aldehydes, ketone, ketene, and the corresponding alcohols is considered in this work. The PA is defined as the energy released when a proton is added to a system. Thus, the energy difference between a species and a species with an additional proton (H$^+$) is estimated. It is calculated as the difference in energy (electronic + zero-point energy) between a neutral species and its protonated analog, i.e.,

$$PA = E_X - E_{XH^+},$$

where $E_X$ is the optimized energy of the species, X, and $E_{XH^+}$ is the optimized energy of the protonated species, XH$^+$. To find the optimized energy of all structures, an MP2 method with an aug-cc-pVDZ basis set is again used. This is then verified via harmonic frequency calculations with the equilibrium geometries having only real frequencies. Zero-point correction to energies is not considered to evaluate the PA of the species reported here. The protonation of a neutral species can occur in more than one position, which yields different protonated species with other PAs. To avoid any ambiguity, only the highest PA is noted in Table 5. A protonated form with a higher PA of a neutral species is found to be more stable and abundant (in some cases) and thus may be detectable. In contrast, another protonated form with a lower PA forming from the same neutral species is less stable. This species is very

### Table 4
Calculated BE Values of the Aldehydes, Alcohols, Ketone, and Ketene Considered in This Work

| Species                  | Ground State Used | CO Monomer | CH$_3$OH Monomer | H$_2$O Monomer | H$_2$O Tetramer (Scaled by 1.188) | Available |
|--------------------------|-------------------|------------|------------------|----------------|----------------------------------|-----------|
| Methanal                 | Singlet           | 641        | 2942             | 2896           | 3242$^c$ (3851)                  | 2050$^b$, 4500 ± 1350$^b$ |
| Methanol                 | Singlet           | 1247       | 3227             | 3124           | 4368$^b$ (5189)                  | 5534$^b$, 5000 ± 1500$^b$ |
| Ethanal                  | Singlet           | 1015       | 1964             | 3189           | 3849$^b$ (4573)                  | 2450$^b$, 5400 ± 1620$^b$ |
| Ethanol                  | Singlet           | 873        | 3408             | 2824           | 5045$^b$ (5993)                  | 6584$^b$, 5400 ± 1620$^b$ |
| Propanal                 | Singlet           | 680        | 3679             | 3522           | 3396 (4034)                      |           |
| 1-Propanol               | Singlet           | 1298       | 3932             | 2609           | 4791 (5692)                      |           |
| Propenal                 | Singlet           | 1043       | 3454             | 2958           | 3495 (4152)                      | 5400 ± 1620$^b$ |
| Allyl alcohol            | Singlet           | 1381       | 3625             | 3170           | 3964 (7085)                      |           |
| Propynal                 | Singlet           | 1174       | 3072             | 2318           | 3379 (4014)                      |           |
| Propargyl alcohol        | Singlet           | 1031       | 4119             | 2870           | 4284 (5089)                      |           |
| Glycolaldehyde           | Singlet           | 826        | 3524             | 2871           | 5131 (6096)                      |           |
| Ethylene glycol          | Singlet           | 933        | 4666             | 3144           | 4602 (5467)                      |           |
| Acetone                  | Singlet           | 728        | 3769             | 3623           | 4420 (5251)                      | 3500$^b$  |
| Isopropanol              | Singlet           | 1369       | 3640             | 2879           | 5230 (6213)                      |           |
| Ethenone                 | Singlet           | 732        | 1450             | 1317           | 2847 (3382)                      | 2200$^b$, 2800 ± 840$^b$ |
| Vinyl alcohol            | Singlet           | 1236       | 3407             | 2836           | 3786 (4497)                      |           |

**Notes.**
- $^a$ Das et al. (2018).
- $^b$ KIDA old BE.
- $^c$ KIDA new BE (Wakelam et al. 2017).
reactive, and the high reactivity of this protonated species may reduce its interstellar abundance. We notice that ethenone has the highest and methanal has the lowest PA among all of the species considered for this study.

