

MICROWAVE DETECTION OF INTERSTELLAR VINYL ALCOHOL, $\text{CH}_2=\text{CHOH}$

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ABSTRACT

Vinyl alcohol ($\text{CH}_2=\text{CHOH}$) has been detected in emission toward Sagittarius B2N by means of its millimeter-wave rotational transitions. The simplest enol, vinyl alcohol is an important intermediate in many organic chemistry reactions. All three stable isomers of the $\text{C}_2\text{H}_4\text{O}$ family, vinyl alcohol, ethylene oxide ($c\text{-C}_2\text{H}_4\text{O}$), and acetaldehyde ($\text{CH}_3\text{-CHO}$) have now been identified in the interstellar medium, as have the three members of the $\text{C}_2\text{H}_4\text{O}_2$ isomeric group (Hollis, Lovas, and Jewell). These complex species cannot be produced in detected amounts by quiescent gas-phase chemistry models, and grain processes have long been envisioned. Our analysis of the abundances of the six species suggests that evaporation from grains of copious amounts of less complex species such as CH_3OH and H_2CO , followed by gas-phase reactions among the evaporated species, explain the high abundance of four of the species, while isomerization (on grains) of the less stable glycol aldehyde and vinyl alcohol species accounts for their lower abundances. The role of catalysis on grains remains unclear.

Subject headings: ISM: abundances — ISM: individual (Sagittarius B2) — ISM: molecules — line: identification

1. INTRODUCTION

An important question in astrochemistry is the relative role of gas-phase (ion-molecule) and grain processes in forming molecules. Based on detailed models of the relevant reactions, it appears very unlikely that quiescent gas-phase processes can account for “complex” species such as EtOH, EtCN, VyCN, dimethyl ether, methyl formate, acetaldehyde, and formamide. Detailed models are hard to develop for molecule formation on grains because of the uncertain nature of the grains, surface mobilities, desorption processes, and so on, but two types of comparison may establish important guidelines. The first comparison is among species with a common backbone but different degrees of hydrogenation (hence differing numbers of atoms). Thus, the backbone C-C-O can give rise to CCO, HCCO, H_2CCO , VyOH, CH_3CHO , and EtOH. Comparison of families with different backbones may offer clues about the mobility of heavy atoms on grain surfaces. Second, complex molecules can form isomeric families, in which the same number and type of atom can form more than one molecular species. Several isomeric groups have been known in the interstellar medium (ISM) for some time among species believed to form in the gas phase (e.g., HCN/HNC , $\text{CH}_3\text{CN/CH}_3\text{NC}$, and HCCCN/HCCNC/HNCCC). The first interstellar isomeric triplet containing species believed unable to form via quiescent gas-phase processes is that of methyl formate (MeF; CH_3OCHO), acetic acid [AA; $\text{CH}_3\text{C(O)OH}$], and the recently discovered glycol aldehyde (GA; $\text{HO-CH}_2\text{-CHO}$); see Hollis, Lovas, & Jewell (2000). These species are believed to involve grain chemistry. Such isomeric groups have the same generic formula ($\text{C}_2\text{H}_4\text{O}_2$), but the members do not have the same heavy-atom backbone. Relative abundances within an isomeric family may contain information on the rearrangement processes on grains and on the relative desorption efficiencies of the various members.

To explore this possibility, we have assembled lists of iso-

meric families containing some members already identified in the ISM, and we have begun searches for the other members. We selected first the $\text{C}_2\text{H}_4\text{O}$ family, comprised of acetaldehyde [AC; $\text{CH}_3\text{-C(H)=O}$], ethylene oxide (EO; $c\text{-C}_2\text{H}_4\text{O}$), and vinyl alcohol (VA; $\text{CH}_2=\text{CH-OH}$). The first two species have been known in the ISM for some time. Here we report the detection of the third member, vinyl alcohol.

