Complex Organic Molecules in Taurus Molecular Cloud-1

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Abstract

We have observed the millimeter-wave rotational spectral lines of CH3CHO, H2CCO, cyclopropenone, and H2CO toward the cyanopolyyne peak of Taurus Molecular Cloud-1 (TMC-1 CP). The spectral line profile of CH3CHO is found to reveal a well-separated double peak. It is similar to the line profile of CH3OH, but is much different from those of carbon-chain molecules and C34S. The different line profiles mean different distributions along the line of sight. The similarity of the spectral line profiles between CH3CHO and CH3OH suggests that CH3CHO is mainly formed on dust grains as CH3OH or through gas-phase reactions starting from CH3OH. On the other hand, the spectral line profiles of H2CCO and cyclopropenone are rather similar to those of carbon-chain molecules and C34S, implying their gas-phase productions. H2CO shows a composite spectral line profile reflecting the contributions of both gas-phase and grain-surface productions. In addition, we have detected the spectral lines of CH3CHO and HCOOCH3 toward the methanol peak near TMC-1 CP. We have also tentatively detected one line of (CH3)2O. Considering the chemical youth of TMC-1, the present results indicate that fairly complex organic species have already been formed in the early evolutionary phase of starless cores. TMC-1 is thus recognized as a novel source where formation processes of complex organic molecules can be studied on the basis of the line profiles.

Key words: ISM: abundances – ISM: individual objects (TMC-1) – ISM: molecules

1. Introduction

Recently, we observed the millimeter-wave rotational emission lines of CH3OH toward the representative starless core, the cyanopolyyne peak of TMC-1 (referred to hereafter as TMC-1 CP), at high velocity resolution, and found that their spectral line profiles are much different from those of carbon-chain molecules and C34S (Soma et al. 2015). Spectral line profiles of carbon-chain molecules and C34S observed toward TMC-1 CP show complex features reflecting a complex internal structure of the core (e.g., Hirahara et al. 1992; Langer et al. 1995; Dickens et al. 2001). On the other hand, the CH3OH line has a double-peaked profile separated by 0.5 km s⁻¹, and its total velocity range is slightly wider than those of carbon-chain molecules and C34S. The double-peaked profile is also observed for 13CH3OH, indicating that it is not due to the self-absorption effect. The difference of the line profiles mentioned above indicates that the emitting region of CH3OH is different from that of the other molecules. According to the mapping observations of the CH3OH and C34S lines, their different distributions have indeed been confirmed. In TMC-1 CP, CH3OH is preferentially distributed in the less dense (1–4 × 10⁴ cm⁻³) gas possibly surrounding the dense core traced by carbon-chain molecules and C34S.

Since the gas-phase production of CH3OH is inefficient (Geppert et al. 2006), CH3OH is thought to be produced on dust grains through hydrogenation of CO, as confirmed by the laboratory experiment (Watanabe & Kouchi 2002). CH3OH produced on dust grains seems to be liberated by nonthermal processes, including desorption by surplus reaction energy, desorption by cosmic-ray induced UV radiation, and photodesorption around the cloud peripheries, although it has recently been suggested that the photodesorption of CH3OH is less efficient than previously thought (Bertin et al. 2016; Martín-Doménech et al. 2016). The grain origin of CH3OH was recently supported by the measurement of the 12C/13C ratio (Soma et al. 2015). In contrast, carbon-chain molecules and CS are thought to be produced in a dense core through gas-phase reactions (e.g., Herbst & Leung 1989; Suzuki et al. 1992; Aikawa et al. 2001; Yamamoto 2017). Since TMC-1 CP has a rather complex internal structure and kinematics as mentioned above, the different distributions of molecules produced in the gas-phase reactions and those liberated from dust grains could be disentangled on the basis of the spectral line profile.

CH3OH is the most representative saturated organic molecule formed on dust grains. More complex organic molecules (COMs), such as CH3CHO, HCOOCH3 and (CH3)2O, would also be produced on dust grains. So far, these molecules are widely detected toward hot cores of high-mass star-forming regions (e.g., Blake et al. 1987; Bisschop et al. 2007), and hot corinos of low-mass star-forming regions (e.g., Cazaux et al. 2003; Bottinelli et al. 2004; Sakai et al. 2006; Imai et al. 2016). In these sources, COMs formed on dust grains are sublimated in a hot region near protostars. In addition, COMs are also detected in the outflow-shocked region L1157 B1, where COMs are liberated into the gas phase by sputtering (Arce et al. 2008; Sugimura et al. 2011). On the other hand, COMs have been detected in relatively cold sources. Although CH3CHO is detected in various cold sources (e.g., Matthews et al. 1985; Öberg et al. 2010; Vastel et al. 2014; Potapov et al. 2016), the detection of HCOOCH3 and/or (CH3)2O has been limited to the two starless cores.
L1689B, and L1544 (Bacmann et al. 2012; Jimenez-Serra et al. 2016) and the cold star-forming core B1b (Oberg et al. 2010; Cernicharo et al. 2012). In the cold sources, COMs would probably be liberated by the nonthermal desorption, as in the case of CH$_3$OH detected in TMC-1 CP. Alternatively, COMs may be formed through gas-phase reactions starting from CH$_3$OH (Vasyunin & Herbst 2013; Balucani et al. 2015). The detections of COMs in L1689B and L1544 suggest that more COMs besides CH$_3$OH could also be found in TMC-1 CP and their line profile would be similar to that observed for CH$_3$OH. In other words, we can study the formation mechanisms of COMs in TMC-1 CP on the basis of their line profile without extensive mapping observations of the faint lines. Although CH$_3$CHO was detected in TMC-1 CP (Matthews et al. 1985; Kaifu et al. 2004), its line profile was not well resolved. With these in mind, we conducted sensitive observations of several COMs and their related species at a high velocity resolution.

2. Observations

Observations in the 40 GHz band were carried out with the Robert C. Byrd Green Bank Telescope of the National Radio Astronomy Observatory in 2013 April and 2014 September. We employed the Q-band receiver, whose simultaneous bandwidth is 4 GHz. The system noise temperature typically ranged from 85 to 120 K toward the source. The beam size and the beam efficiency of the telescope were 16" and 0.70, respectively. The pointing of the telescope was checked by observing nearby continuum sources every hour, and was maintained to be better than 5". The frequency-switching mode with a frequency offset of ±2.5 MHz was employed for the observations. The back end was a bank of autocorrelators, whose bandwidth and frequency resolution were 12.5 MHz and 3 kHz, respectively. The frequency resolution corresponds to a velocity resolution of 0.019 km s$^{-1}$ at 47.2 GHz. The intensity scale was calibrated by noise injection.

