Tentative detection of ethylene glycol toward W51/e2 and G34.3+0.2*,

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ABSTRACT

Context. With only a few low- and high-mass star-formation regions studied in detail so far, it is unclear what role the environment plays in complex molecule formation. In this light, a comparison of relative abundances of related species between sources might be useful for explaining any observed differences.

Aims. We seek to measure the relative abundance between three important complex organic molecules, ethylene glycol ((CH₂OH)₂), glycolaldehyde (CH₂OCHO) and methyl formate (HCOOCH₃), toward high-mass protostars and thereby provide additional constraints on their formation pathways.

Methods. We use IRAM 30 m single-dish observations of the three species toward two high-mass star-forming regions – W51/e2 and G34.3+0.2 – and report a tentative detection of (CH₂OH)₂ toward both sources.

Results. Assuming that (CH₂OH)₂, CH₂OCHO, and HCOOCH₃ spatially coexist, relative abundance ratios, HCOOCH₃/(CH₂OH)₂, of 31 and 35 are derived for G34.3+0.2 and W51/e2, respectively. CH₂OCHO is not detected, but the data provide lower limits to the HCOOCH₃/(CH₂OH)₂ abundance ratios of ≥193 for G34.3+0.2 and ≥550 for W51/e2. A comparison of these results to measurements from various sources in the literature indicates that the source luminosities may be correlated with the HCOOCH₃/(CH₂OH)₂ and HCOOCH₃/(CH₂OH)₂ ratios. This apparent correlation may be a consequence of the relative time scales each source spend at different temperature ranges in their evolution. Furthermore, we obtain lower limits to the ratio of (CH₂OH)₂/CH₂OCHO for G34.3+0.2 (≥6) and W51/e2 (≥16). This result confirms that a high (CH₂OH)₂/CH₂OCHO abundance ratio is not a specific property of comets, as previously speculated.

Key words. ISM: molecules – ISM: abundances – ISM: individual objects: W51/e2 – methods: observational – astrochemistry – ISM: individual objects: G34.3+0.2

1. Introduction

How complex organic – and potentially prebiotic – molecules are formed in regions of low- and high-mass star formation remains a central question in astrochemistry. To date there has been no consensus about how complex organic molecules (COMs hereafter) form in dense regions of the interstellar medium, despite the increasing number of detections (e.g., Herbst & van Dishoeck 2009). One promising suggestion was that warm gas phase chemistry, following evaporation of simple ices, could be a primary formation pathway (e.g., Millar et al. 1991; Charnley et al. 1992). However, more recent laboratory experiments and chemical modeling has shown that this mechanism is not effective enough to account for the observed abundances (e.g., Geppert et al. 2006). An alternative formation mechanism involves UV induced radicals. Garrod et al. (2008) propose that, during the warm up phase, radicals can migrate on the grains surfaces and form complex species that are then released into the gas phase at higher temperatures. The initial ice composition and the amount of UV radiation have also proved to play an important part in the formation process (Oberg et al. 2009). To determine the formation pathway of COMs, it is useful to determine abundance ratios between different related species because these ratios, in comparison with the predicted abundance ratios from chemical models, can provide constraints on the formation processes. Indeed, variations in the abundance profiles can reflect the physical and chemical conditions that are occurring. It is therefore important to observe these species in different environments.

Some of the simplest species in this context include the oxygen-bearing COMs associated to glycolaldehyde, CH₂OCHO, including its isomer methyl formate (HCOOCH₃ or CH₃OCHO) and the reduced alcohol version of CH₂OCHO, ethylene glycol, (CH₂OH)₂ (also commonly known as anti-freeze). By constraining the relative abundances of these species in different environments the hope is to be able to explore, for instance, the importance of initial chemical conditions, temperature and irradiation in the formation for comparison, such as for laboratory experiments (e.g., Oberg et al. 2009) and as input for sophisticated chemical models (e.g., Garrod et al. 2008). For example, in their laboratory experiments Oberg et al. (2009) show that the relative abundances of HCOOCH₃ to CH₂OCHO and
(CH$_2$OH)$_2$ strongly depend on both the ice temperature and exact ice composition in terms of the relative amounts of CO and CH$_3$OH.

So far, (CH$_2$OH)$_2$ has been detected toward high-mass sources such as the Galactic center source Sgr B2(N) by Hollis et al. (2002), marginally toward W51 e1/e2 by Kalenskii & Johansson (2010), and recently also toward the Orion Kleinmann-Low (KL) nebula by Brouillet et al. (2015).