### 4. Chemical Modeling

The chemical model for molecular clouds (CMMC; Das et al. 2015a, 2015b, 2019, 2021; Gori and et al. 2017a, 2017b, 2020; Sil et al. 2018, 2021; Bhat et al. 2021) is implemented for studying the formation of aldehydes, ketone, ketene, and their corresponding alcohols. The low metallic elemental abundances are used as the initial abundances (Wakeham & Herbst 2008; EA1 set). The gas-phase pathways of the CMMC are mainly adopted from the UMIST database (McElroy et al. 2013). Additionally, a complete network for the formation of alcohols and aldehydes is considered. For the construction of these reaction sets, the ice-phase reactions noted in Table 3 are considered. The activation energy barriers calculated by the CCSD(T)/aug-cc-pVTZ level are adopted. Since, for reaction 13a of Table 3, a true TS was not obtained with the CCSD(T)/aug-cc-pVTZ level of theory, the activation barrier obtained with the B3LYP/6-31+G(d,p) level of theory is used. For the gas-phase destruction of these species, interstellar photoreactions, cosmic ray–induced reactions, and ion–molecular reactions with major ions (He+, H+, HCO+, H2O+, C+, etc.) are considered. The destruction of some of these reactions was already available in McElroy et al. (2013). If it is not available, a very similar reaction with the same rate constants is adopted for these reactions. A cosmic-ray rate of $1.3 \times 10^{-7}$ s$^{-1}$ is considered in all of our models. Cosmic ray–induced and chemical desorption with an efficiency of 1% is considered. For the all-grain surface species, a photodesorption rate of $3 \times 10^{-3}$ per incident UV photon (Öberg et al. 2007) is adopted. A sticking coefficient of 1.0 is considered for the neutral species. Sticking coefficients of H and H$_2$ are taken from Chaabouni et al. (2012). On the grain surface, the diffusive surface reaction can lead to chemical complexity. However, to successfully continue the diffusive reaction mechanism, the reactants should be in close proximity until they react. There is a possibility that two reactants can move apart or be desorbed back to the gas phase. So it is essential to consider the competition between diffusion, desorption, and reaction. Following Garrod & Pauly (2011), this possibility is included here. At a high density ($\sim 10^7$ cm$^{-3}$) and around 10 K, a notable portion of the grain surface would be covered by molecular hydrogen. At this stage, an encounter desorption of H$_2$ (Hincelin et al. 2015; Chang et al. 2021; Das et al. 2021) needs to be considered to avoid an unnecessary surge in the grain molecular hydrogen. The grain mantle chemical composition at this phase is crucial to delivering the surface species into the gas phase during the warm-up stage. Here the encounter desorption mechanism of H$_2$ is considered in our model.

The BE ($E_d$) of the surface species plays a decisive role in controlling the chemical complexity of the interstellar ice. A straightforward relation between the diffusion energy ($E_d$) of a species with the BE is considered by following $E_d = R E_d$, where $R$ may vary between 0.35 and 0.8 (Garrod et al. 2007). Here $R = 0.35$ and 0.50 are used to show their effects on the chemical complexity. These BEs are taken from either the KIDA database$^{13}$ or Das et al. (2018). Das et al. (2018) provided BE values for some relevant interstellar species with the water surface. They computed the interaction energies, varying the size of the substrate. They showed that their method will yield a minimum deviation with the experimentally obtained BE values when a higher-order cluster is used. Table 4 shows the computed BEs of these aldehydes, alcohols,

### Table 5

| Species                  | Protonation Reactions                                                                 | PA (kJ mol$^{-1}$) | Available          |
|--------------------------|---------------------------------------------------------------------------------------|--------------------|-------------------|
| Methanal                 | HCHO + H$^+$ → CH$_2$OH$^+$                                                          | 692                | 712.9 ± 1.1$^a$   |
| Ethanol                  | CH$_3$OH + H$^+$ → CH$_3$OH$_2^+$                                                    | 740                | 754.3$^a$         |
| Ethanal                  | CH$_3$CHO + H$^+$ → CH$_3$CHOH$^+$                                                   | 749                | 768.5 ± 1.6$^a$   |
| 1-Propanol               | CH$_3$CH$_2$OH + H$^+$ → CH$_3$CH$_2$OH$_2^+$                                       | 764                |                   |
| Propenal                 | CH$_3$CH$_2$CHO + H$^+$ → HCH$_2$CH$_2$CHO$^+$                                      | 764                |                   |
| Allyl alcohol            | CH$_3$CH$_2$CHOH + H$^+$ → CH$_3$CH$_2$CHOH$_2^+$                                   | 773                |                   |
| Propynal                 | HC$_3$CHO + H$^+$ → HC$_3$CHOH$^+$                                                   | 733                |                   |
| Propargyl alcohol        | HC$_3$CH$_2$OH + H$^+$ → HC$_3$CH$_2$OH$_2^+$                                       | 742                |                   |
| Glycolaldehyde           | HOCH$_2$CHO + H$^+$ → H$_2$OCH$_2$CHO$^+$                                           | 759                |                   |
| Ethylene glycol          | HOCH$_2$CH$_2$OH + H$^+$ → HOCH$_2$CH$_2$OH$_2^+$                                   | 797                |                   |
| Acetone                  | CH$_3$COH + H$^+$ → CH$_3$COH$^+$                                                   | 793                | 825.3 ± 3$^a$     |
| Isopropanol              | CH$_3$CHOH$_2$ + H$^+$ → CH$_3$CHOH$_2$CH$_2$OH$^+$                                | 782                |                   |
| Ethenone                 | CH$_2$CO + H$^+$ → CH$_2$CO$^+$                                                     | 822                | 882.8$^b$         |
| Vinyl alcohol            | CH$_2$CHOH + H$^+$ → CH$_2$CHOH$^+$                                                  | 800                |                   |

Notes.