Observations in the 70 GHz band were conducted with the Nobeyama 45 m telescope. We employed the T70 receiver, whose system noise temperature was 200–300 K depending on the frequency. The beam size and the beam efficiency of the telescope were 20" and 0.4, respectively. The pointing of the telescope was checked by observing nearby SiO maser source (NML Tau) every hour, and was maintained to be better than 7". The position-switching mode was used for the observations, where the offset was taken as ($\alpha_\text{2000}$, $\delta_\text{2000}$) = (04h42m35s92, 25°53′23″34′′) (Soma et al. 2015). The back end was the autocorrelator SAM4S, whose frequency resolution was set to be 30.52 kHz. This frequency resolution corresponds to a velocity resolution of 0.13 km s$^{-1}$ at 70 GHz.

Observations in the 140 GHz band were carried out with the IRAM 30 m telescope at Pico Veleta in 2011 April. The SIS receiver, EMIR, was used as a front end, whose system noise temperature ranged from 100 to 200 K. The beam size and the main beam efficiency of the telescope were 17" and 0.80 at 145.1 GHz, respectively. The telescope pointing was checked every hour by observing nearby continuum sources, and was maintained to be better than 4". The autocorrelator VESPA was used as a back end. We set the individual bandwidth and resolution to be 20 MHz and 20 kHz, respectively. The frequency resolution corresponds to a velocity resolution of 0.04 km s$^{-1}$ at 140 GHz. The frequency-switching mode was used for the observation.

We observed the spectral lines listed in Table 1 toward TMC-1 CP (($\alpha_\text{2000}$, $\delta_\text{2000}$) = (04h41m42s88, 25°41′27.7″)) and the CH$_3$OH peak of TMC-1 (referred to hereafter as TMC-1 MP). TMC-1 MP is apart from TMC-1 CP by 2: ($\alpha_\text{2000}$, $\delta_\text{2000}$) = (04h41m38.6′2, 25°42′09.8″). Note that no infrared sources are associated with TMC-1 CP and TMC-1 MP. In all the observations, the two orthogonal polarization signals were averaged to improve the signal-to-noise ratio.

3. Results for TMC-1 CP

We detected the lines of CH$_3$CHO, H$_2$CCO, cyclopropenone (c-C$_2$H$_3$O), H$_2$CO, C$^{34}$S, CCS, and HC$_2$N in our observation. Figure 1 shows the line profiles detected toward TMC-1 CP, which are compared with the CH$_3$OH line profile. The line parameters are summarized in Table 2. The line profiles of C$^{34}$S, CCS, and HC$_2$N are narrower than that of CH$_3$OH, and have complicated velocity structures, as reported by Soma et al. (2015). This indicates that the spatial distributions of C$^{34}$S, CCS, and HC$_2$N are different from that of CH$_3$OH. In the following subsections, we describe the result for CH$_3$CHO, H$_2$CCO, cyclopropenone, and H$_2$CO.

3.1. CH$_3$CHO

Toward TMC-1 CP, we detected the 2$_{02}$–1$_{01}$ (A and E), and 2$_{11}$–1$_{00}$ (E) lines of CH$_3$CHO at 38.5 GHz and 39.4 GHz, respectively. Their spectral line profiles show a well-separated double-peak structure, and hence, they are fitted to the double-Gaussian function to derive the line parameters for the blueshifted and redshifted components. The results are shown in Table 2. The spectral line profiles are similar to that of CH$_3$OH, and are different from those of C$^{34}$S, CCS, and HC$_2$N, as shown in Figure 1. The separation of two peaks of CH$_3$CHO is 0.49 km s$^{-1}$ on average. The separation is similar to that of CH$_3$OH (0.46 km s$^{-1}$), while it is, for example, different from that of HC$_2$N (0.20 km s$^{-1}$). On the other hand, the velocity widths of the two components of the double-peak structure are slightly narrower for CH$_3$CHO (0.25 km s$^{-1}$ and 0.1 km s$^{-1}$ on average for the red and blueshifted components, respectively) than for CH$_3$OH (0.30 km s$^{-1}$ and 0.26 km s$^{-1}$ for the red and blueshifted components, respectively). Hence, the emission is very faint at the intermediate velocity around 5.8 km s$^{-1}$ between the two peaks, and thus the two components are well-separated. Regardless of the difference of the line width, similarity of the spectral line shapes between CH$_3$CHO and CH$_3$OH indicates their spatial coexistence. We note that the slightly narrower line width of each component for CH$_3$CHO may mean more compact distribution than that of CH$_3$OH. The similar line profile to CH$_3$OH suggests that CH$_3$CHO is formed on dust grains and is liberated into the gas phase through nonthermal desorption mechanisms as CH$_3$OH. Alternatively, CH$_3$CHO may be formed from CH$_3$OH through gas-phase processes (Johnson et al. 2000).

In TMC-1 CP, CH$_3$CHO was first detected by Matthews et al. (1985). Kaifu et al. (2004) also detected the CH$_3$CHO lines in the spectral line survey toward TMC-1 CP. However, the spectral resolution in these observations was not high enough to reveal the above characteristic line profiles, although the observed line widths look slightly broad. The present high spectral resolution observation allowed us to reveal that the line shape of CH$_3$CHO is different from the rest of the other molecules.
3.2. H$_2$C$\text{CO}$ and Cyclopropenone

In grain-surface chemistry, it is proposed that CH$_3$CHO is formed as an intermediate species during sequential hydrogenation of H$_2$CCO: H$_2$CCO $\rightarrow$ H$_2$C$\text{CO}$ $\rightarrow$ CH$_3$CHO $\rightarrow$ C$_2$H$_4$O $\rightarrow$ C$_2$H$_5$OH (e.g., Herbst & van Dishoeck 2009). If this mechanism is the case, H$_2$CCO should also exist on dust grains as a parent molecule forming CH$_3$CHO. With this in mind, we also observed H$_2$CCO in TMC-1 CP.

We detected the 4$_{03}$--3$_{03}$ (para) and 4$_{13}$--3$_{12}$ (ortho) lines of H$_2$CCO in the 81 GHz region. As shown in Figure 1, the spectral line profile of H$_2$CCO looks slightly different from those of CH$_3$OH and CH$_3$CHO. Although it shows a double-peaked structure, the two components are substantially blended. The separation of the two components evaluated by the double Gaussian fitting is 0.37 km s$^{-1}$ for the ortho lines and 0.35 km s$^{-1}$ for the para line. These values are smaller than that of CH$_3$OH (0.49 km s$^{-1}$).