(CH$_2$OH)$_2$ has also been observed toward the low-mass Class 0 protostars IRAS 16293–2422 (Jørgensen et al. 2012, and in prep.) and NGC 1333 IRAS 2A (Maury et al. 2014; Coutens et al. 2015) as well as toward the intermediate-mass protostar NGC 7129 FIRS2 (Fuente et al. 2014). CH$_3$OCHO has been detected toward Sgr B2(N) (Hollis et al. 2000, 2001, 2004; Halfen et al. 2006; Requena-Torres et al. 2008), the high-mass hot molecular core G31.41+0.31 (Beltrán et al. 2009), in IRAS 16293–2422 by Jørgensen et al. (2012) and recently also in NGC 7129 FIRS2 (Fuente et al. 2014), NGC 1333 IRAS 2A (Coutens et al. 2015; Taquet et al. 2015) and NGC 1333 IRAS 4A (Taquet et al. 2015). HCOOCH$_3$ is the most abundant isomer of CH$_2$OCHO, and it has previously been observed in numerous hot cores and corinos (e.g., Blake et al. 1987; Bisschop et al. 2007; Demyk et al. 2008; Favre et al. 2014, 2011). There are some notable differences in terms of the abundance ratios. For example, Coutens et al. (2015) find a (CH$_2$OH)$_2$/CH$_3$OCHO ratio of ~5 in NGC 1333 IRAS 2A, while Jørgensen et al. (2012 and in prep.) find a lower value of ~1 in IRAS 16293-2422. These changes hint that it might be useful to explore these ratios in different sources sampling similar physical conditions.

This paper presents IRAM 30 m observations of (CH$_2$OH)$_2$ and CH$_3$OCHO toward the high-mass protostars W51/e2 (distance = 5.4 kpc, Sato et al. 2010) and G34.3+0.2 (distance = 3.8 kpc, Kurtz et al. 2000). The aim of this study is to determine the relative abundance of (CH$_2$OH)$_2$ and CH$_3$OCHO to HCOOCH$_3$ and compare to other sources from the literature. Overall our aim is to investigate the use of abundance ratios of species that are believed to be chemically related to explore the origin of complex molecules in the dense interstellar medium. In Sect. 2, the IRAM 30 m observations are presented. Data modeling, results and analysis are presented in Sect. 3 and discussed in Sect. 4.

3. Analysis and results

Spectra from both sources show a rich forest of lines characteristic of high-mass sources. A total of 21 and 19 lines have peak temperatures above 5 K for W51/e2 and G34.3+0.2, respectively. The strongest lines in both spectra are the CS 5–4 transition at 244 935 MHz. It is important to know that there is still a remnant oscillation in the baseline even after the removal of the standing wave in the spectra. This increases the rms noise of the spectra, which complicates the analysis of faint lines. Therefore, in addition to the global baseline subtraction, an additional local zero-, or first-order baseline subtraction was therefore performed before making a Gaussian fit of the (CH$_2$OH)$_2$ lines. This additional baseline subtraction is applied in a range of ±100 km s$^{-1}$ for each line. As for the data reduction, CLASS was used for the additional baseline subtraction, as well as for Gaussian profile fits to the detected lines. The resulting rms of the local baseline is ~60 mK for the 1 mm observations and ~7 mK for the 3 mm observations.

To ensure proper line identification, we checked the line observations against entries in the Splatalogue database for astronomical spectroscopy\(^\text{2}\). In addition, we made a reference model where we produced synthetic spectra for the line emission of common species (CH$_3$OCH$_3$, HCOOH, CH$_3$CHO, CH$_3$OH, C$_2$H$_5$OH and CH$_3$CN) in order to visually exclude lines that are blended with any of these molecules. Table 1 lists spectroscopic parameters for the (CH$_2$OH)$_2$ transitions that can be excited in the observed frequency range. Transitions with log($A_{ul}$) < -5 for the 3 mm observations and log($A_{ul}$) < -6 and $E_{up}$ > 3000 K for the 1 mm observations have been excluded from the table, because these transitions are predicted from the synthetic spectra to have peak intensities ≤0.02 K, i.e., are not detectable.