2. VINYL ALCOHOL

Vinyl alcohol (ethenol), the simplest enol, has been extensively studied theoretically (Apeloig 1990). It was proposed as a reaction intermediate more than 100 yr ago (Ehrenmeyer 1881), but it was identified experimentally only in 1976 by Saito (1976), who decomposed ethylene glycol into AC and smaller amounts of EO as well as VA. Theoretically and experimentally, VA is found to be planar and to occur in two conformations, of which the “syn” form is more stable than the “anti” form (see Fig. 1). Among the members of this isomer triplet, AC is the lowest energy isomer, with syn-VA and anti-VA, respectively, 0.65 and 0.745 eV higher and EO more than 1 eV higher than AC. Interestingly, EO is kinetically stable in the laboratory, whereas VA requires unusual conditions for its preparation because it tends to isomerize into AC. How this happens is important in the interstellar context: VA actually has a very high energy barrier to unimolecular rearrangement to AC, but detailed calculations (see Apeloig 1990) show that there are low-energy paths for rearrangement in the presence of other molecules such as H_2O and C_2H_2 , which form a series of intermediate species. Presumably interaction with H_2 , which does not form intermediaries, would not produce rearrangement. Thus, the lifetime of interstellar VA in the gas phase is probably limited by protonation because the calculated proton affinity is high, 211 kcal mol⁻¹, and probably leads directly to protonated AC.

Spectroscopically, the more stable syn-VA has been the object of several microwave studies, with that of Kaushik (1977) providing good coverage up to 120 GHz, which with quartic

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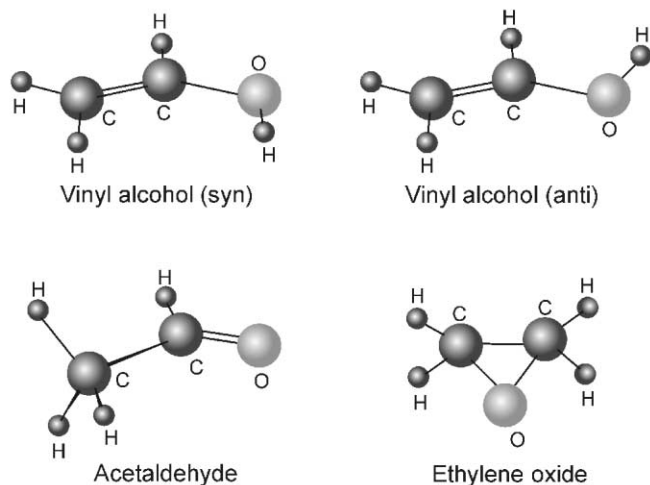


FIG. 1.—Geometry of the C_2H_2O family. Both forms of VA (and EO) are planar, with all atoms lying in the plane of the paper. Only the methyl group on AC is nonplanar, the tapered connectors to the methyl hydrogen atoms indicating relative positions in and out of the plane of the paper.

centrifugal distortion corrections can be extrapolated to the 2 mm band with confidence, using the Watson A—reduced constants and I' representation. Only one study of the less stable anti-VA has been done (Rodler 1985), covering frequencies up to 50 GHz; comparison of our predicted spectrum with an extensive set of measurements again suggests adequate precision in the 2 mm band. Dipole moments are $\mu_a = 0.616$ and $\mu_b = 0.807$ D for syn-VA and $\mu_a = 0.547$ and $\mu_b = 1.702$ D for anti-VA. If syn and anti abundances were the same, b -type transitions should be 4.4 times stronger for anti-VA.

3. OBSERVATIONS AND RESULTS

The observations were made in 2001 May and June with the Kitt Peak 12 m telescope equipped with the dual-channel 3 mm SIS mixer receiver tuned to single sideband and the 256-channel filter-bank spectrometer with 1 MHz resolution. Chopper-vane calibration was used, providing results on the T_R^* scale with an uncertainty of 15% and including corrections for atmospheric extinction and telescope spillover losses but not for error-beam losses or the forward-beam coupling to the source. At 72, 89, 107, 139, and 154 GHz, the FWHP beam sizes are 87", 71", 59", 53", and 41", respectively, while the main-beam efficiencies varied from 0.90 to 0.66. Data were obtained in the position-switching mode with offset 30' west in azimuth.