The overall line shape is rather similar to those of C$^{34}$S and CCS, indicating that the distribution of H$_2$CCO would resemble those of CCS and C$^{34}$S. A similarity of the line shape of H$_2$CCO to those of C$^{34}$S and CCS is also confirmed at TMC-1 MP, as described in Section 4.1. CS and CCS are thought to be produced by the gas-phase processes (e.g., Aikawa et al. 2001; Suzuki et al. 1999). Actually, the distribution of C$^{34}$S is much different from that of the dust-origin species, CH$_3$OH, as reported in Soma et al. (2015). Hence, these results imply that H$_2$CCO would also be formed mainly through gas-phase reactions in TMC-1 CP, as Irvine et al. (1989) suggested on the basis of the chemical model calculation by Herbst & Leung (1986).

In addition to H$_2$CCO, we detected the 3$_{13}$--2$_{12}$ line of cyclopropenone (c-C$_3$H$_2$O). Its spectral line profile is found to be blueshifted by $\sim$0.3 km s$^{-1}$. This shift corresponds to the frequency shift of 40 kHz, and probably originates from insufficient accuracy of the rest frequency, because the uncertainty of this transition is as large as 30 kHz according to CDMS (Müller et al. 2005). Apart from this overall velocity shift, the spectral line profile of cyclopropenone has three (or more) velocity components and resembles those of C$^{34}$S and CCS. Hence, its production would not be related directly to CH$_3$OH and CH$_3$CHO. According to Herbst & van Dishoeck (2009), this molecule is also thought to be produced on dust grains. However, the observed spectral profile suggests that this molecule is mainly produced through gas-phase processes in TMC-1 CP, as in the case of CS and CCS. Recently, Loison et al. (2016) conducted the survey observations of cyclopropenone and propynal (HCCCHO) toward several starless cores including TMC-1, and argued the gas-phase production of these molecules. Their conclusion is consistent with ours. Since the line profile is complicated, only the integrated intensity is given for the cyclopropenone line in Table 2.

### Table 1

| Molecule | Transition | Frequency (MHz)$^a$ | $E_{\text{up}}$ (K) | $S_{ij}/\mu$ (Debye)$^c$ | Observations$^d$ |
|----------|------------|-------------------|-------------------|-------------------|-----------------|
| H$_2$CO$^e$ | 1$_{01}$--0$_{00}$ | 72837.948(10) | 3.5 | 5.44 | CP |
| CH$_3$OH$^f$ | 1$_{01}$--0$_{00}$ A$^i$ | 48373.457(70) | 2.3 | 0.809 | CP, MP |
| H$_2$CCO$^g$ | 1$_{01}$--0$_{00}$ | 48376.892(10) | 15$^h$ | 0.808 | MP |
| CH$_3$CHO$^h$ | 2$_{01}$--1$_{01}$ A | 38206.0348(13) | 2.9 | 4.03 | MP |
| HCOOCH$_3$ | 4$_{02}$--3$_{02}$ | 47534.09(50) | 5.8 | 10.5 | CP |
| H$_2$CO | 4$_{02}$--3$_{02}$ | 47536.01(50) | 5.8 | 10.5 | CP |
| H$_2$CO | 4$_{14}$--3$_{13}$ | 45395.79(50) | 6.1 | 9.95 | MP |
| H$_2$CO | 4$_{14}$--3$_{13}$ | 45397.38(50) | 6.1 | 9.95 | MP |
| (CH$_3$)$_2$O$^i$ | 1$_{01}$--0$_{00}$ EE | 47674.9576(47) | 2.3 | 27.1 | MP |
| c-C$_3$H$_2$O (Cyclopropenone)$^j$ | 3$_{13}$--2$_{12}$ | 39956.70(30) | 5.0 | 154 | CP |
| C$^{34}$S$^k$ | 1 -- 0 | 48206.940(20) | 2.3 | 3.83 | CP, MP |
| C$^{34}$S$^k$ | 2 -- 1 | 96412.995(22) | 6.9 | 1.34 | MP |
| CCS$^l$ | 3$_{13}$ | 38866.420(25) | 12 | 337 | MP |
| HCN$^l$ | 18 -- 17 | 47927.2746(20) | 22 | 953 | CP |
| HCN$^l$ | 41 -- 40 | 46246.9780(11) | 47 | 0.809 | CP |

Notes.

$^a$ The error denotes one standard deviation in units of the last significant digits.

$^b$ Observed position: CP: Cyanopolyne peak; MP: Methanol peak. See the text.

$^c$ Taken from CDMS (Müller et al. 2005).

$^d$ Measured from the 0$_{00}$ level of the A state. $E_{\text{up}}$ is 7.5 K, if it is measured from the lowest E state (1$_{11}$).

$^e$ Taken from JPL (http://spec.jpl.nasa.gov/ftp/pub/catalog/catalogdir.html).

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3.3. H$_2$CO

We observed the 1$_{01}$--0$_{00}$ and 2$_{02}$--1$_{01}$ lines of para-H$_2$CO. Their line profiles are apparently broader than that of HC$_2$N, as shown in Figure 1. The apparent width of the H$_2$CO line, especially that of the skirt part, is comparable to that of CH$_3$OH. On the other hand, two peaks are only marginally separated, and the central dip is not as clear as in the case of CH$_3$OH. Since the line profile is complicated, only the integrated intensity is given.
for the H$_2$CO lines in Table 2. Relative intensities of the blueshifted and redshifted components are different between the two lines of H$_2$CO. The blueshifted component is relatively weak in the $^2_{02-1_{01}}$ emission. According to the CH$_3$OH observation (Soma et al. 2015), the H$_2$ densities of the blueshifted and redshifted components are $(1.7 \pm 0.5) \times 10^4$ cm$^{-3}$ and $(4.3 \pm 1.2) \times 10^4$ cm$^{-3}$, respectively. Since the critical densities of the $1_{01}-0_{00}$ and $(2_{02}-1_{01})$ lines of H$_2$CO are $1.5 \times 10^5$ cm$^{-3}$ and $5.2 \times 10^5$ cm$^{-3}$, respectively, according to the Einstein coefficients and the collisional cross sections.

Figure 1. Line profiles observed toward TMC-1 CP. The spectrum of the CH$_3$OH $1_{01}-0_{00}$ line is overlaid on the spectra of the other species (gray). The horizontal bars represent the uncertainties of the rest frequencies.

