The Formation of $C_3O_3H_6$ Structural Isomers in the Gas Phase through Barrierless Pathways: Formation and Spectroscopic Characterization of Methoxy Acetic Acid

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Abstract

Gas phase formation processes feasible at low temperatures are determined theoretically for 38 isomers obeying the $C_3O_3H_6$ empirical formula, one of them, the simplest ketose dihydroxyacetone, has been observed in gas phase sources. A preliminary search for isomeric forms first targets ethoxy formic acid ($C_2H_5-O-COOH$) as the most stable isomer followed by lactic acid. Profiles corresponding to the minimum energy pathways reveal that the favored conformers of 14 of these isomers can be formed in the gas phase through 29 barrierless processes involving the OH^* , CH_3O^* , HCO^* , CH_3^* , CH_2OH , $HCOO^*$, and $OHCO^*$ radicals, all of them observed in the interstellar medium. Kinetic rates are provided at 200, 298, and 500 K, confirming the suitability of 16 processes at low temperatures. Faster processes involve the OH hydroxyl radical whereas, to a lesser degree, the processes involving the $HOCO$ radical and the methoxy methyl radical CH_3O^* , are quite significant. Spectroscopic parameters (rovibrational and torsional) are obtained for methoxy acetic acid (CH_3-O-CH_2COOH) for which two low-lying isoenergetic conformers can be produced from the $CH_3OCH_2^*$ radical predicted to be a precursor of abundant observed molecules. Profiles and spectroscopic properties make methoxy acetic acid a good candidate to be detected in the gas phase of extraterrestrial sources.

Unified Astronomy Thesaurus concepts: [Molecular physics \(2058\)](#); [Molecule formation \(2076\)](#); [Molecular spectroscopy \(2095\)](#)

Supporting material: figure set, machine-readable table

1. Introduction

As has already been emphasized in previous works (Herbst & van Dishoeck 2009; Lovas et al. 2010), isomerism plays a remarkable function in the gas-phase chemistry. Structural isomerism is extensive in interstellar clouds (Lovas et al. 2010), where the detection of new species is often followed by the observation of its isomers. In complex organic molecules (COMs), isomers can share fragments and functional groups and can be derived from the same reagents in formation processes of increasing complexity.

Many COMs have been observed in extraterrestrial gas phase sources where they are considered organic precursors (Herbst & van Dishoeck 2009). Some of them are objects of frequent studies in the gas phase because they are abundant in the interstellar medium or they are listed as volatile organic compounds (VOCs), taking part in important processes of the Earth atmosphere as precursors for secondary organic aerosols (Kroll & Seinfeld 2008; Nozière et al. 2015). The participation of COMs in tropospheric ozone formation processes and atmosphere radical cycles is generally accepted (Atkinson et al. 2004). To understand their chemical lifecycles, the possible formation routes, as well as their contribution to other chemical processes have been extensively studied (Atkinson et al. 2004).

Although, it is generally accepted that the formation of COMs in the interstellar medium is more viable on ice mantles (Fedoseev et al. 2017), gas-phase processes cannot be ignored (Laas et al. 2011; Cernicharo et al. 2012; Balucani et al. 2015;

Eckhardt et al. 2018; Skouteris et al. 2018; Cooke & Sims 2019). In a recent paper, Balucani et al. (2015) recognized that grain-surface chemistry is not necessarily present in the formation of all the COMs. They verified that gas-phase reactions are major actors in the formation of methyl formate, dimethyl ether, and the methoxy radical in cold gas. The role of gas-phase neutral processes, missing in previous astrochemistry databases, has been evidenced in an extended study of the gas-phase formation of glycolaldehyde, acetic acid, and formic acid (Skouteris et al. 2018).

In the formation of COMs, barrierless bimolecular reactions can play an important role (Laas et al. 2011; Cernicharo et al. 2012; Barone et al. 2015; Eckhardt et al. 2018; Cooke & Sims 2019). Mostly, these processes involve radicals and ions. Their study can be made using experimental techniques that are not always feasible (Cooke & Sims 2019). Experiments are a particular challenge for reactions involving volatile organic species that can condense and dimerize at low temperature, or for reactions involving only ions and radicals. For many systems, theoretical procedures provide unique suitable information. Thus, quantum chemical calculations have been employed to demonstrate that formamide can be formed from the NH_2 and H_2CO precursors through a barrierless process (Barone et al. 2015).

Radicals and molecular fragments are ubiquitous in extraterrestrial environments. First detected species were small radicals. Their formation is frequently related to ionization and photodissociation processes, or reactions in solid surfaces (Kaiser 2002).