The spectroscopic data for (CH$_2$OH)$_2$ come from Christen & Müller (2003) and Christen et al. (1995) and are available from the CDMS database\(^3\) (Müller et al. 2001, 2005), while the spectroscopic data for HCOOCH$_3$ and CH$_3$OCHO are from Ilyushin et al. (2009) and Carroll et al. (2010) respectively, available from the JPL database\(^4\) (Pickett et al. 1998). For the analysis, the (CH$_2$OH)$_2$ lines that are reasonably well separated and

\(^1\) http://www.iram.fr/IRAMFR/GILDAS

\(^2\) http://www.splatalogue.net

\(^3\) http://www.astro.uni-koeln.de/cdms

\(^4\) http://spec.jpl.nasa.gov/home.html
### Table 1. Transitions of (CH$_2$OH)$_2$ in the observed frequency range.

| Transition   | Frequency [MHz] | $E_{up}$ [K] | $\log_{10}(A_{ul})$ [s$^{-1}$] | Rotational diagram |
|--------------|-----------------|-------------|-------------------------------|-------------------|
| 9$\_1$, $v$ = 1 – 8$\_1$, $v$ = 0 | 100 333.6424 | 23.6 | -6.773 | W51/e2 |
| 9$\_2$, $v$ = 1 – 8$\_2$, $v$ = 0 | 100 490.6121 | 27.0 | -6.800 |
| 11$\_1$, $v$ = 1 – 10$\_1$, $v$ = 1 | 102 064.0770 | 33.9 | -6.692 |
| 10$\_2$, $v$ = 1 – 9$\_2$, $v$ = 0 | 102 291.5860 | 26.2 | -5.798 |
| 9$\_2$, $v$ = 1 – 8$\_2$, $v$ = 0 | 102 539.4267 | 25.0 | -6.355 |
| 10$\_3$, $v$ = 1 – 9$\_3$, $v$ = 0 | 102 689.8384 | 26.1 | -4.449 |
| 11$\_2$, $v$ = 0 – 10$\_1$, $v$ = 1 | 105 574.9490 | 72.2 | -4.934 |
| 10$\_2$, $v$ = 0 – 10$\_3$, $v$ = 1 | 105 644.1940 | 63.9 | -4.579 |
| 11$\_1$, $v$ = 0 – 10$\_2$, $v$ = 1 | 105 701.0020 | 33.6 | -3.646 |
| 11$\_2$, $v$ = 0 – 10$\_1$, $v$ = 1 | 105 735.3520 | 56.5 | -4.405 |
| 11$\_3$, $v$ = 0 – 10$\_2$, $v$ = 1 | 105 834.6960 | 36.9 | -5.676 |
| 11$\_6$, $v$ = 0 – 10$\_5$, $v$ = 1 | 105 866.9546 | 50.1 | -4.322 |
| 11$\_7$, $v$ = 0 – 10$\_6$, $v$ = 1 | 106 072.0524 | 44.7 | -6.197 |
| 11$\_5$, $v$ = 0 – 10$\_5$, $v$ = 1 | 106 068.9178 | 44.8 | -5.104 |

**Notes.** Catalog values for the (CH$_2$OH)$_2$ transitions that can be excited in the observed frequency range for W51/e2 and G34.3+0.2. Some faint transitions have been excluded from this table, please Sect. 3. The source names are listed for the lines that are used in the rotational diagram analysis.

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Fig. 1. Observed (black) and synthetic (red) spectra of the five transitions of (CH$_2$OH)$_2$ in W51/e2 that are used for the analysis. Also shown are the synthetic spectra of all other species investigated in this study (blue) to demonstrate that the (CH$_2$OH)$_2$ lines in question are not blended. The transitions are located at 239 883.56, 240 807.88, 242 656.23, 242 948.29 and 100 333.64 MHz – denoted by black vertical lines in the plot. The displayed frequency region in each plot corresponds to $\sim$200 km s$^{-1}$.

Fig. 2. Same as for Fig. 1 but for G34.3+0.2. The transitions are located at 240 807.88 and 242 656.23 MHz – indicated by black vertical lines in the plot.

have a peak temperature above $3\sigma$ were selected. For W51/e2 we included the lines at $\sim$100 333 and $\sim$242 656 MHz, although they are partially blended, because it is possible to distinguish the (CH$_2$OH)$_2$ peak from the other peaks and perform a multiple Gaussian fit that includes all relevant peaks.

Figures 1 and 2 show a zoom-in of the area of $\sim$200 km s$^{-1}$, which corresponds to $\sim$160 MHz in the 1 mm observations and $\sim$70 MHz in the 3 mm observations, around each detected line in both sources after the local baseline subtraction. Superimposed onto the observed spectra are the synthetic spectra of (CH$_2$OH)$_2$ as well as the other species investigated here, as to demonstrate that the chosen (CH$_2$OH)$_2$ lines are not blended. The fit to the entire observed spectra for both sources are shown in Figs. B.1–B.8 in the appendix. Table A.1 in the appendix lists the estimated column densities of the molecules in the reference model. Table 2 lists spectroscopic parameters and the observed quantities from the fits of the (CH$_2$OH)$_2$ lines: the integrated line intensity ($\int T_{mb} \Delta v$), position ($V_{LSR}$), line width ($\Delta v$) and peak temperature (Peak $T_{mb}$).