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Table 2

| Molecule | Transition | $T_{MB}$ (K) | $\Delta V$ (km s$^{-1}$) | $V_{LSR}$ (km s$^{-1}$) | $\int T_{MB}dv$ (K km s$^{-1}$) | Res. $^b$ (km s$^{-1}$) | rms $^c$ (K) |
|----------|------------|--------------|-------------------------|-------------------------|-----------------------------|--------------------------|-------------|
| CH$_3$OH$^d$ | $1_01$--$0_0$ A$^+$ | blue | 0.702(36) | 0.298(3) | 5.622(1) | 0.365(2)$^e$ | 0.019 | 0.014 |
| | | red | 0.491(25) | 0.263(4) | 6.085(2) |
| CH$_3$CHO$^i$ | $2_{02}$--$1_{01}$ E | blue | 0.080(24) | 0.255(89) | 5.607(38) | 0.043(8)$^e$ | 0.048 | 0.042 |
| | | red | 0.201(47) | 0.083(24) | 6.128(8) |
| | $2_{01}$--$1_{01}$ A | blue | 0.096(27) | 0.235(75) | 5.691(32) | 0.048(7)$^e$ | 0.048 | 0.035 |
| | | red | 0.160(46) | 0.076(3) | 6.188(12) |
| | $2_{11}$--$0_{10}$ E | blue | 0.042(5) | 0.258(32) | 5.636(14) | 0.022(1)$^e$ | 0.046 | 0.006 |
| | | red | 0.054(7) | 0.142(18) | 6.079(8) |
| (CH$_3$)$_2$O$^j$ | $5_{14}$--$5_{05}$ EE | blue | 0.054(7) | 0.142(18) | 6.079(8) | <0.003 | <0.003 |
| H$_2$CO | $1_{01}$--$0_{00}$ | blue | 0.952(21)$^f$ | 0.063 | 0.106 |
| | $2_{02}$--$1_{01}$ | red | 0.346(4)$^f$ | 0.040 | 0.029 |
| c-C$_3$H$_2$O | $3_{12}$--$2_{12}$ | blue | 0.022(1)$^f$ | 0.046 | 0.007 |
| H$_2$CCO$^d$ | $4_{04}$--$3_{03}$ | red | 0.151(18) | 0.363(84) | 5.913(34) | 0.104(7)$^e$ | 0.113 | 0.026 |
| | | blue | 0.161(27) | 0.202(46) | 5.567(23) |
| | $4_{13}$--$3_{12}$ | red | 0.205(32) | 0.197(45) | 6.039(20) | 0.142(9)$^e$ | 0.112 | 0.035 |
| | | blue | 0.290(27) | 0.297(40) | 5.678(16) |
| C$^{34}$S | 1--0 | red | 0.475(25)$^f$ | 0.019 | 0.026 |
| | | blue | 0.479(3)$^f$ | 0.061 | 0.023 |
| CCS | $3_{12}$--$2_{12}$ | red | 0.335(13)$^f$ | 0.047 | 0.085 |
| | | blue | 0.208(8) | 0.208(15) | 5.981(8) | 0.031(1)$^e$ | 0.020 | 0.015 |
| HC$_5$N$^j$ | 41--40 | red | 0.111(8) | 0.143(15) | 5.783(6) | 0.031(1)$^e$ | 0.020 | 0.015 |

Notes.

$^a$ The numbers in parentheses represent one standard deviation in units of the last significant digits. The uncertainties for $T_{MB}$, $\Delta V$, and $V_{LSR}$ are derived from the Gaussian fitting. The uncertainties of the integrated intensities, $\Delta S$, are calculated as $\Delta S = (\Delta T_{MB}/\sqrt{N})\Delta V$, where $\Delta T_{MB}$ represents the rms noise per spectral resolution and $N$ the number of spectrum resolution channels over the line width ($\Delta V$).

$^b$ Velocity resolution of the spectrum shown in Figure 1.

$^c$ rms noise per spectral resolution shown in Figure 1.

$^d$ Line parameters are obtained by a Gaussian fit.

$^e$ Total integrated intensity for the red and blue components.

$^f$ Lines are not detected. The upper limits correspond to a $3\sigma$ detection level. Line widths are estimated by using those of CH$_3$CHO lines.

$^g$ Since the line profile is complicated, only the integrated intensity is given.

(LAMDA: Schöier et al. 2005; Wisenfeld & Faure 2013), the two lines are subthermally excited. Hence, the higher excitation line ($2_{02}$--$1_{01}$) of H$_2$CO becomes weaker for the blueshifted component because of the slightly lower H$_2$ density. The lack of a clear central dip may suggest that the H$_2$CO lines are optically thick. Alternatively, the dense core component, which is traced by the spectral lines of C$^{34}$S, CCS, and HC$_5$N, may fill up the dip structure. Actually, the peak positions of the two velocity components coincide with the outer two of the three velocity components in the C$^{34}$S ($J = 1$--0) and CCS lines. Above all, the spectral line profiles of H$_2$CO may suggest the mixed characteristics of the gas-phase and dust-grain origins. The partial contribution of the gas-phase production seems reasonable, because H$_2$CO can be formed, for instance, through ion-molecule reactions such as

$$\text{CH}_3^+ + O \rightarrow \text{CH}_2O^+ + H \quad (1)$$

$$\text{CH}_2O^+ + H_2 \rightarrow \text{CH}_2OH^+ + H \quad (2)$$

$$\text{CH}_2OH^+ + e^- \rightarrow \text{H}_2\text{CO} + H. \quad (3)$$

Protonated H$_2$CO (CH$_2$OH$^+$) was recently detected in the starless core L1689B (Bacmann et al. 2016). Its detection in TMC-1 CP will give a constraint on the contribution of the gas-phase production.

4. Results for TMC-1 CP

Following the above results in TMC-1 CP, we searched for more complex organic species such as HCOOCH$_3$ and (CH$_3$)$_2$O in TMC-1 MP, because the CH$_3$OH emission is brighter by a factor of 2 in the CH$_3$OH peak than in TMC-1 CP. This position is based on the mapping observations of CH$_3$OH (Soma et al. 2015). As mentioned in Section 2, no infrared source is associated with TMC-1 MP.

The lines observed toward TMC-1 MP are listed in Table 1. We successfully detected the CH$_3$CHO, H$_2$CCO, HCOOCH$_3$, and (CH$_3$)$_2$O lines in addition to the CH$_3$OH, C$^{34}$S, CCS, and HC$_5$N lines. Here the detection of (CH$_3$)$_2$O is tentative. Figures 2 and 3 show the line profiles for TMC-1 MP. The line parameters are summarized in Table 3. As in the case of TMC-1 CP, the overall line profiles of C$^{34}$S, CCS, and HC$_5$N are narrower than that of CH$_3$OH. The two peaks of the CH$_3$OH line have a wider separation than the line width of C$^{34}$S, CCS, and HC$_5$N, the redshifted component being brighter than the blueshifted component. In the following subsections, we describe the results of CH$_3$CHO, H$_2$CCO, HCOOCH$_3$, and (CH$_3$)$_2$O.