$^a$ Hunter & Lias (1998), $^b$ Turner & Apponi (2001)

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ketone, and ketene with various substrates. The ground state used to calculate the BE of these molecules is also pointed out along with the BE values in Table 4. Das et al. (2018) suggested a scaling factor of ∼1.188 while using the tetramer water configuration for the computation of the BE. The scaled BE values are also noted in Table 4. Except for the glycolaldehyde and ethylene glycol pair, for all cases, obtained BEs with the tetramer configuration are noted to be comparatively higher than their related aldehyde, ketone, or ketene. These new sets of BEs with the tetramer configuration of water molecules are included in our chemical model with appropriate scaling.

Depending on the BEs and $R$ values, four sets of BEs are constructed (see Table 6). For sets 1 and 2, BEs are used from the KIDA database (Wakelam et al. 2017). The only difference between sets 1 and 2 is that for set 1, $R = 0.5$ is used, whereas for set 2, $R = 0.35$ is used. Recently, Das et al. (2018) provided a set of BEs for 100 relevant interstellar species with the water surface. They used the tetramer configuration of water molecules for this calculation. They suggested using a scaling factor of 1.188 with this to estimate the BEs of these species. Set 3 is constructed with the BE values provided by Das et al. (2018). Sil et al. (2017) reported the BEs of H and H$_2$ for a comprehensive collection of surfaces (benzene, silica, and water). They showed that the BEs of H and H$_2$ are very sensitive to the choice of substrates. These variations should be expected for all species if various substrates are considered. But showing all of the changes here would be outside the scope of this work. Here one additional BE set is considered, where the BE of H and H$_2$ are kept the same as in KIDA, but for the others, it is the same as in set 3. Thus, in set 3, BEs of H and H$_2$ of 148 and 627 K, respectively, are used from Das et al. (2018) after scaling by 1.188, whereas in set 4, 650 and 440 K, respectively, are used for H and H$_2$ (Wakelam et al. 2017). Here $R = 0.35$ is considered for both set 3 and set 4.

**Table 6**  
Different Sets of BE Used Based on the Ratio of the Diffusion Energy to BE ($R$)

| Set  | BEs Used                  | $R$ |
|------|---------------------------|-----|
| 1    | Wakelam et al. (2017)     | 0.5 |
| 2    | Wakelam et al. (2017)     | 0.35|
| 3    | $1.188 \times$ BE of Das et al. (2018) | 0.35|
| 4    | $1.188 \times$ BE of Das et al. (2018), BE of H and H$_2$ from Wakelam et al. (2017) | 0.35|

4.1. Physical Conditions

Here a physical condition is used that is suitable to explain the properties of a hot core. Three models (A, B, and C) are implemented to describe the chemical complexity around this region. The physical condition of our model A is divided into three distinct stages. In the first stage ($10^5$–$10^6$ yr), an isothermal (gas and grain temperature are kept the same) collapse of the cloud is considered. The BE values are derived from a minimum hydrogen number density ($n_{H_{\text{min}}}$) of $3 \times 10^3$ cm$^{-3}$ to a maximum hydrogen number density ($n_{H_{\text{max}}}$) $10^7$ cm$^{-3}$. During this stage, the visual extinction parameter ($\chi_V$) can gradually increase due to increased density. The following relation between $\chi_V$ and $n_H$ is used to consider this situation (Lee et al. 1996; Das & Chakrabarti 2011; Gorai et al. 2020):

$$\chi_V = \max (\chi_{V_{\text{min}}}, (\sqrt{n_H/n_{H_{\text{min}}} - 1})/(\sqrt{n_{H_{\text{max}}}/n_{H_{\text{min}}} - 1}) \times \chi_{V_{\text{max}}})$$

(7)

It is considered that $\chi_V$ can vary from a minimum value ($\chi_{V_{\text{min}}} = 2$) to a maximum value ($\chi_{V_{\text{max}}} = 200$). In the second stage ($5 \times 10^4$ yr), the cloud remains constant at $n_{H_{\text{max}}}$, $\chi_{V_{\text{max}}}$ - At the end of this stage, the gas and dust temperatures can reach up to 200 K. The third or last stage is a post–warm-up stage (period of $1.0 \times 10^5$ yr), where $n_H$, $\chi_V$, and temperature are kept fixed at their respective highest values.