In a previous work, we attended the spectroscopy and the formation of $C_2O_2H_4$ isomers starting by 62 reactants (Senent 2001a, 2004; Senent et al. 2005; Gámez et al. 2019a). With this

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new paper, devoted to the $C_3O_3H_6$ family, we want to take a step forward in complexity by taking care of larger species. Many possible isomers containing organic acid, alcohols, ketones, peroxides, etc., take part in this new family for which a limited number of previous studies is available. The main objective of the present work is to find spectroscopic parameters and reliable formation pathways in low density environments at low temperatures with participation of free radicals. In this paper, we use accurate theoretical procedures suitable for the study of kinetic rates and large amplitude vibrations. Density functional theory and highly correlated ab initio calculations are combined to obtain equilibrium geometries and potential energy surfaces.

The $C_3O_3H_6$ family relevance for the interstellar chemistry has attracted a crescent interest although low abundances are expected and detections are predicted to occur within the confusion limit (Lovas et al. 2010). The interest has been satisfied by the discovery in the gas phase sources of one of the molecules in the series, the simplest ketose dihydroxyacetone ($CH_2OH-CO-CH_2OH$) (Widicus-Weaver & Blake 2005; Apponi et al. 2006b), while the search for the three-carbon sugar glyceraldehyde ($CH_2OH-CHOH-COH$) has been unproductive (Hollis et al. 2004). Efficient mechanisms increasing the number of C–C bonds responsible for the formation of detected species such as glycolaldehyde and ethylene glycol also holds the potential to form the next larger members in these series, glyceraldehyde and glycerol (Fedoseev et al. 2017).

To our knowledge, few published works pay attention to the formation in the gas phase and spectroscopy of the $C_3O_3H_6$ isomers, although the detection of new species requires a previous spectroscopic characterization at the laboratory level. Radio-astronomy represents the main technique for the search of extraterrestrial or rare abundant atmospheric COMs. Its application implies previous measurements and assignments of the rotational spectra in the microwave, millimeter, and submillimeter regions. In species showing nonrigidity, assignments infer to attend to the large amplitude motions, which are involved in the conformer interconversion that can occur at very low temperatures. As far as we know, with the exception of dihydroxyacetone (Lovas et al. 2003; Widicus-Weaver et al. 2005), glyceraldehyde (Lovas et al. 2003), lactic acid (Pszczółkowski et al. 2005; Apponi et al. 2006a), methyl glycolate (Meyer et al. 1989; Jarmelo et al. 2000), and dimethyl carbonate (McGuire et al. 2011) measurements of the infrared and microwave spectra of the $C_3O_3H_6$ isomers are not available. In addition, a low resolution spectrum of methoxy acetic acid (MAA, CH_3O-CH_2-COOH) is available (NIST SRD.), and several structural theoretical works have been published (Vogt et al. 2009; Lattalais et al. 2010; Karton & Talbi 2014; Boussessi et al. 2015).

MAA remains as an uncharacterized species, although it has been taken into account in a previous list of $C_3O_3H_6$ isomers (Lovas et al. 2010) and represents a relatively stable isomer. Throughout the work, we point out the properties that support its relevance. To cover the lack of experimental and theoretical data, as a second goal of the present paper, we include a spectroscopic study of MAA providing accurate parameters describing the far-infrared region. For this goal, a theoretical variational model that takes into consideration the minimum interconversion, is employed.

2. Results and Discussion

2.1. Electronic Structure Calculations

This paper is focused on reactivity and spectroscopy. The kinetic rate constants were computed using the code POLY-RATE (Zheng et al. 2017). The spectroscopic constants were obtained using the vibrational second-order perturbation theory (VPT2; Barone 2007) and a variational procedure implemented in our code ENEDIM (Senent 1998a, 1998b, 2001b). In all cases, the starting points were geometries and potential energy surfaces computed using highly correlated ab initio calculations or density functional theory.

The electronic structure calculations were achieved using both codes: Gaussian (Frisch et al. 2016) and Molpro (Werner et al. 2012). Different levels of theory were employed and combined searching for a coherent balance between computational efficiency and accuracy. The number of involved geometries and the necessary precision, different for the different properties, were considered.

The search for stable geometries obeying the $C_3O_3H_6$ empirical formula was performed using the second-order Möller–Plesset theory (MP2) implemented in Gaussian and the aug-cc-pVTZ basis set (denoted by AVTZ; Kendall et al. 1992). The search for the gas phase formation processes was performed using the density functional theory implemented in Gaussian, the M052X functional (Zhao et al. 2006), and the 6-311+G(d,p) basis set (Krishnan et al. 1980).