Our results toward Sagittarius B2N are given in Table 1 and

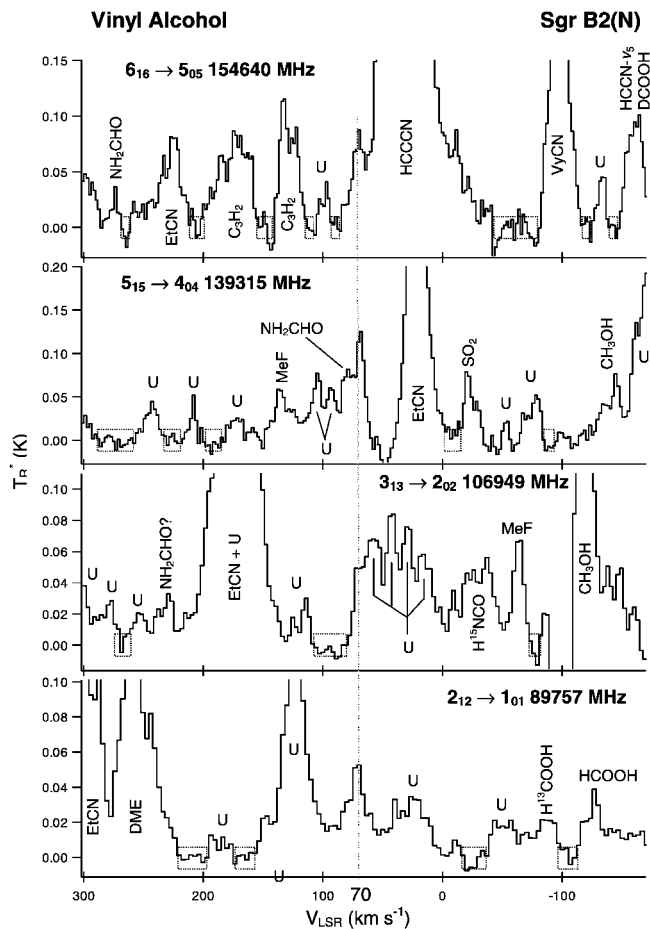


FIG. 2.—VA seen toward Sgr B2N at 1 MHz resolution. The spectra are highly crowded with molecular lines so that the baseline is almost obscured. The theoretical rms noise is 2, 3, 7, and 8 mK for the lowest to highest frequency spectra, respectively. Rest frequencies for the observed transitions are 71830.39, 89757.11, 106949.49, 139315.20, and 154640.52 MHz for anti-VA and 86557.60, 103706.01, 135877.28, and 151085.12 MHz for syn-VA. A velocity of 65.0 km s⁻¹ was assumed.

Figure 2. The higher energy anti-VA species is seen in all five transitions searched, whereas the lower energy syn-VA is seen in only two transitions, as a result both of its lower b -type dipole moment and the presence of contaminating lines in three other transitions. It may also appear that two of the anti-VA transitions are contaminated. Lines of MeF lie close to the $4_{14} \rightarrow 3_{03}$ and $5_{15} \rightarrow 4_{04}$ transitions, but the velocities of these lines, if MeF, would be 71 km s⁻¹, differing distinctly from the MeF velocity of 63.7 km s⁻¹ observed by Maio et al. (1995).