4.1. CH$_3$CHO

Toward TMC-1 MP, we clearly detected the spectral line ($2_{11}$--$0_{10}$ E) of CH$_3$CHO. Its spectral line profile is similar to that of the CH$_3$OH line, but is significantly different from those of
the CCS and HC$_3$N lines. The CH$_3$CHO line is brighter by a factor of 2 than that in TMC-1 CP. As in the case of TMC-1 CP, the velocity widths of the two components (0.20 km s$^{-1}$ and 0.18 km s$^{-1}$ for the red and blueshifted components, respectively) are slightly narrower than those for the CH$_3$OH A$^1$ transition (0.30 km s$^{-1}$ and 0.23 km s$^{-1}$ for the red- and blueshifted components, respectively). However, it is comparable to those of the CH$_3$OH E transition (0.18 km s$^{-1}$ and 0.15 km s$^{-1}$ for the red and blueshifted components, respectively), whose upper state energy is higher than that of the A$^1$ species. The similarity of the line shapes between CH$_3$OH and CH$_3$CHO in TMC-1 MP further suggests the dust-grain origin of these molecules: CH$_3$CHO is formed on dust grains as in the case of CH$_3$OH or through gas-phase reactions driven by CH$_3$OH released from dust grains. The spectral lines are fitted to the double-Gaussian function to obtain the line parameter for the blueshifted and redshifted components separately. The result is shown in Table 3.

4.2. H$_2$CCO

We detected the H$_2$CCO line in TMC-1 MP, as in the case of TMC-1 CP. The H$_2$CCO line shows a double-peaked line profile, where the velocity difference between the two components (0.33 km s$^{-1}$) is slightly smaller than those for CH$_3$OH (0.36 km s$^{-1}$ on average) and CH$_3$CHO (0.41 km s$^{-1}$). Moreover, the blueshifted component is brighter than the redshifted component for H$_2$CCO, which is opposite to the CH$_3$OH and CH$_3$CHO cases, and is rather similar to the C$_3$S and CCS cases. Although we marginally identify the difference of the line shape between CH$_3$OH/CH$_3$CHO and H$_2$CCO in TMC-1 CP, the difference can be confirmed in TMC-1 MP. Since the line profile of H$_2$CCO is similar to those of C$_3$S and CCS, the gas-phase reactions seem to play an important role in the production of H$_2$CCO.

4.3. HCOOCH$_3$ and (CH$_3$)$_2$O

Since the CH$_3$CHO line was detected with moderate intensity, we searched for the spectral lines of more complex species, HCOOCH$_3$ and (CH$_3$)$_2$O, toward TMC-1 MP. As shown in Figure 3, we detected the four lines of HCOOCH$_3$, although each detection is at the (9−15)$\sigma$ confidence level in integrated intensity (\textit{\textbf{TS$_{MB}$dv}}). The line parameters of HCOOCH$_3$ are obtained by the Gaussian fitting, and are summarized in Table 3. The spectral line profiles of the three lines (4$_{04}$−4$_{03}$ A, 4$_{14}$−3$_{13}$ A, and 4$_{14}$−3$_{13}$ E) are similar to one another, where only the redshifted velocity component (∼5.9 km s$^{-1}$) of the double-peaked feature of the CH$_3$OH lines is seen. Note that the 4$_{04}$−3$_{03}$ E line has been detected at a slightly different velocity (velocity shift of ∼0.15 km s$^{-1}$). However, the difference (∼24 kHz) is smaller than the uncertainty of the rest frequency (50 kHz), and hence the 4$_{04}$−3$_{03}$ E line is likely detected.

The spectral line profile of HCOOCH$_3$ is peculiar, which only shows the redshifted velocity component out of the two components seen in the CH$_3$OH and CH$_3$CHO lines. This result does not necessarily mean that HCOOCH$_3$ preferentially exists in the redshifted component, but may originate from some excitation effects. The redshifted and blueshifted components in TMC-1 MP are physically related to the corresponding redshifted and blueshifted components in TMC-1 CP, respectively (Soma et al. 2015). The redshifted component is denser than the blueshifted component in TMC-1 CP, and this trend is also true in TMC-1 MP, as shown later (Section 4.4). Although the collisional cross sections of this molecule are not available for all the rotational levels, that for the 2$_{02}$ level is reported by Faure et al. (2014). By employing this value, we roughly estimated the critical density of the
observed lines to be $3 \times 10^4$ cm$^{-3}$. This value is almost comparable to or higher than the H$_2$ density of the blueshifted component (see Section 4.4), and hence, only the redshifted component could be detected due to the excitation effect in the limited signal-to-noise ratio. Detection of the three (or possibly four) lines of HCOOCH$_3$ at the velocity of the redshifted velocity component of CH$_3$OH suggests that HCOOCH$_3$ has the dust-grain origin as in the case of CH$_3$OH and CH$_3$CHO.

In addition to HCOOCH$_3$, we tentatively detected the $1_{11}-0_{00}$ EE line of (CH$_3$)$_2$O in TMC-1 MP with the confidence level of 4.8$\sigma$ in integrated intensity ($\int T_{mb} dv$), as shown in Figure 3. Unfortunately, we observed only one line, because the other internal rotation components of this transition, which fall in the observing band are weaker at least by a factor of 2.7. Hence, we still need confirmation observations to claim definitive detection. Nevertheless, the spectral line profile is similar to that observed for the HCOOCH$_3$ lines: only the redshifted component appears. The line parameters are obtained by the Gaussian fitting and are summarized in Table 3.

Recently, the gas-phase production of the COMs including HCOOCH$_3$ and (CH$_3$)$_2$O from CH$_3$OH are proposed (Vasyunin & Herbst 2013; Balucani et al. 2015). If the liberation of CH$_3$OH into the gas phase enhances the gas-phase production of the COMs, the similarity of the line shape of CH$_3$OH with those of HCOOCH$_3$ and (CH$_3$)$_2$O for the redshifted component could also be explained. Even in this case, HCOOCH$_3$ and (CH$_3$)$_2$O have the dust-grain origin in their production indirectly, which is reflected in their distributions (and in their line shapes).