In the case of model B, the prestellar collapsing stage is considered instead of the initial isothermal collapsing stage. In this stage, the dust temperature is allowed to decrease as the collapse proceeds. The gas temperature is kept constant at 10 K during this collapse. The other two stages are considered the same as model A. The dust temperature of the prestellar collapsing stage is calculated by using the following empirical relation proposed by Hocuk et al. (2017) and used in Shimonishi et al. (2020):

$$T_d^\text{Hoc} = [11 + 5.7 \tanh (0.61 - \log_{10} (\chi_V))] \chi_{UV}^{1/5.9}$$

(8)

where $\chi_{UV}$ is the Draine UV field strength (Draine 1978) corresponding to 1.7$G_0$ using the Habing field (Habing 1968). Here $G_0$ is the far-ultraviolet radiation field in the Habing unit ($\sim 1.6 \times 10^{-3}$ erg cm$^{-2}$ s$^{-1}$) integrated over the energy range 6–13.6 eV. Here $\chi_{UV} = 1$ is used.

Model C is the same as model A. The only difference between model A and model C is the isothermal collapsing timescale of the first stage. In model C, a shorter timescale ($10^5$ yr) for the isothermal collapse is considered. It is more relevant for high-mass star-forming regions. Thus, in the case of model A, we have a density slope of $\sim 10$ cm$^{-3}$ yr$^{-1}$, whereas it is $\sim 100$ cm$^{-3}$ yr$^{-1}$ in the collapsing stage. The warm-up and post–warm-up timescales are kept the same as in model A.

The physical conditions described here are summarized in Figure 3. The time evolution of density, temperature, and visual extinction in the three distinct stages is shown for models A, B, and C. The left axis of Figure 3 represents the variation of the temperature and visual extinction parameters in the linear scale, whereas the right axis represents the density curve in the logarithmic scale. For better visibility, in the top panel, temperature is plotted by scaling by a factor of 2. Models A and B start with an isothermal collapsing stage. In this case, the dust and gas temperatures are kept the same. Here a region having an initial temperature between 8 and 20 K is explored to check the sensitivity of our model A to the initial choice of temperature. The temperature range for the initial stage of models A and C is highlighted with the red shaded region. The visual extinction for the initial stage (isothermal collapsing stage) of models A and C is kept constant at 2. In the case of model B, the gas temperature of the first stage is kept fixed at 10 K, and the dust temperature is estimated based on Equation (8). The initial visual extinction of model B is varied between 0.1 and 10 (corresponds to an initial dust temperature of 16–5 K from Equation (8)) to check its effect on chemical evolution. The initial choice of visual extinction parameter and the estimated dust temperature of model B are highlighted in green and yellow, respectively, in Figure 3. In the warm-up stage of models A, B, and C, $\chi_V$ and $n_H$ are kept constant at
their highest value, and the temperature is allowed to increase up to 200 K. It is the typical temperature of a hot core (Garrod et al. 2008). In the post–warm-up stage, both of the models have identical conditions.

### 4.2. Modeling Results

#### 4.2.1. Abundances

In model A, various cases starting with the initial temperature between 8 and 20 K are considered. Figure 4 shows the variation of peak abundances with respect to H$_2$ obtained during the simulation timescale. Six pairs of aldehyde–alcohol, one pair of ketone–alcohol, and one pair of ketene–alcohol shown. Observed abundances in G10, G31, Sgr B2(N), and Orion KL are shown in solid blue, red, cyan, and orange curves, respectively. In Figure 4, the solid violet line represents the case with set 1 BEs reported in Table 6. The solid black line represents the case with set 2. A lower value of $R$ provides more mobility to the surface species keeping the same resident time on grains. It yields a dramatic change in the production of surface species. The changes in the chemical composition of interstellar ice would reflect a significant difference between the gas-phase abundances of the species shown in Figure 4. The case with set 3 is represented with a solid green line in Figure 4. The set 4 case is represented with a solid brown line in Figure 4. It is evident from Figure 4 that the resulting peak abundance is highly sensitive to the choice of initial temperature—more specifically, the dust temperature. Some cases of model A are tested with a different gas temperature than dust and do not find significant differences in the peak abundance.

It is noticed that the set 1 and 2 BEs are helpful to explain the abundances of these aldehydes and alcohols, except glycolaldehyde and ethylene glycol. The set 3 BEs deviate very much from the observed value. This is mainly because of the adopted BE values of H (148 K) and H$_2$ (627 K). However, with the set 4 BEs, the observed abundance of ethylene glycol could be explained. This is because set 4 considered the BE of H and H$_2$ to be the same as that in sets 1 and 2 (650 and 440 K, respectively, for H and H$_2$). The ice-phase origin of these species is evident from the results obtained from model A. The results obtained from model A seem to be highly sensitive to the initial dust temperature, which suggests that either these species were formed during the initial cold phase or the seeds of these species were produced during the initial stage. The final gas-phase abundance of these species is highly affected by the surface species present at the beginning of the warm-up stage. The surface species at the warm-up stage are reprocessed with the elevated temperature, where radicals take an active part in building the chemical complexity. Once the warm-up stage starts, the desorption of the surface species enhances and might reach their respective sublimation temperatures and populate the gas phase. With the set 4 BE and model A, it is possible to explain the observed abundances, except for glycolaldehyde.