A total of 35 and 52 well separated lines have been detected above the $3\sigma$ level in the 1 mm and 3 mm data for HCOOCH$_3$ in W51/e2 and G34.3+0.2, respectively. For (CH$_2$OH)$_2$, four and
two lines toward W51/e2 and G34.3+0.2 respectively, are detected in the 1 mm observations; while only one line is detected at 3 mm toward W51/e2. Many other (CH$_2$OH)$_2$ lines, as well as some potential CH$_3$OHCHO lines are present in both data sets, but they are either blended with other species or too faint to be properly detected above a 3σ limit.

3.1. Modeling

Assuming LTE and optically thin emission, the rotational diagram method can be used to determine the column density, $N_{	ext{rot}}$, and the rotational temperature, $T_{	ext{rot}}$ (Goldsmith & Langer 1999). The approach used in this work follows the formalism described by Goldsmith & Langer (1999) with the following assumptions:

1. (CH$_2$OH)$_2$, CH$_3$OHCHO, and HCOOCH$_3$ are emitting from the same region and thus have the same source size, $\theta_{\text{source}}$.
2. (CH$_2$OH)$_2$, CH$_3$OHCHO, and HCOOCH$_3$ are in LTE, which implies that the excitation temperature, $T_{\text{ex}}$, is equal to the kinematic temperature, $T_{\text{kin}}$, for all three species. Using the rotational diagram method, one obtains the rotational temperature, which in LTE is $T_{\text{rot}} = T_{\text{kin}} = T_{\text{ex}}$.
3. The observations at 1 mm and 3 mm trace the same gas.

According to our assumptions, the source size and $T_{\text{rot}}$ derived from the HCOOCH$_3$ analysis can be used to derive the column density of (CH$_2$OH)$_2$ and set an upper limit on the column density of CH$_3$OHCHO. A possible caveat is that the large beam size of our observations compared to the source sizes does not guarantee that the measured lines arise from species present in the same gas. Specifically, we obtain similar mean values of $V_{\text{LSR}}$ for (CH$_2$OH)$_2$ and HCOOCH$_3$ in both sources ($56.4 \pm 0.5$ km s$^{-1}$ and $56.0 \pm 0.8$ km s$^{-1}$ in W51/e2 along with $57.7 \pm 0.5$ km s$^{-1}$ and $58.4 \pm 1.2$ km s$^{-1}$ in G34.3+0.2 for (CH$_2$OH)$_2$ and HCOOCH$_3$, respectively), so here the assumption appears reasonable.

The same formalism in Goldsmith & Langer (1999) as was used to create a rotational diagram can also be used to generate a synthetic spectrum of the line emission of a specific molecule by using the source size, $\theta_{\text{source}}$, the rotational temperature, $T_{\text{rot}}$, the line width, $\Delta v$, and the column density, $N_{\text{rot}}$, as input parameters. It is possible to correct for the optical depth of the line emission in case it deviates from being completely optically thin (Goldsmith & Langer 1999). A synthetic spectrum generated with input parameters derived from the rotational diagram therefore serves as a check for the self-consistency of the result. We use adopted source sizes from the literature and determine the rotational temperatures and column densities in the following analysis.

The observed width of the detected lines have been determined from the Gaussian fit. For HCOOCH$_3$ in W51/e2, we obtain mean values of $\Delta v = 6.4 \pm 0.8$ km s$^{-1}$ in the 1 mm data and $\Delta v = 6.1 \pm 1.1$ km s$^{-1}$ in the 3 mm data. In the same source, the mean value of the line width of the (CH$_2$OH)$_2$ lines is $6.3 \pm 0.9$ km s$^{-1}$ for the 1 mm data, and the only detected value is $5.5$ km s$^{-1}$ in the 3 mm data. For G34.3+0.2, we find $\Delta v = 6.5 \pm 1.5$ km s$^{-1}$ in the 1 mm data and $\Delta v = 7.3 \pm 1.3$ km s$^{-1}$ in the 3 mm data for HCOOCH$_3$ and $\Delta v = 4.5 \pm 0.5$ km s$^{-1}$ for the (CH$_2$OH)$_2$ lines in the 1 mm data. In the analysis below, a fixed line width of 6.0 km s$^{-1}$ was chosen as input parameter in synthetic spectra for all species.