The work requires very accurate properties of methoxy acetic acid, suitable for further assignments of experimental rotational spectra. For this reason, the eight equilibrium geometries were computed with explicitly correlated coupled cluster theory with single and double substitutions augmented by a perturbative treatment of triple excitations (CCSD(T)-F12b) (Werner et al. 2007; Knizia et al. 2009) implemented in Molpro using the default options and the AVTZ atomic orbitals and the corresponding functions for the density fitting and the resolutions of the identity. In previous papers (Spackman et al. 2016), the accuracy of CCSD(T)-F12 has been confirmed and compared with CCSD(T) computations. In addition, previous calculations (Hochlaf et al. 2015) show the ability of the explicitly correlated methods to reproduce good potential shapes. For the spectroscopic parameters, the accuracy of CCSD(T)-F12/AVTZ is similar to CCSD(T)/AV5Z.

The core-valence electron correlation effects on the rotational constants were introduced using CCSD(T) (Hampel et al. 1992) and the cc-pCVDZ basis set (denoted by CVDZ; Woon & Dunning 1995). Anharmonic rovibrational parameters were derived using VPT2 implemented in Gaussian and an anharmonic MP2/cc-pVTZ force field.

Since VPT2 theory does not take into consideration the minimum interconversion, the far-infrared region and the torsional transitions are analyzed using a variational three-dimensional procedure. For this purpose, MP2/AVTZ potential energy surfaces were computed and later on, they were vibrationally corrected at the B3LYP/AVTZ level of theory.

2.2. The $C_3O_3H_6$ Family

The work was initiated by the search for all the possible $C_3O_3H_6$ isomeric structures. Given the large number of possible arrangements of 12 atoms, initial geometries were produced using a standardized computing tool (Isomer generator.). The procedure provides 102 structures of a reasonable stability. To

Table 1
MP2/AVTZ Relative Energies (E_r , in cm^{-1}), Equilibrium Rotational Constants (A_e , B_e , and C_e , in MHz), and Dipole Moment (μ , in D) of the Most Stable Conformers of the $\text{C}_3\text{O}_3\text{H}_6$ Isomers