The results obtained with model B are also shown in Figure 4. All four cases mentioned in the context of model A are also considered with model B. To visualize the differences between model A and model B, the model B cases are shown with dashed curves in the same colors. It is interesting to note that for model B, significant changes of abundance for the adopted BE parameters are noticed. Like model A, the results of model B are not very sensitive to the initial choice of dust temperature. The reason behind this deviation is the adopted dust temperature at the first stage of models A and B (see Figure 3). In model A, the dust remains at a constant temperature for $\sim 10^3$ yr, whereas in model B, in between a few times $10^3$ yr, it drops down to a temperature of $< 10$ K. This affects the mobility of the surface species. Since it stays at $< 10$ K during its first stage of evolution, model B does not show dramatic changes between the variation of the initial dust temperature.

The orange curve of Figure 4 represents the variation of the peak abundances of these species with set 4 and model C. It is interesting to note that with the shorter collapsing timescale (relevant for the hot core) of model C, the peak abundances of
the COMs are significantly enhanced. Most of the observed abundances could be explained with set 4 of model C. The increase in the abundances of the COMs with the shorter collapsing time is not so straightforward. Many parameters are involved in it. But the shorter collapsing time leads to a much steeper slope for the density, which means that the depletion will be much faster, and the complex molecules, once produced, will have a comparatively shorter time to be destroyed further. In Figure 5, the time evolution of the gas- and ice-phase abundances of aldehydes, alcohols, ketone, and ketene with respect to H2 are shown. Only the results obtained with model C by considering an initial gas and ice temperature of 10 K are shown. There is some uncertainty in the observations. Additionally, the chemical model includes lots of estimated parameters (BEs, reaction pathways, reaction rates, interaction with dust, etc.) that can induce severe skepticism. For these reasons, it is not easy to match all of the observed abundances simultaneously. In Figure 4, the peak abundance is taken beyond the isothermal collapsing stage. Figure 5 shows that beyond the isothermal stage, these peak gas-phase abundances appeared during the warm-up stage, when the temperature varied between ~100 and 120 K. So our time uncertainty is relatively small (~10^4 yr).

A comparison between our obtained gas-phase peak abundance and the observational results is shown in Table 7. Only the results obtained with set 4 of model C are used to show this comparison. Minimum and maximum peak abundances obtained within the initial temperature range considered for model C and set 4 are noted in Table 7. The errors in the obtained abundances are only shown for those species that are identified in G10. The errors are calculated by taking the uncertainty in estimating the H2 column density and the column density obtained from rotation diagram analysis. Gorai et al. (2020) obtained an average column density of \( \sim 1.35 \times 10^{25} \) cm\(^{-2}\). The error in estimating the column density was \( \pm 1.0 \times 10^{22} \) cm\(^{-2}\), which mainly arose from the uncertainty of the measured flux. The error in estimating the column density of the species is taken from Table 2. For estimating the abundance errors for glycolaldehyde, the only uncertainty in predicting the H2 column density is considered.

It is noticed that our results can successfully explain the observed abundances.
4.2.2. Molecular Ratios

In Figure 6, the temperature variation of the ratio obtained between the peak abundance of six pairs of alcohol–aldehyde, one pair of alcohol–ketone, and one pair of alcohol–ketene for model A (solid curve), model B (dashed curve), and model C (dotted–dashed curves) is shown. The observed ratios for G31, G10, Sgr B2(N), and Orion KL are shown with red, blue, cyan, and orange solid lines, respectively. The simulated ratio between the peak abundance of alcohol and aldehyde/ketone/ketene obtained with set 4 and model C, along with the observed abundances of these species, is noted in Table 7. Table 7 depicts the observed abundances in G31, G10, Sgr B2, and Orion KL, along with our modeled abundance. Mainly, the interferometric observations (wherever available) are noted to facilitate a comparative study of the chemical complexity of these hot cores. However, it is worth pointing out that all of these observations are carried out with different facilities with very diverse angular and spatial resolutions. The facility used for each observation, along with the H$_2$ column density used to derive the abundances, is noted in the footnotes of Table 7. Here only the band 4 archival data of G10 are analyzed and report only one alcohol–aldehyde pair (ethylene glycol–glycolaldehyde pair). These two species are recognized for the first time in this source. Earlier, Rolffs et al. (2011) obtained the methanol–methanal pair. Any transitions of methanal are not identified within our spectral bands. So, a direct comparison between our obtained ratios and others could not be performed. For example, Table 7 denotes a higher methanol abundance than ours, obtained by Rolffs et al. (2011). This is because the beam size of our band 4 observation of ALMA varies between 1″39 and 2″44 (~12,000–21,000 au, considering 8.6 kpc distance). In contrast, the beam size of the Submillimeter Array observation at 345 GHz of Rolffs et al. (2011) is 0″3 (~2600 au, considering 8.6 kpc distance). The integrated emission map of the methanol transitions shown in