**Figure 3.** Line profiles of HCOOCH$_3$ and (CH$_3$)$_2$O observed toward TMC-1 MP. The spectrum of the CH$_3$OH $1_{01}-0_{00}$ A$^+$ line is overlaid on the spectra of the other species (gray). The horizontal bars represent the uncertainties of the rest frequencies.
### Table 3

| Molecule  | Transition | $T_{	ext{MB}}$ (K) | $\Delta V$ (km s$^{-1}$) | $V_{15}$ (km s$^{-1}$) | $\int T_{	ext{MB}}dv$ (K km s$^{-1}$) | Res. (km s$^{-1}$) | rms (K) |
|-----------|------------|---------------------|--------------------------|------------------------|-------------------------------|-----------------|--------|
| CH$_3$OH  | 1$_{01}$–0$_{00}$ A$^+$ | blue | 0.712(6) | 0.301(4) | 5.604(2) | 0.503(2)$^a$ | 0.004 | 0.030 |
|           |            | red | 1.101(6) | 0.229(2) | 5.967(1) | | | |
|           | 1$_{01}$–0$_{00}$ E | blue | 0.046(6) | 0.175(28) | 5.641(12) | 0.0316(12)$^d$ | 0.018 | 0.015 |
|           |            | red | 0.145(7) | 0.154(8) | 6.007(4) | | | |
| CH$_3$CHO | 2$_{11}$–1$_{01}$ E | blue | 0.097(9) | 0.195(21) | 5.567(9) | 0.034(2)$^d$ | 0.046 | 0.009 |
|           |            | red | 0.136(10) | 0.175(14) | 5.979(6) | | | |
| HCOOCH$_3$| 4$_{02}$–3$_{03}$ A | red | 0.030(5) | 0.220(46) | 5.975(19) | 0.0089(8) | 0.036 | 0.009 |
|           | 4$_{02}$–3$_{03}$ E | red | 0.067(7) | 0.123(25) | 5.850(10) | 0.0056(6) | 0.036 | 0.009 |
|           | 4$_{12}$–3$_{13}$ A | red | 0.043(6) | 0.124(20) | 6.029(9) | 0.0079(5) | 0.038 | 0.008 |
|           | 4$_{12}$–3$_{13}$ E | red | 0.059(6) | 0.095(12) | 5.959(5) | 0.0058(4) | 0.038 | 0.007 |
| (CH$_3$)$_2$O | 1$_{11}$–0$_{00}$ EE | red | 0.028(6) | 0.184(47) | 6.040(20) | 0.0053(11) | 0.072 | 0.010 |
| H$_2$CCO  | 2$_{02}$–1$_{01}$ | red | 0.073(9) | 0.131(19) | 5.988(8) | 0.0433(15)$^d$ | 0.045 | 0.010 |
|           |            | blue | 0.123(6) | 0.226(15) | 5.654(6) | | | |
| C$^{14}$S | 1–0 | red | 0.707(8) | 0.272(7) | 5.902(3) | 0.4137(11)$^d$ | 0.004 | 0.030 |
|           |            | blue | 0.844(6) | 0.223(4) | 5.622(2) | | | |
| CCS       | 3$_{12}$–2$_{11}$ | red | 0.327(24) | 0.151(15) | 5.904(6) | 0.221(4)$^d$ | 0.047 | 0.034 |
|           |            | blue | 0.714(21) | 0.204(9) | 5.645(3) | | | |
| HC$_5$N   | 18–17 | red | 1.298(13) | 0.136(2) | 5.897(1) | 0.5100(14)$^d$ | 0.004 | 0.031 |
|           |            | blue | 1.400(8) | 0.216(3) | 5.700(1) | | | |

**Notes.**

$^a$ The numbers in parentheses represent one standard deviation in units of the last significant digits. The uncertainties of the integrated intensities, $\Delta S$, are calculated as $\Delta S = (\Delta T_{\text{MB}}/\sqrt{N})\Delta V$, where $\Delta T_{\text{MB}}$ represents the rms noise per spectral resolution and $N$ the number of spectral resolution channels over the line width ($\Delta V$).

$^b$ Velocity resolution of the spectrum shown in Figures 2 and 3.

$^c$ rms noise per spectral resolution shown in Figures 2 and 3.

$^d$ Total integrated intensity for the red and blue components.

### Table 4

| Species | Blueshifted Component | Redshifted Component |
|---------|-----------------------|----------------------|
|         | $T_{\text{rot}} = 3.8$ K | 4.8 K | 5.8 K | 4.7 K | 5.7 K | 6.7 K |
| CH$_3$OH A$^a$ | $(1.7 \pm 0.3) \times 10^{13}$ | | | $(9.3 \pm 1.0) \times 10^{12}$ | | |
| CH$_3$OH E$^a$ | $(1.5 \pm 0.3) \times 10^{13}$ | | | $1.0 \times 10^{13}$ | | |
| CH$_3$CHO | $(2.0 \pm 0.3) \times 10^{12}$ | $(1.4 \pm 0.3) \times 10^{12}$ | $(1.3 \pm 0.2) \times 10^{12}$ | $(1.0 \pm 0.2) \times 10^{12}$ | $(9.5 \pm 1.7) \times 10^{11}$ | $(9.5 \pm 1.7) \times 10^{11}$ |
| (CH$_3$)$_2$O$^b$ | $\leq 1.1 \times 10^{13}$ | $\leq 4.6 \times 10^{12}$ | $\leq 3.0 \times 10^{12}$ | $\leq 3.3 \times 10^{12}$ | $\leq 2.1 \times 10^{12}$ | $\leq 1.6 \times 10^{12}$ |
| H$_2$CCO$^b$ | $(1.3 \pm 0.2) \times 10^{13}$ | $(6.9 \pm 1.0) \times 10^{12}$ | $(5.1 \pm 0.7) \times 10^{12}$ | $(4.7 \pm 0.9) \times 10^{12}$ | $(3.4 \pm 0.7) \times 10^{12}$ | $(2.8 \pm 0.6) \times 10^{12}$ |

**Notes.**

$^a$ Column densities reported by Soma et al. (2015).

$^b$ The upper limits are derived by the rms noise ($\leq N$).

$^c$ Blue and redshifted components of this molecule do not exactly correspond to those of CH$_3$OH and CH$_3$CHO (see Figure 1 and Section 3.2).

### 4.4. Physical Conditions of TMC-1 MP

We derive the H$_2$ density from the 1$_{01}$–0$_{00}$ A$^+$ and 1$_{01}$–0$_{00}$ E lines of CH$_3$OH by using the statistical equilibrium calculation (Goldreich & Kwan 1974). We employ the RADEX code (van der Tak et al. 2007) for this purpose, where the gas kinetic temperature is assumed to be a typical value for starless cores (10 K; e.g., Benson & Myers 1989). We also assume the same abundances of the A and E species of CH$_3$OH. The H$_2$ density for the blueshifted and redshifted components are evaluated to be $3.5 \times 10^4$ and $1.6 \times 10^4$ cm$^{-3}$, respectively. These H$_2$ densities are slightly higher than those derived for TMC-1 CP (Soma et al. 2015). The column density of CH$_3$OH is also derived to be $(2.2 \pm 0.6) \times 10^{13}$ and $(4.0 \pm 1.4) \times 10^{13}$ cm$^{-2}$ for the blueshifted and redshifted components of TMC-1 MP, respectively. The total column density is higher by a factor of 1.5 than that derived toward TMC-1 CP (Soma et al. 2015).