3.2. HCOOCH$_3$

In the rotational diagram analysis for W51/e2, a source size of 2.4″ (Zhang et al. 1998) is applied and results in a rotation temperature of $T_{\text{rot}} = 120$ K and a column density of $1.1 \times 10^{16}$ cm$^{-2}$. We estimate a 40 K uncertainty on the rotational temperature, which contribute to a ~20% error on the column density. This, combined with an observational uncertainty of ~30% returns an estimated overall error of 30%-40% for the column density. For G34.3+0.2 a source size of 7.6″ (Remijan et al. 2003) is applied and results in $N_{\text{rot}} = 5.8 \times 10^{16}$ cm$^{-2}$, and $T_{\text{rot}} = 140$ K for HCOOCH$_3$. As in the case for W51/e2, the estimated uncertainty of the column density is 30%-40% and 40 K for the temperature. Results from both sources are given in Table 3, and we have checked the validity of these results by generating synthetic spectra and comparing these to the observed spectra.

3.3. (CH$_2$OH)$_2$

Numerous (CH$_2$OH)$_2$ lines are blended with other species or have line intensities below 3σ. A total of two and five reasonable well separated lines above the 3σ limit toward G34.3+0.2 and W51/e2, respectively, were chosen for this analysis (see Tables 2 and 1 for the spectroscopic data and Figs. 1 and 2 for the zoom-in of the spectra around the lines). With only two to
five unblended lines, the assignment of (CH$_2$OH)$_2$ cannot be considered as a firm detection. However, even if our tentative detection of (CH$_2$OH)$_2$ is not confirmed, this measurement represents a useful upper limit for the column density of (CH$_2$OH)$_2$, which still can provide important information when compared to the HCOOCH$_3$ detection.

When only a few data points are available, a statistically reliable result of the rotational temperature cannot be obtained from the traditional use of the rotational diagram method. Thus, we assume that (CH$_2$OH)$_2$ and HCOOCH$_3$ emit at the same $T_{\text{rot}}$, which in LTE is equal to $T_{\text{rot}}$. The uncertainty of the column density is, as for HCOOCH$_3$, estimated to 30%–40%.

Using $\theta_{\text{source}} = 7.6'$ and $T_{\text{rot}} = 140$ K, a column density of $1.9 \times 10^{15}$ cm$^{-2}$ is derived for (CH$_2$OH)$_2$ toward G34.3+0.2. For W51/e2, a source size of 2.4'' and $T_{\text{rot}} = 120$ K returns $N_{\text{rot}} = 3.1 \times 10^{16}$ cm$^{-2}$ for (CH$_2$OH)$_2$. These results, listed in Table 3, are used as input parameters for synthetic spectra in order to perform a sanity check. We checked each line in the synthetic spectra against the observed spectra for each source, and they all seem to provide a reasonable match, at least within the estimated uncertainty. Figures 1 and 2 shows the comparison of the synthetic spectra against the observed spectra. It is evident from Fig. 1 that the synthetic spectrum in the 1 mm data toward W51/e2 slightly overproduces the observed spectrum, while it reproduces the observed line in the 3 mm data. Since this line has a lower $E_{\text{up}}$, this could indicate that a lower excitation temperature would give a better fit. Indeed a fixed $T_{\text{rot}} = 70$ K in the rotational diagram returns the same column density, $N_{\text{rot}} = 3.1 \times 10^{16}$ cm$^{-2}$.

### 3.4. CH$_2$OHCHO

Several lines in the data might be assigned to CH$_2$OHCHO. However, they are either blended with the emission of other molecules or too faint (i.e., below the 3σ limit), thus we cannot claim a detection. Nevertheless, we are able to obtain an upper limit for the column density. Following the assumptions stated in Sect. 3.1, synthetic spectra were generated using $\theta_{\text{source}}$, $T_{\text{rot}}$ and $\Delta v$ in Table 3, allowing $N_{\text{rot}}$ to vary. More specifically, the upper limit of the column density is then determined by increasing the value until the synthetic spectra overproduces the observed spectra intensities at the locations of the CH$_2$OHCHO lines in the observed spectra. The upper limit on the column density is $\lesssim 3 \times 10^{16}$ cm$^{-2}$ toward G34.3+0.2 and $\lesssim 2 \times 10^{15}$ cm$^{-2}$ toward W51/e2. The uncertainty of the column density is, as for HCOOCH$_3$, estimated to 30%–40%.