![Figure 5](image-url). The chemical evolution of aldehyde, ketone, ketene, and their corresponding alcohols is shown with set 4 of CMMC model C while the initial dust temperature is kept at 10 K. The X-axis of the figure shows the logarithmic scale for the isothermal collapsing stage, whereas beyond that, it is shown on the regular scale. Gas-phase abundances are represented with solid curves, whereas the ice phase is shown with dashed curves. Additionally, the time evolution of propynal, methyl formate, and dimethyl ether is shown.
Figure 6. Obtained ratios of six pairs of alcohol and aldehyde, along with the ratios of alcohol–ketone and alcohol–ketene. The observed ratio is marked in red (G31), blue (G10), cyan (Sgr B2(N)), and orange (Orion KL). Model A results are highlighted with solid curves, model B is represented with dashed curves, and model C is represented with dotted-dashed curves.

Table 7

Comparison between the Observed Abundance and Our CMMC Results with Model C (Set 4)

| Species | Obtained Abundances from Model | Obtained Abundance Ratio from Model | G31 | Sgr B2 (N) | G10 |
|---------|-------------------------------|-----------------------------------|-----|------------|-----|
| Methanol | 3.3(−9) − 5.8(−7) | 1.0(1) − 5.3(1) | [1.9(−7)] | [3.2(−8)] | [6.1(−7)] |
| Methanol | 3.5(−8) − 1.4(−5) | 1.9(−6) | [7.7(−7)] | [7.1(−6)] | [2.2(−7)] | [3.2 ± 2.5(−7)] | [1.8(−6)] |
| Ethanol | 1.8(−13) − 5.0(−9) | 8.0(−2) − 2.6(4) | [1.0(−9)] | [1.4(−8)] | [9.5(−8)] | [5.0 ± 0.8(−10)] |
| Ethanol | 7.4(−10) − 9.7(−8) | 2.0(−8)[1.3(−9)] | [1.1(−7)] | [3.6(−7)] | [1.3(−8)] | [1.2(−7)] |
| Propanal | 7.3(−10) − 4.8(−8) | 2.4(−12) − 1.1(−7) | 2.6(−4) − 1.3(2) | [1.8 ± 0.2(−8)] |
| 1-Propanol | 2.0(−13) − 1.9(−9) | 3.6(−2) − 2.9(0) | | |
| Allyl alcohol | 8.7(−15) − 1.7(−9) | 1.4(−4) − 1.0(−2) | [1.2(−10)] |
| Propargyl alcohol | 6.4(−15) − 1.3(−11) | 5.5(−17) − 1.6(−5) | 1.9(−2) − 4.45(2) | [1.7(−10)] | [4.1(−10)] |
| Glycolaldehyde | 6.6(−14) − 1.7(−8) | 1.2(−13) − 4.4(−9) | 9.7(−2) − 7.4(3) | [2.6(−8)] | [4.0 ± 0.5(−8)] | [1.0(−7)] |
| Ethylene glycol | 4.6(−13) − 5.5(−9) | 3.5(−11) − 1.4(−8) | 1.90(0) − 7.7(1) | [8.0(−8)] | [≤2.3(−9)] |
| Methyl formate | 2.3(−11) − 1.3(−6) | 3.5(−9) − 1.5(−7) | 1.2(−1) − 1.5(2) | [2.6(−9)] | [7.7(−8)] | [9.5(−8)] | [6.7 ± 0.5(−8)] | [1.4(−7)] |

Note.

G31 observation: Gorai et al. (2021); used ALMA with $\theta_{b} = 0".98−1".19$ and $N_{H_2} = 1.53 \times 10^{25}$ cm$^{-2}$; Rivilla et al. (2017); used SMA with $\theta_{b} = 0".75−3".05$ and $N_{H_2} = 1.2 \times 10^{26}$ cm$^{-2}$; Nommelin et al. (1998); used SEST and IRAM with $\theta_{b} = 10"$ and $N_{H_2} = 1.6 \times 10^{23}$ cm$^{-2}$; Sgr B2 observation: Belloche et al. (2014); used ALMA with $\theta_{b} = 1".2−1".9$ and $N_{H_2} = 5.6 \times 10^{24}$ cm$^{-2}$; Belloche et al. (2014); used SMA with $\theta_{b} = 1".2−1".9$ and $N_{H_2} = 2.0 \times 10^{24}$ cm$^{-2}$; Favre et al. (2011); Belloche et al. (2014); used SMA with $1".29−2".0$ and $N_{H_2} = 2.0 \times 10^{24}$ cm$^{-2}$; Favre et al. (2011). G10 observation: This work (used ALMA with $\theta_{b} = 1".39−2".44$ and $N_{H_2} = 1.35 \times 10^{25}$ cm$^{-2}$); Rolfs et al. (2011); used SMA with $\theta_{b} = 3".28−4".27$ and $N_{H_2} = 5 \times 10^{24}$ cm$^{-2}$; Dickens et al. (2001); used SERT and NRAO for possible detection of propenal and upper limit for vinyl alcohol with $\theta_{b} = 45"$ and $N_{H_2} = 10^{23}$ cm$^{-2}$.