### 5. Discussions

#### 5.1. Column Densities

The column densities of the detected COMs are derived from the observed intensities by assuming the local thermodynamic equilibrium (LTE) conditions. When the blueshifted and redshifted components are well separated, they are treated individually. Since we observed only one transition or multiple transitions having the similar upper state energies for the most species, we have to assume the excitation temperature. For CH$_3$CHO in TMC-1 CP, we employ the LTE excitation temperature for the two velocity components of CH$_3$OH reported by Soma et al. (2015); $T_{\text{ex}}$ is 4.8 K and 5.7 K for the blueshifted and redshifted components, respectively. The results are shown in Table 4. Variations of the column densities by a change in the assumed excitation temperature by $\pm 1$ K are also given in Table 4. The upper limits to the column...
The ortho-to-para ratio is assumed to be 3.

respectively.

Note.

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Table 5
Column Densities of CH$_3$CHO, HCOOCH$_3$, (CH$_3$)$_2$O, and H$_2$CCO in TMC-1 MP

| Species     | 4.2 K Column Density (cm$^{-2}$) | 5.2 K Column Density (cm$^{-2}$) | 6.2 K Column Density (cm$^{-2}$) |
|-------------|----------------------------------|----------------------------------|----------------------------------|
| CH$_3$CHO   | blue $(2.8 \pm 0.4) \times 10^{12}$ | $(2.4 \pm 0.3) \times 10^{12}$ | $(2.3 \pm 0.3) \times 10^{12}$ |
|             | red $(3.4 \pm 0.4) \times 10^{12}$ | $(3.1 \pm 0.3) \times 10^{12}$ | $(3.0 \pm 0.3) \times 10^{12}$ |
| HCOOCH$_3$  | red $(1.9 \pm 0.2) \times 10^{12}$ | $(1.6 \pm 0.1) \times 10^{12}$ | $(1.5 \pm 0.1) \times 10^{12}$ |
| (CH$_3$)$_2$O | red $(2.0 \pm 0.7) \times 10^{12}$ | $(1.9 \pm 0.6) \times 10^{12}$ | $(2.1 \pm 0.7) \times 10^{12}$ |
| H$_2$CCO$^a$ | blue $(4.8 \pm 0.4) \times 10^{12}$ | $(4.0 \pm 0.3) \times 10^{12}$ | $(3.7 \pm 0.3) \times 10^{12}$ |
|             | red $(1.6 \pm 0.3) \times 10^{12}$ | $(1.4 \pm 0.3) \times 10^{12}$ | $(1.3 \pm 0.2) \times 10^{12}$ |

Note.

$^a$ Blue and redshifted components of this molecule do not exactly correspond to those of CH$_3$CHO, HCOOCH$_3$, and (CH$_3$)$_2$O (see Figure 2 and Section 4.2). The ortho-to-para ratio is assumed to be 3.

density for (CH$_3$)$_2$O in TMC-1CP are calculated in the same way from the root-mean-square noise of the spectrum. We also evaluate the column density of H$_2$CCO for the blueshifted and redshifted components, assuming the above excitation temperatures. The results are listed in Table 4. However, it should be noted that these two components of H$_2$CCO do not exactly correspond to those of CH$_3$OH and CH$_3$CHO, as mentioned in Section 3.2.

On the other hand, the LTE analysis of H$_2$CO in TMC-1 CP is unsuccessful, probably because of the subthermal populations and the relatively high optical depths. Hence, we employ the non-LTE code (RADEx) to evaluate the column density of H$_2$CO. We only evaluate the total column density, because the blueshifted and redshifted components are not well resolved for the H$_2$CO lines. The column density and the H$_2$ density are derived to be $1.2 \times 10^{13}$ cm$^{-2}$ and $2 \times 10^4$ cm$^{-3}$, respectively. The line profile is also complicated for cyclopropenone. Hence, only the total column density is derived for this species to be $(5.6 \pm 0.3) \times 10^{11}$ cm$^{-2}$ under the assumption of the LTE conditions with the average excitation temperature of the blueshifted and redshifted components of CH$_3$OH (5.2 K). The column density is $(6.6 \pm 0.3) \times 10^{11}$ cm$^{-2}$ and $(5.4 \pm 0.2) \times 10^{11}$ cm$^{-2}$, if the excitation temperature is 4.2 and 6.2 K, respectively.

For CH$_3$CHO, HCOOCH$_3$, and (CH$_3$)$_2$O in TMC-1 MP, we derive the column densities by using the average rotation temperature (5.2 K) of the two velocity components of CH$_3$OH in TMC-1 CP. As in the case of TMC-1 CP, the total column densities for the blueshifted and redshifted components are derived for H$_2$CCO, although these components would not exactly correspond to those of CH$_3$CHO, as mentioned in Section 4.1. The results are summarized in Table 5. Variations of the column densities by a change in the assumed rotation temperature by $\pm 1$ K are also shown in Table 5.

5.2. Comparison with other Sources

Although COMs have long been thought to be specific to hot cores in high-mass star-forming regions and hot corinos in low-mass star-forming regions, their existence in cold starless cores has recently been revealed, as mentioned in Section 1. If COMs are produced on dust grains, some desorption mechanisms are necessary for their radio detection in cold starless cores. Desorption by surplus reaction energy, cosmic-ray or cosmic-ray-induced UV radiation, as well as photodesorption by the interstellar UV radiation in cloud peripheries are considered (Bacmann et al. 2012; Caselli et al. 2012), although the photodesorption processes were recently suggested to be less efficient than previously thought (Bertin et al. 2016; Martín-Doménech et al. 2016). Alternatively, the gas-phase formation of COMs is also proposed to account for the result by involving new radiative association reactions (Vasyunin & Herbst 2013; Balucani et al. 2015). Thus, the formation of COMs still remains controversial. However, the similarity of the distribution of COMs and CH$_3$OH inferred from the similar spectral line shapes in this study favors the dust-grain origin for cold starless cores. At least, the formation of COMs would be triggered by liberation of CH$_3$OH from dust grain, even if the final production pathways to the COMs are the gas-phase ones.