### 3.5. Relative abundances

Following the three assumptions listed in Sect. 3.1, it is possible to calculate the relative abundance of the species at the rotational temperature and source size found for each source. The following abundance ratios have been computed: HCOOCH$_3$/(CH$_2$OH)$_2$, HCOOCH$_3$/CH$_2$OHCHO and (CH$_2$OH)$_2$/OHCHO. As CH$_2$OHCHO is not detected, it is only possible to set an upper limit on the column density. The HCOOCH$_3$/CH$_2$OHCHO and (CH$_2$OH)$_2$/CH$_2$OHCHO ratios are therefore lower limits. All three relative abundance ratios for W51/e2 and G34.3+0.2 are listed in Table 4 along with previous measurements toward high-mass stars-forming regions, a hot core, an intermediate-mass protostar, low-mass protostars, molecular clouds toward the Galactic center and comets.

### 4. Discussion

(CH$_2$OH)$_2$ has previously been detected in several other sources (Sgr B2(N), NGC 7129 FIRS2, NGC 1333 IRAS 2A and Orion-KL), with additional marginal/tentative detections in W51 e1/e2 and IRAS 16293–2422 (Hollis et al. 2002; Fuente et al. 2014; Maury et al. 2014; Coutens et al. 2015; Kalenskii & Johansson 2010; Jorgensen et al. 2012). In this paper we have identified (CH$_2$OH)$_2$ and HCOOCH$_3$ in two high-mass protostellar sources, W51/e2 and G34.3+0.2, and in addition been able to give an upper limit for the column density of CH$_2$OHCHO in the same sources. The results from this study are roughly similar to the estimates ratios seen in Orion KL (Favre et al. 2011; Brouillet et al. 2015) for the HCOOCH$_3$/CH$_2$OHCHO and HCOOCH$_3$/(CH$_2$OH)$_2$ ratios while the upper limits for (CH$_2$OH)$_2$/CH$_2$OHCHO are similar to the results for NGC 1333 IRAS 2A (Coutens et al. 2015), as well as the upper limits results for comets (Biver et al. 2014; Bockelée-Morvan et al. 2000; Crovisier et al. 2004a,b) (Table 4).

When investigating the conditions leading to differences in observed abundance ratios, it is important to take both the formation processes and the destruction processes of the molecules into consideration. Garrod et al. (2008) combined a gas-grain chemical network with a physical model to test whether the chemistry can reproduce the observed abundances of previously detected organic molecules in physical conditions characteristic of star-forming regions. The physical model used in Garrod et al. (2008) is based on Viti et al. (2004) and consist of an isothermal collapse followed by a warm-up phase with temperatures from 10 K to 200 K, assuming absolute time scales for the warm-up phases are $1 \times 10^5$, $2 \times 10^5$, and $5 \times 10^5$ yr representing low-, intermediate-, and high-mass star formation respectively. However, Aikawa et al. (2008) argue that the relation should be reversed, because the warm-up time scale should be relative and should depend on the ratio of the size of the warm region to the infall speed instead of the overall speed of star formation. Either way, Garrod et al. (2008) and Aikawa et al. (2008) agree that the time scales, whether absolute or relative, at the different temperature ranges are important for the chemistry.

For all the sources in Table 4, HCOOCH$_3$ is more abundant than CH$_2$OHCHO from a factor of $>550$ in W51/e2 to a factor of $>2$ in comet Hale-Bopp. According to Garrod et al. (2008), HCOOCH$_3$ and CH$_2$OHCHO have similar formation pathways, which are based on the addition of HCO and CH$_3$O or CH$_3$OH at 30 K–40 K. Garrod et al. (2008) find that the production rates of CH$_3$O and CH$_3$OH are the same, which leads to similar abundances for HCOOCH$_3$ and CH$_2$OHCHO. Intuitively this makes sense because the two molecules are isomers, but it
contradicts observations because HCOOCH$_3$ is observed to be much more abundant than CH$_2$OHCHO in all the sources reported so far. As suggested by Garrod et al. (2008), this discrepancy could be due to the differences in the CH$_3$O/CH$_2$OH branching ratio. According to Öberg et al. (2009), HCOOCH$_3$ forms at a lower temperature than CH$_2$OHCHO, which can also have an impact on the resulting ratio of the two species. Another explanation for the high HCOOCH$_3$/CH$_2$OHCHO ratio is the assumptions regarding thermal evaporation for these two species. Garrod et al. (2008) suggest that CH$_2$OHCHO remains on the grains until co-desorbs with water (at ~110 K) while HCOOCH$_3$ evaporates at 70–80 K. This leaves CH$_2$OHCHO to be destroyed by OH radicals at higher temperatures on the grains prior to evaporation. As Öberg et al. (2009) conclude, the ratio of HCOOCH$_3$/CH$_2$OHCHO does not depend greatly on the initial ice composition, and so the observed variations will most likely be linked to the different temperature conditions of the different sources.