TABLE 1
OBSERVATIONS OF VINYL ALCOHOL TOWARD SGR B2N

Transition	ν (MHz)	T_R^* (mK)	V (km s ⁻¹)	δV (km s ⁻¹)	W (K km s ⁻¹)	E_u (cm ⁻¹)	$S\mu^2$	log L
Anti-VA								
$1_{11} \rightarrow 0_{00}$	71830.39	30	78	11	0.312	0.000	2.90	11.38
$2_{12} \rightarrow 1_{01}$	89757.11	35	72.3	13	0.455	0.648	3.24	11.27
$3_{13} \rightarrow 2_{02}$	106949.49	34	71.3	8	0.272	1.942	5.83	10.85
$4_{14} \rightarrow 3_{03}$	139315.20	119	68.3	8	0.952	6.462	9.05	11.08
$5_{15} \rightarrow 4_{04}$	154460.95	50	71.7	7	0.750	9.680	10.83	10.86
Syn-VA								
$2_{12} \rightarrow 1_{01}$	86557.60	27	70.2	16	0.432	0.651	0.98	11.89
$3_{13} \rightarrow 2_{02}$	103706.01	49	71.7	8	0.392	1.953	1.31	11.67

Furthermore, the energies of these MeF transitions lie much too high according to the detailed excitation models of Turner (1991). The $4_{14} \rightarrow 3_{03}$ line is also confused by a multiplet of NH_2CHO lines that, together with the VA line, have an intensity of 120 mK, while detailed excitation models of NH_2CHO (Turner 1991) predict 90 mK from NH_2CHO alone. The difference of 30 mK, attributed to VA, is precisely as expected based on the intensities of the other VA lines. Unsuccessful searches for the $2_{12} \rightarrow 1_{01}$ and $3_{13} \rightarrow 2_{02}$ lines of anti-VA were also made toward Orion KL.

We have used a “rotation diagram analysis” (Turner 1991) of the five observed lines of anti-VA. For anti-VA, we find $T_{\text{rot}} = 11.6^{+13.5}_{-4.7}$ K and $N = (2.4 \pm 0.6) \times 10^{13} \text{ cm}^{-2}$. For syn-VA, the two transitions listed in Table 1 yield $N = 2.0 \times 10^{14} \text{ cm}^{-2}$, which is a highly uncertain value, but of order 10 times the anti-VA column depth. T_{rot} is not determined and is assigned the anti-VA value. The total abundance of VA is therefore $2.2 \times 10^{14} \text{ cm}^{-2}$.

It is difficult to compare the Sgr B2N abundances within the $\text{C}_2\text{H}_4\text{O}$ isomer triplet, even though all three species have been observed with similar telescopes. For EO toward Sgr B2N, Dickens et al. (1997) find that $N = (3.3 \pm 0.9) \times 10^{14} \text{ cm}^{-2}$ and $T_{\text{rot}} = 18 \pm 3$ K. In a study of seven hot star-forming cores, Nummelin et al. (1998) find that $N = (0.6\text{--}1.0) \times 10^{14} \text{ cm}^{-2}$ and $T_{\text{rot}} = 16\text{--}38$ K. For AC toward Sgr B2, Turner (1991) finds that $N = 2.2^{+1.1}_{-0.8} \times 10^{14} \text{ cm}^{-2}$ and $T_{\text{rot}} = 9.4$ K, while toward seven hot star-forming cores, Nummelin et al. (1998) find that $N = (2\text{--}5) \times 10^{14} \text{ cm}^{-2}$ and $T_{\text{rot}} = 16\text{--}38$ K. All these studies use the same LTE, optically thin analysis and give highly similar results. For Sgr B2N, they give abundance ratios of VA/EO/AC = 1/1.5/1, a surprising result in view of the much stronger lines exhibited by AC than by VA and in view of the likely rapid isomerization of VA to AC under terrestrial conditions. However, Turner (1991) cited extensive evidence for much higher AC abundances, based on observed intensity ratios of weak to strong transitions that exceeded those consistent with small opacities by large factors. The suitable correction factor for AC resulted in $N = (0.7\text{--}3.0) \times 10^{17} \text{ cm}^{-2}$ —a factor of 300–1000 times larger than the optically thin values. Thus, the abundance ratios for the members VA, ethylene oxide, and AC of the $\text{C}_2\text{H}_4\text{O}$ family are either 1/1.5/1 if all three species are optically thin or 1/1.5/800 if AC is optically thick.