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Figure C3 suggests that the methanol is more compact. So, as expected, with the higher spatial resolution, Rolffs et al. (2011) could trace the more inner region of the G10; thus, they obtained a higher abundance than us. Furthermore, for deriving the abundances from Rolffs et al. (2011), a hydrogen column density of $5 \times 10^{24}$ cm$^{-2}$ is used. In contrast, our abundance is derived by considering $1.35 \times 10^{25}$ cm$^{-2}$ (Gorai et al. 2020), which might also create significant variation. Since our chemical model does not consider the spatial variation of the abundances, explaining the observed ratio with the suitable beam size is also outside the scope of this work.

The observed ratio is calculated from the observed pair from the same source (if available). It shows that the methanol-to-methanol abundance ratio in these sources can vary between 2.95 and 23.8, whereas our calculated methanol-to-methanol ratio varies between 10 and 53. The observed ratio of ethanol to ethanol varies between 5 and 261, whereas our model results show it ranges between 0.08 and 25,600. The observed ethylene glycol–to–glycolaldehyde ratio varies between 1.3 and 37, whereas our model derives 0.019–445. The observed ratio of vinyl alcohol to ethenone is 0.021, whereas our chemical model estimates 1.78–77. In brief, the observed ratio of three alcohol–aldehyde pairs (methanol–methanol, ethanol–ethanol, and glycolaldehyde–ethylene glycol) is $>1$ in G10, G31, Sgr B2(N), and Orion KL. Thus, in the high-mass star-forming regions, the abundances of these alcohols are generally higher than their respective aldehydes. Our estimated molecular ratios for these alcohol–aldehyde pairs are similar to the observed values in the temperature range 12–18 K (see Figure 6). However, in the case of vinyl alcohol to ethenone, the observed abundance ratio could not be explained. It could be because of the consideration of the upper limit of the vinyl alcohol observation from the single-dish observation of Dickens et al. (2001) for deriving the molecular ratio. A little ambiguity between our obtained ratio of dimethyl ether (DE) and methyl formate (MF) is obtained. Here DE/MF $< 1$ is received from our observational analysis, whereas Rolffs et al. (2011) noted it as $>1$ for the same source. Also, in other high-mass sources, the ratio is $>1$ (4.5 for Sgr B2, 2 for G31, and 2.5 for Orion KL). Our modeling results find that the ratio of DE to MF can vary between 0.12 and 152.

5. Conclusions

Here our CMMC model, coupled with the observational study, is used to explain the abundance of some interstellar aldehydes, ketone, and ketene, along with their corresponding alcohols. It is noticed that there is both observational and theoretical evidence for the production of alcohols via hydrogenation of precursor aldehydes, ketones, and ketenes. The following are the main highlights of this paper.

1. Various aldehydes, alcohols, and a ketene are identified in G10. Among them, ethylene glycol and propanal are detected for the first time in G10, and glycolaldehyde is tentatively detected.

2. The column densities and fractional abundances of the observed molecules are estimated assuming LTE conditions. The kinetic temperatures of the gas are also evaluated, which vary from 72 to 234 K.

3. The spatial distributions of the observed species are investigated, and their zeroth-order moment maps and emitting regions are provided. However, molecular emissions are not well spatially resolved or, at best, marginally resolved to an extent. Thus, we need high angular resolution data to understand their detailed distributions in G10.

4. Successive hydrogenation reactions can lead to the formation of alcohol starting from the aldehyde/ketone/ketene. Extensive quantum chemical calculations are carried out to yield the TS of some of these reactions. The first step of the hydrogen addition reactions has an activation barrier, whereas the second step could be considered barrierless radical–radical reactions. Our higher-level (CCSD(T)/aug-cc-pVTZ) ice-phase calculations depict the first step of the hydrogenation reaction at the carbon atom position for all pairs (except acetone–isopropanol) and are comparatively more favorable than the oxygen atom position. In the acetone–isopropanol pair, an actual TS could not be obtained for the hydrogenation to the carbon atom position. However, the lower-level calculation (DFT-B3LYP/6-31+G(d,p)) in the ice phase shows the same trend.