In Table 4 the sources are listed in order with a decreasing HCOOCH$_3$/CH$_2$OHCHO ratio, which in turn also roughly correspond to a descending order of luminosity, which is also listed in the table. The top plot in Fig. 3 shows a schematic bar plot of HCOOCH$_3$/CH$_2$OHCHO against $L_{bol}$. On the x-axis the sources in Table 4 have been plotted in descending order from left to right, but not to scale. As illustrated by Fig. 3 (top) a rough correlation between HCOOCH$_3$/CH$_2$OHCHO and $L_{bol}$ exists: more luminous sources show a high HCOOCH$_3$/CH$_2$OHCHO ratio, while low-luminosity sources show a low HCOOCH$_3$/CH$_2$OHCHO ratio with intermediate values in between. The apparent correlation between HCOOCH$_3$/CH$_2$OHCHO and source luminosity supports the hypothesis that the HCOOCH$_3$/CH$_2$OHCHO ratio depends mainly on the temperature, which in turns depends on the luminosity of the source. Even if the chemistry and the temperature profile in all the sources were quite similar, the differences in time scales of the different temperature ranges (low, intermediate, to high temperature) are not. A higher HCOOCH$_3$/CH$_2$OHCHO ratio in more luminous sources could simply be a consequence of i) more luminous sources having experienced a longer time scale at temperatures that are either more favorable to the formation of HCOOCH$_3$ and/or to the destruction of CH$_2$OHCHO; or ii) less luminous sources experience a shorter time scale at high temperature, which would conserve a greater fraction of CH$_2$OHCHO than their more luminous counterparts. One should of course keep in mind that the sources discussed here have temperature profiles that covers a range of temperatures falling with radius and that hot core regions are permeated by shocks that also produce a range of temperatures. For the Galactic center molecular clouds from the study by Requena-Torres et al. (2008), no luminosities are listed: these are warm, low-density clouds with no sign of star formation. However, judging by the HCOOCH$_3$/CH$_2$OHCHO and HCOOCH$_3$/CH$_3$OH$_2$ ratios, they appear to be closer to the low-mass protostars than to the hot cores and high-mass star-forming regions.

In the bottom plot in Fig. 3, the HCOOCH$_3$/CH$_3$OH$_2$ abundance ratio also shows a decrease with $L_{bol}$ similar to that of HCOOCH$_3$/CH$_2$OHCHO. If the same temperature time scale argument is applied to this correlation, one would expect an opposite trend, because (CH$_3$OH)$_2$ is formed at high temperatures (Garrod et al. 2008). A possible explanation for this seeming contradiction is that less luminous sources might experience high temperatures on time scales, that are just long enough for (CH$_2$OH)$_2$ to form, but not long enough for (CH$_3$OH)$_2$ to be destroyed again. Another possible explanation is that the initial ice composition affects the abundance ratio. While the HCOOCH$_3$/CH$_2$OHCHO ratio is independent of initial ice composition, the formation of (CH$_3$OH)$_2$ is strongly correlated to the CH$_3$OH:CO composition of the ice (Öberg et al. 2009). Öberg et al. (2009) show that pure CH$_3$OH ice enhances the (CH$_3$OH)$_2$ abundance as compared to ice mixes containing CO. This is in agreement with the predictions by Garrod et al. (2008).
Fig. 3. Schematic bar plot of HCOOCH$_3$/CH$_2$OHCHO (top) and HCOOCH$_3$/CH$_2$OHCHO$_2$ (bottom) against $L_{bol}$. The sources from Table 4 have been plotted in descending order of luminosity from left to right on the x-axis, but not to scale, and the sources have been grouped into high-mass sources (blue), intermediate-mass protostar (red) and low-mass protostars (green). The white bars for four of the high-mass sources are upper or lower levels, which is indicated by the direction of the arrow. The luminosity for the top plot spans from Sgr B2(N) with $L_{bol} = 10^7 L_{\odot}$ to IRAS NGC 1333 4A with $L_{bol} = 7.7 L_{\odot}$, while it spans from W51/e2 with $L_{bol} = 4.7 \times 10^6 L_{\odot}$ to IRAS NGC 1333 4A with $L_{bol} = 20 L_{\odot}$ in the bottom plot.

where the (CH$_2$OH)$_2$ abundance actually drops two to three magnitudes when the initial CH$_3$OH ice-composition in their model is reduced by a factor of 10. However, to date there is no observational evidence that the ice contents on the grains vary in any statistically significant way from high-mass protostars to low-mass protostars (Öberg et al. 2011).