It is useful to compare abundances for the $\text{C}_2\text{H}_4\text{O}_2$ family with those of our $\text{C}_2\text{H}_4\text{O}$ group. The ratio GA/AA/MeF = 4/1/26 is given by Hollis et al. (2000) on the assumption that all three species are located in the small (5”) hot core component of the Large Molecular Heimat (LMH). Subsequent observations of GA with the BIMA array show GA to be extended in a 60” region well outside the small hot core (Hollis et al. 2001), resulting in a revised abundance ratio of 1/2/52. Array observations also give $N = 1.9 \times 10^{17} \text{ cm}^{-2}$ for MeF, in good agreement with the result of Turner (1991), who obtained $N = (0.7\text{--}1.4) \times 10^{17} \text{ cm}^{-2}$ after correcting the LTE analysis for opacity effects. A large column density of $7 \times 10^{16} \text{ cm}^{-2}$ was also obtained for AA (Mehring et al. 1997). Single-dish data provide a good measure of the average line-of-sight abundance ratio if the emission sources for different molecules are smaller than the telescope beam. This is clearly not the case for GA. For VA, we note in Table 1 a probable trend of decreasing line widths as beam size decreases, which would suggest that VA is also extended beyond the LMH. Just such a very strong trend may also be seen in the EO data (Table 1 in Dickens et al. 1997).

Finally, the velocities are important in formulating a model. The species MeF, AA, AC, and EO (and dimethyl ether [DME])

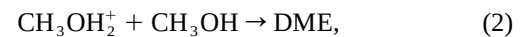
all have velocities of $63.4^{+0.6}_{-1.4} \text{ km s}^{-1}$, while GA and VA have distinctly different velocities, 71.5 and 70.9, respectively (EtOH is at 59.8 km s^{-1}).

4. DISCUSSION

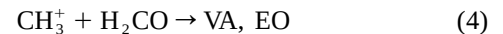
Of the six species comprising the $\text{C}_2\text{H}_4\text{O}$ and $\text{C}_2\text{H}_4\text{O}_2$ isomeric triplets, it appears from the velocities that four of them (EO, AC, AA, and MeF) occur only within the hot, 5” LMH core, coincident with the dust, and are formed either by grain processes or by the warm gas-phase chemistry of the products of sudden evaporation of grain mantles. The other two species (GA and VA) are of much lower abundance and appear to reside in the cooler outer regions of the LMH. Quiescent, purely gas-phase chemical models (Lee, Bettens, & Herbst 1996; Turner, Terzieva, & Herbst 1999) fail to produce observed abundances of these species by orders of magnitude, but the following gas-phase processes may produce them if the reactant abundances are high enough:



(see Caselli, Hasagawa, & Herbst 1993),



(see Dickens et al. 1997), and



(this work).

Reaction (1), which produces the $\text{C}_2\text{H}_4\text{O}_2$ family, may have a high barrier (E. Herbst 2001, private communication of work by H. Mollendahl), but this may be surmounted if the LMH core is hot enough. The product ion could be $\text{H}_2\text{CCOOCH}_3^+$, leading to MeF, $\text{H}_3\text{CCOOH}_2^+$, which forms AA, or $\text{HOCH}_2\text{CHOH}^+$, which forms GA. The latter is unlikely because of the extensive rearrangement of bonds. Similarly, the $\text{C}_2\text{H}_4\text{O}$ family could be produced by reactions (3) and (4) or by $\text{CH}_3^+ + \text{EtOH} \rightarrow \text{C}_2\text{H}_5\text{O}^+ + \text{CH}_4$ (Dickens et al. 1997). Of these processes, reaction (3) very likely forms AC rather than EO or VA because no bond rearrangement is necessary. Assuming the above reactions as written, one can produce the observed velocities and abundances of all six isomeric species as follows. MeF, AA, and AC are produced in the hot core at high abundance by reactions (1) and (3). VA is produced in the cooler halo at lower abundance. To produce EO at 71 km s^{-1} rather than at 64 km s^{-1} , reaction (4) cannot produce EO, while reaction (3) must operate in the hot core (64 km s^{-1}) but not in the cooler halo (71 km s^{-1}), implying an energy barrier for the process. Furthermore, EO must not isomerize in the hot core. To explain GA in the halo (71 km s^{-1}) but not in the core (64 km s^{-1}), GA must isomerize in the hot dense core but not in the less dense halo. Reaction (2) would operate in both the core and the halo but would operate less efficiently in the halo owing to a slower evaporation rate for grain mantles. Note that DME is also explained by this scheme but that EtOH is not.