5. The BEs of these species are computed with various substrates, such as H$_2$O, CH$_3$OH, and CO. For most cases, the BE of alcohols is found to be greater than that of the corresponding aldehyde/ketone/ketene. On average, the computed BE with the CH$_3$OH monomer is found to be $\sim 1.16$ times higher, and with the CO monomer, it is $\sim 2.85$ times lower than that of the water monomer. These new sets of BEs will help in understanding the chemical complexity, where CO and CH$_3$OH will also efficiently cover the icy mantle. The BEs of the species reported in this study for the alcohol, aldehyde, ketone, and ketene is a little bit on the higher side ($\sim 3000$ K) with the H$_2$O c-tetramer configuration. Comparatively, a higher surface temperature is needed to transfer these surface species in the gas phase. Such a high temperature is usually achieved deep inside the cloud in the hot-core stage. If the grain surface pathways are the only deriving route, then species with lower BE are expected to have more extended emission than species with relatively higher BE. Since our observed beam size is large, it is not possible to spatially resolve the inner region and comment on the dependency between the BE and size of the emitting region.

6. Our CMMC model with the shorter collapsing timescale ($\sim 10^{5}$ yr) was able to reproduce the observed abundance and ratio between various species.

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Software: Gaussian 09 (Frisch et al. 2013), CASA 4.7.2 (McMullin et al. 2007), CASSIS (Vastel et al. 2015).

Appendix A
Emitting Diameter

The emitting diameter of each transition of the observed molecules is shown in Table A1. Here the average emitting diameter refers to the average source size. Two-dimensional Gaussian fittings of a region (the area enclosing a 50% line peak) of the moment map image are performed. After averaging the semiminor and semimajor axes, the emission region’s diameters are obtained.

Table A1
Emitting Diameter of Each Transition of Observed Species toward G10

| Species               | $J_{K_a}K_a$ - $J_{K_a}K_a'$ | Frequency (GHz) | $E_u$ (K) | Emitting Diameter (Average) $\theta_e$ |
|-----------------------|-------------------------------|----------------|----------|----------------------------------------|
| Methanol (CH3OH)      | 110,11 - 111,11, E, $v_t = 0$ | 154.425832     | 166.1    | 1.81                                   |
| Ethylene glycol (g-HOCH2CHO) | 88,8 - 7,5, 1-0            | 153.567383     | 25.4     | 1.83                                   |
| Acetaldehyde (CH3CHO) | 81,5 - 7,5, A                | 154.2746864    | 53.7     | 1.49                                   |
| Propanal (CH3CH2CHO)  | 92,2 - 9,3, A                | 148.05042      | 49.6     | 1.18                                   |
| Glycolaldehyde (HOCH2CHO) | 153,597995     | 60.5           | 1.26     |
| Acetone (CH3COCH3)    | 112,11 - 111,10, AA          | 153.927999     | 44.1     | 1.28                                   |
| Methyl formate (CH3OCHO) | 112,10 - 102,9, A           | 153.016790     | 40.7     | 1.87                                   |

Note. Optically thick.
Appendix B

Observed Spectra toward G10

The observed, fitted, and LTE spectra of the observed transitions are shown in Figure B1.

Figure B1. The observed spectra (solid black lines), the fitted Gaussian profile (solid green lines), and the LTE synthetic spectrum with our derived parameters (rotation temperature and column density) from the rotation diagram analysis (solid blue lines) are shown. For the LTE calculation, a source size of 2'' and an average FWHM obtained from the Gaussian fitting (noted in Table 1) of each species are used. The dashed red line shows the systematic velocity ($V_{LSR}$) of the source at $\sim$68 km s$^{-1}$. In addition, the name of the species, their respective transitions (in GHz), and the optical depth of each transition are given in each panel. The optical depths of all transitions are calculated based on the parameters assumed during LTE modeling. The last two transitions of methanol are optically thick and largely overproduced with the LTE consideration. The intensity of all of the transitions of dimethyl ether is underproduced, possibly because of our overestimated FWHM for dimethyl ether.
Appendix C

Line Maps

The integrated intensity distribution of all observed molecules is shown in Figures C1–C4. The integrated intensity is obtained in the velocity range where the emission line is seen. It is typically obtained between 58 and 78 km s$^{-1}$. This range slightly varies for some species. Figures C1 and C2 show the intensity distribution of the observed molecules with an upper energy state of $<100$ K, and Figures C3 and C4 show the intensity distribution for the molecules with an upper energy state of $>100$ K.

Figure C1. Integrated emission maps of observed transitions with an upper energy state of less than 100 K. The name of the molecule and its respective transition (in GHz) and upper energy state (in K) are given in each panel. The contours are shown at 20%, 50%, and 80% of maximum flux. The observed beam is shown in the lower left corner of each figure. Three black crosses indicate the position of three HII regions B1, B2 and A (Cesaroni et al. 2010).
Figure C2. Same as Figure C1.
Figure C3. Integrated emission maps of observed transitions with an upper energy state of greater than 100 K. The contours are shown at 20%, 50%, and 80% of maximum flux. The observed beam is shown in the lower left corner of each figure. Three black crosses indicate the position of three HII regions B1, B2 and A (Cesaroni et al. 2010).
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Figure C4. Same as Figure C3.