Isomers (ISO)	E_r	A_e	B_e	C_e	μ	Previous Works
1 $\text{C}_2\text{H}_5\text{-O-COOH}$	0 ^a	7741.9	2452.9	2152.0	0.882	
2 $\text{CH}_3\text{-CHOH-COOH}$	1019	5143.1	3311.8	2262.0	2.512	Pszczółkowski et al. (2005), Apponi et al. (2006a), Lovas et al. (2010)
3 $\text{OHCH}_2\text{-CH}_2\text{-COOH}$	2041	7443.3	2448.6	1961.6	0.471	Lovas et al. (2010)
4 $\text{CH}_3\text{-CO-OCH}_2\text{OH}$	2635	7867.8	2544.8	2149.1	2.224	Lovas et al. (2010)
5 $\text{CH}_3\text{-CHOH-OCHO}$	3084	7448.2	2726.9	2186.5	1.901	
6 $\text{CH}_3\text{O-CO-OCH}_3$	4884	10380.0	2387.4	1989.4	0.350	Lovas et al. (2010), McGuire et al. (2011), Boussessi et al. (2015)
7 $\text{CH}_3\text{O-CO-CH}_2\text{OH}$	5895	9999.8	2221.6	1860.0	3.070	Meyer et al. (1989), Jarmelo et al. (2000), Lovas et al. (2010)
8 $\text{CH}_3\text{-CO-CH(OH)}_2$	6170	5145.4	3301.5	2266.7	2.804	
9 t- $\text{CH}_3\text{O-CH}_2\text{-COOH}$	6781	9442.1	2097.1	1753.9	5.696	Lovas et al. (2010), NIST SRD
c- $\text{CH}_3\text{O-CH}_2\text{-COOH}$	6840	7583.8	2396.7	2041.7	2.299	
10 $\text{OHCH}_2\text{-CH}_2\text{-OCHO}$	7131	5667.6	3147.3	2203.7	3.361	Lovas et al. (2010)
11 $\text{CH}_3\text{-C(OH)}_2\text{-CHO}$	7181	5084.2	2938.4	2902.6	2.691	
12 $\text{CH(OH)}_2\text{-CH}_2\text{-CHO}$	7482	5354.3	2952.2	2662.2	2.984	Atkinson et al. (2004), Kroll & Seinfeld (2008), Fedoseev et al. (2017), Cooke & Sims (2019)
13 $\text{OHCH}_2\text{-CO-CH}_2\text{OH}$	9357	9828.0	2068.0	1745.5	2.241	Lovas et al. (2003), Widicus-Weaver & Blake (2005), Widicus-Weaver et al. (2005), Apponi et al. (2006b), Vogt et al. (2009), Lovas et al. (2010)
14 $\text{CH}_3\text{O-CH}_2\text{-OCOH}$	9798	6331.1	2809.4	2236.4	0.607	Lovas et al. (2010)
15 $\text{OHCH}_2\text{-CHOH-CHO}$	10018	5480.0	2817.5	2436.2	2.693	Lovas et al. (2003), Hollis et al. (2004), Widicus-Weaver et al. (2005), Vogt et al. (2009), Lovas et al. (2010)
16 $\text{CH}_3\text{-CHOH-C(OH)}_2$	10478	5086.1	3334.0	2049.2	1.038	
17 $\text{OHCH}_2\text{-CH=C(OH)}_2$	10757	7674.9	2486.1	1977.7	3.527	
18 OHCH=CH-CH(OH)_2	11068	8207.6	1957.2	1684.2	0.909	
19 $\text{CH}_3\text{O-CHOH-CHO}$	12814	8155.5	2398.7	2007.0	2.751	
20 $\text{OHCH}_2\text{-COH-CHOH}$	13000	8070.1	2129.9	1832.1	2.640	
21 $\text{OHCH}_2\text{-O-CH}_2\text{-CHO}$	13091	5760.3	3076.5	2337.1	3.001	
22 $\text{OHCH=CH-O-CH}_2\text{OH}$	15177	12654.4	1744.5	1596.9	1.808	
23 $\text{CH}_3\text{O-CH=C(OH)}_2$	15722	8656.2	2148.7	1851.7	1.202	
24 $\text{CH}_3\text{O-COH=CHOH}$	16426	7704.8	2314.5	1954.7	2.528	
25 $\text{C}_2\text{H}_5\text{-COOOH}$	22999	9066.5	2205.7	1890.3	2.769	Lovas et al. (2010)
26 $\text{CH}_3\text{-CO(OO-CH}_3\text{)}$	26870	7873.4	2463.1	2131.5	3.496	
27 $\text{C}_2\text{H}_5\text{-O-O-CHO}$	28210	8360.5	2177.6	1900.4	2.334	
28 $\text{CH}_3\text{-CO-CH}_2\text{OOH}$	29919	7437.8	2450.7	2042.5	4.338	
29 $\text{CH}_3\text{-CH(OOH)-CHO}$	31166	4358.3	3716.0	2234.7	3.645	
30 $\text{CHO-CH}_2\text{-CH}_2\text{-OOH}$	32142	5332.5	3165.2	2156.1	5.168	
31 $\text{C}_2\text{H}_5\text{-COH-OOH}$	33226	5687.0	2751.0	1988.0	2.134	
32 $\text{CH}_3\text{-C(OOH)-CHOH}$	33583	4713.0	3097.2	2045.6	2.310	
33 $\text{OHCH=CH-CH}_2\text{OOH}$	34108	5708.6	2913.9	2163.7	1.641	
34 $\text{CH}_3\text{-COH-CHOOH}$	34678	7412.8	2118.6	1816.0	1.361	
35 $\text{CH}_3\text{O-O-CH}_2\text{-CHO}$	35535	9602.5	1851.2	1667.4	3.316	
36 $\text{OHCH}_2\text{-CH=CH-OOH}$	35872	5379.0	3198.1	2299.7	3.397	
37 $\text{CH}_3\text{O-O-CH=CHOH}$	37685	10353.7	1863.6	1713.6	1.744	
38 $\text{CH}_3\text{O-CH=CH-OOH}$	40670	7872.1	2262.1	1869.6	4.473	

Note.

^a $E_0 = -343.079283$ au.

establish some limits to the present work, we retained the 38 most stable nonrigid molecules. Each selected isomer presents various equilibrium geometries (conformers) transforming through internal rotation. Structures containing carbenes or carbon cycles were neglected. The MP2/AVTZ relative energies of the most stable conformers and the corresponding equilibrium rotational constants and dipole moments are summarized in Table 1. All the 38 isomers present real harmonic fundamentals at the MP2/AVTZ level of theory. The energies shown in Table 1 correspond to the most stable conformer of each isomer.