If the assumptions we have made are borne out, what is the role of grains in the chemistry of complex species? First, grain catalysis of some of the $\text{C}_2\text{H}_4\text{O}$ and $\text{C}_2\text{H}_4\text{O}_2$ species is not precluded, for example, $\text{HCOOH} + \text{CH}_3\text{OH} \rightarrow \text{MeF} + \text{H}_2\text{O}$, and $2\text{H}_2\text{CO} \rightarrow \text{HOCH}_2\text{CHO}$ (GA). These reactions have high

barriers and hence can proceed only in solution or on surfaces. However, for the C_2H_4O family, we have not identified exothermic neutral-neutral reactions that can produce on grains the C_2H_4O species with the large abundances required. Second, gas-phase chemistry as described has not explained EtOH, EtCN, EtNC, or VyCN. Fully saturated species such as EtOH and EtCN probably form on grains, and VyCN is subsequently formed in the gas phase from desorbed EtCN (Caselli et al. 1993). For N-chemistry, there seem to be no analogs to CH_3OH and H_2CO for producing complex gas-phase species from abundant desorbed species. Thus, grain processes may be more important for N species. Third, isomeric conversion is likely efficient on grain surfaces or during the desorption process. We suggest that VA and GA suffer rapid isomerization in the dense core, which explains why they are seen only in the halo. Note that EO and GA, not VA, are the highest energy species in their respective isomeric families but that isomerization depends on the details of interactions as well as the energy of the species and that VA is particularly susceptible to conversion by H_2O .

Although interstellar isomerism appears common, we would not conclude with Hollis et al. (2000) that it suggests that molecular formation routes for such species have common precursors. First, detailed chemical models often show the contrary, e.g., in the case of HCN and HNC (Turner, Pirogov, & Minh 1997), *c*- C_3H and *l*- C_3H , *c*- C_3H_2 and *l*- C_3H_2 (Turner, Herbst, & Terzieva 2000), and the present cases of C_2H_4O and

$C_2H_4O_2$ species according to our arguments. Rather than revealing much about grain processes of the sort argued by Millar et al. (1988), our results seem instead to support the notion that evaporation of grain mantles in hot, dense star-forming regions is the principal mechanism affecting the chemistry of complex species. Specifically, assuming only that CH_3OH and H_2CO remain intact during evaporative desorption, the aforementioned gas-phase reactions can in principle produce seven of the eight complex species containing H, C, O, viz., the six species studied here, and DME. We may hope for more such trends, for the problem of understanding specific gas-phase reactions is much more tractable than that of isolating the properties of grain catalysis. We need more isomeric families of the type $C_nH_mO_p$ to test the boundaries of complex gas-phase chemistry fed by evaporation of grain mantles. We suspect that grain surface processes will be more important for complex N-bearing species than for the O species. Thus, we plan to search for other isomeric families such as CH_2N_2 , C_2H_2O , CH_3NO , C_2H_3N , C_3H_3N , C_3H_4 , and C_3H_5N , which have up to seven members, most of which have at least one member known in the ISM.

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