Until recently it has been speculated that a high (CH$_2$OH)$_2$/CH$_2$OHCHO ratio is a specific property of comets (Biver et al. 2014). But since Coutens et al. (2015) report a value of around five for a low-mass protostar, and both we and Brouillet et al. (2015) report lower limits of $>6$--16 for high-mass sources, then a (CH$_2$OH)$_2$/CH$_2$OHCHO ratio greater than three can be expected to be observed in other sources as well.

5. Conclusions

In summary, we have tentatively detected (CH$_2$OH)$_2$ in G34.3+0.2 for the first time, and our tentative detection in W51/e2 confirms the previous marginally detection by Kalenskii & Johansson (2010). In addition, we derived upper limits for the column density of CH$_2$OHCHO emission in both sources. From these data we determined the relative abundance ratios of (CH$_2$OH)$_2$, HCOOCH$_3$, and CH$_2$OHCHO and compared these to measurements from the literature covering a wide range of source environments and luminosities. The data show what appears to be a correlation between source luminosity and HCOOCH$_3$/CH$_2$OH$_2$, as well as HCOOCH$_3$/CH$_2$OHCHO. This apparent correlation is proposed to be a consequence of the relative time scales each source spends at different temperature ranges in their evolution. Using the upper limit for the column density of CH$_2$OHCHO gives a lower limit for (CH$_2$OH)$_2$/CH$_2$OHCHO of $>16$ and $>6$ for W51/2 and G34.3+0.2, respectively. These results, together with an upper limit of $>12$ for Orion-KL (Brouillet et al. 2015) and (CH$_2$OH)$_2$/CH$_2$OHCHO = 5 for IRAS NGC 1333 2A (Coutens et al. 2015), shows that one can expect to find a high (CH$_2$OH)$_2$/CH$_2$OHCHO abundance ratio in multiple types of environments.

Additional systematic surveys of these and other relevant molecules in additional sources, as well as more model and laboratory work, is needed to fully constrain the formation pathway of complex molecules. In particular, the Atacama Large Millimeter/submillimeter Array (ALMA) shows great potential for successfully revealing the formation processes with its high sensitivity and resolution, making it possible to map the relative spatial distributions of these sources.

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Appendix A: Reference model

Table A.1. Column densities of species in our reference model.

| Molecule   | G34.3+0.2 [cm⁻²] | W51/e2 [cm⁻²] |
|------------|-------------------|---------------|
| CH₃OCH₃   | 4 × 10^{16}       | 3 × 10^{17}   |
| HCOOH t    | 1 × 10^{15}       | 1 × 10^{16}   |
| CH₃CHO    | 2 × 10^{15}       | 1 × 10^{16}   |
| CH₃OH     | 1 × 10^{17}       | 3 × 10^{18}   |
| C₂H₅OH    | 1 × 10^{16}       | 1 × 10^{17}   |
| CH₃CN     | 2 × 10^{15}       | 6 × 10^{16}   |

Notes. Estimated column densities of other relevant organic species. These values are used to create synthetic spectra, which serves as a reference model when identifying lines.

Appendix B: Observed and synthetic spectra

Fig. B.1. Synthetic spectra (red: (CH₂OH)₂, yellow: HCOOCH₃, green: CH₂OHCHO, blue: the molecules listed in Table A.1) on top of observed spectrum (black) at 1 mm for W51/e2 in the frequency range ~238–242 GHz.
Fig. B.2. Same as Fig. B.1 but for ~242–246 GHz.
Fig. B.3. Synthetic spectra (red: (CH$_2$OH)$_2$, yellow: HCOOCH$_3$, green: CH$_2$OHCHO, blue: the molecules listed in Table A.1) on top of observed spectrum (black) at 1 mm for G34.3+0.2 in the frequency range $\sim$238–242 GHz.
Fig. B.4. Same as for Fig. B.3 but for ∼242–246 GHz.
Fig. B.5. Synthetic spectra (red: (CH$_2$OH)$_2$, yellow: HCOOCH$_3$, green: CH$_3$OHCHO, blue: the molecules listed in Table A.1) on top of observed spectrum (black) at 3 mm for W51/e2 in the frequency range $\sim$100–103 GHz.
Fig. B.6. Same as for Fig. B.5 but for ~103–106 GHz.
Fig. B.7. Synthetic spectra (red: (CH$_2$OH)$_2$, yellow: HCOOCH$_3$, green: CH$_3$OHCHO, blue: the molecules listed in Table A.1) on top of observed spectrum (black) at 3 mm for G34.3+0.2 in the frequency range $\sim$100–103 GHz.
Fig. B.8. Same as for Fig. B.7 but for $\sim$103–106 GHz.