In this study, we detected CH$_3$CHO, HCOOCH$_3$, and (CH$_3$)$_2$O toward TMC-1 MP, although the detection of (CH$_3$)$_2$O is tentative. First, we compare the relative abundances of these three species relative to CH$_3$OH observed in TMC-1 MP with those in the other cold sources L1544, L1689B, and B1b (Öberg et al. 2010; Bacmann et al. 2012; Jimenez-Serra et al. 2016), as shown in Table 6. Although the ratios are different by a factor of a few among the three sources, we would say in this stage that the relative abundances of these three COMs could be similar to one another among the four sources in a sense of the order-of-magnitude estimate. This result suggests that a common chemistry for the above COMs is occurring in these sources. We need better quality data and their analyses to discuss their source-to-source differences.

In TMC-1 MP, the column density of CH$_3$CHO is roughly comparable to those of HCOOCH$_3$ and (CH$_3$)$_2$O. CH$_3$CHO is often regarded as a “cold molecule,” because its excitation temperature is lower than those of hot corino/hot core molecules (Bisschop et al. 2007). Hence, formation processes of CH$_3$CHO were thought to be different from those of the other COMs. However, the present observation shows on the basis of the spectral line shape that CH$_3$CHO has the dust-grain origin as in the case of the other COMs for TMC-1 MP and TMC-1 CP.
|           | TMC-1 MP (blue) ($T_{\text{ex}} = 5.2$ K) | TMC-1 MP (red) ($T_{\text{ex}} = 5.2$ K) | L1544$^{+b}$ (center) | L1544$^{+c}$ (CH$_3$OH peak) | B1b$^{d}$ (Core) | L1689B$^{+e,f}$ ($T_{\text{ex}} = 30$ K) | L1157$^{+g}$ | IRAS 16293-2422$^{+h}$ |
|-----------|----------------------------------------|----------------------------------------|-----------------------|-------------------------------|-----------------|---------------------------------------|---------------|--------------------------|
| CH$_3$CHO/CH$_3$OH | 0.110 ± 0.034                          | 0.077 ± 0.028                          | 0.04                  | 0.05                          | 0.012 ± 0.002  | 0.050 ± 0.003                      | 0.0036 ± 0.018 | 0.17                     |
| HCOOCH$_3$/CH$_3$OH | 0.039 ± 0.014                          | 0.16 ± 0.15                            | 0.04 ± 0.02           | 0.023 ± 0.005                 | 0.084 ± 0.013  | 0.007 ± 0.003                      | 1.3           |                          |
| CH$_3$OCH$_3$/CH$_3$OH | 0.048 ± 0.023                          | 0.056 ± 0.012                          | 0.012 ± 0.002         | <0.008                        | 0.084 ± 0.008  | <0.005                             | 0.80          |                          |
| $N$(CH$_3$OH) [cm$^{-2}$] | $(2.2 \pm 0.6) \times 10^{13}$        | $(4.0 \pm 1.4) \times 10^{13}$         | $(2.7 \pm 0.6) \times 10^{13}$ | $6.3 \times 10^{13}$          | $3.6 \times 10^{13}$ | $1.2 \times 10^{14}$               | $(6.24 \pm 0.02) \times 10^{15}$ | $2.25 \times 10^{16}$ |

Notes.

$^a$ Jimenez-Serra et al. (2016).
$^b$ Spezzano et al. (2016).
$^c$ Bizzocchi et al. (2014). The CH$_3$OH column density is taken from their Figure 3.
$^d$ Öberg et al. (2010).
$^e$ Bacmann & Faure (2016).
$^f$ Bacmann et al. (2016). Column densities for the excitation temperature of 8 K are employed.
$^g$ Sugimura et al. (2011). Beam averaged values (~20$''$).
$^h$ Cazaux et al. (2003).
16293-2422 may originate from this effect. Alternatively, the difference may reflect the difference of the evaporation mechanism. In the hot corino, the COMs are thought to be thermally evaporated, while in starless cores they come out into the gas phase through nonthermal processes mentioned above. In the former case, all the ice mantles will be evaporated, but not in the latter case. If the ice composition has a layered structure, the different evaporation mechanisms would cause the different gas-phase compositions.

It is interesting to compare the abundances with those in the outflow-shocked region, L1157 B1, where CH$_3$CHO, HCOOCH$_3$ ($\text{CH}_3$)$_2$O, and C$_2$H$_5$OH were detected by Arce et al. (2008) and Sugimura et al. (2011). The CH$_3$CHO/CH$_3$OH and HCOOCH$_3$/CH$_3$OH ratios in L1157 B1 are significantly lower than the ratios in TMC-1 MP. If CH$_3$OH, CH$_3$CHO, and HCOOCH$_3$ are supplied from dust grains by sputtering in the shocked region, the CH$_3$CHO and HCOOCH$_3$ abundances relative to CH$_3$OH on dust grains in L1157 B1 should be lower than those in TMC-1 MP. L1157 B1 is a shocked region caused by the interaction between an ambient cloud and the molecular outflow from IRAS 20386+6751 (Mikami et al. 1992; Umemoto et al. 1992; Bachiller & Pérez Gutiérrez 1997). Hence, the formation of COMs on dust grains may have not well proceeded in comparison with TMC-1 MP. This implication is consistent with the idea that the abundance of CH$_3$OH and COMs gradually increases with time (Garrod & Herbst 2006). Alternatively, COMs may be more easily destroyed in the shocked region than CH$_3$OH, so that their abundances relative to CH$_3$OH become lower. There is also a possibility that the emitting region of COMs are smaller than that of CH$_3$OH.

It is worth noting that Requena-Torres et al. (2007) reported the upper limits of the HCOOCH$_3$/CH$_3$OH ratio in the quiescent dark cloud L183 and the L1448 outflow. They are not stringent, and are consistent with the TMC-1 MP and L1157 B1 values.

TMC-1 CP is known to be a young starless core, because it harbors rich carbon-chain molecules and deficient NH$_3$ and HN$_2$ (Hirahara et al. 1992; Kaifu et al. 2004; Sakai & Yamamoto 2013). TMC-1 MP is spatially close to TMC-1 CP, and both are within the starless core, Core D, of Hirahara et al. (1992). The present detection of COMs in such a young starless core is very important. It is most likely that a substantial amount of COMs has already been formed on dust grains even in the early evolutionary stage of starless cores. At the same time, it is found that H$_2$CCO and cycloprenone are likely formed in gas-phase processes, as proposed by Loison et al. (2016) and Vasyunin & Herbst (2013). This result means that COMs are not always formed on dust grains. Further theoretical, laboratory, and modeling works are awaited to account for the present observation.

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