The set shown in Table 1 contains all the structures that were objects of previous theoretical searches (Vogt et al. 2009; Lattelais et al. 2010; Lovas et al. 2010; Karton & Talbi 2014), as well as new species. References attend to theoretical and experimental inquiries as well as to astrophysical searches and detections. The most complete list of isomers was provided by

Lovas et al. in (2010) who describe 11 linear structures and two rings. In all the previous works (Vogt et al. 2009; Lattelais et al. 2010; Lovas et al. 2010; Karton & Talbi 2014), lactic acid, $\text{CH}_3\text{-CHOH-COOH}$, was considered to be the most stable $\text{C}_3\text{O}_3\text{H}_6$ structure. However, our methodology points to another acid compound, ethoxy formic acid, ($\text{C}_2\text{H}_5\text{-O-COOH}$, ISO1), as the most stable form, 1019 cm^{-1} (2.9 Kcal mol^{-1}) below the lactic acid (see Figure 1). Although stability does not assure detectability (Lattelais et al. 2010), it represents a major factor to support the search for the first isomer, ISO1, although the permanent dipole moment (0.882 D) is relatively small.

The 14 low-lying isomers can be considered good candidates for astrophysical searches and further experimental works. However, to our knowledge, for four of them (the two ethers, $\text{C}_2\text{H}_5\text{-O-COOH}$ (ISO1) and $\text{CH}_3\text{-CHOH-OCHO}$ (ISO5), and the two diols labeled as ISO8 and ISO11), previous works are

not available and they are not listed as relevant isomeric forms. In addition, very little attention has been given to methoxy acetic acid (MAA, ISO9) contemplated in previous lists (Lovas et al. 2010). This isomeric form presents a considerable stability and promising spectroscopic properties for detection, such as a significant permanent dipole moment. In the present paper, we pay attention to MAA considering two points of view, probably formation processes and spectroscopic properties.

Among the 38 structures, more of the less stable isomers are the peroxi compounds. Some of them can be relevant for terrestrial atmosphere studies involving VOC's and radicals. Unsaturated structures of low stability complete the set of Table 1.

2.3. Barrierless Formation Processes in the Gas-phase

Our purpose is to find gas-phase reactions qualified for competing with formation processes on the ice surface. The most efficient ones at low temperatures and pressures are those following barrierless pathways involving low stability species such as reactive radicals. To establish some limits to the present work, we have chosen the set of reactants shown in Table 2. They obey the following conditions:

- (1) They enclose the atomic elements H, C, and O, constituents of the isomers.
- (2) They contain at most 11 atoms because the objective is to select chemical routes of increasing molecular complexity.
- (3) They have been detected in the gas phase of the ISM, or at least, they are listed as probably detectable species.

All the possible chemical routes starting from the selected reactants are automatically generated by the original computer code STAR (Searching Tool for Astrochemical Reactions; Gómez et al. 2019b). This statistical code contains a broad comprehensive molecular database. An implemented algorithm searches for all the likely combinations of reactants leading to a specific molecular species. The processes producing the desired molecule and some by-products are automatically rejected if the viability of these last species cannot be confirmed. The code selects only the exergonic processes for which the change of Gibbs free energies is negative ($\Delta G < 0$).

Two additional conditions are applied:

- (1) The selected processes must occur following a limited number of steps.
- (2) The activation energies must be relatively low.

The number of steps is considered to concur with the sum of breaking and forming bonds. To quantify them, the MNES (Maximum number of Necessary Elementary Steps) parameter is defined. In principle, 127 exergonic processes are derived from STAR, which are provided as supporting data in Table A1. For all of them, ΔG was computed optimizing the geometry with the CBS-QB3 procedure (Montgomery et al. 1999), the CBS-Q (Nyden & Petersson 1981) complete basis set model implemented in Gaussian and modified for the use of the B3LYP hybrid density functional. Although the resulting ΔG shown in Table A1 were computed at room temperature and room pressure, which are not the conditions of the stellar medium sources, the computed parameter allows us to establish the exergonic character of the processes. Whereas ΔG depends of the environment conditions, a variation of the ΔG sign is not

expected at low temperatures and pressures due to the important contribution of the enthalpy variation to ΔG .

Finally, 47 final exergonic reactions for which $MNES < 3$ were found, although 15 of them are restricted by relevant energy barriers or imply endergonic steps. 29 processes categorized as one step exergonic reactions, are summarized in Table 3 and emphasized in italics in the Table A1 of Appendix.

All these processes lead to the formation of the most stable conformer of each isomer, although for methoxy acetic acid, the formation of two minimum energy structures is contemplated. In MAA, two conformers C1 and T1 compete in stability. At low temperatures, their interconversion is hindered by a relatively high barrier.

Profiles support that the preferred conformers of the 14 low-lying isomers can be formed in the gas phase through barrierless processes involving seven radicals (OH^* , CH_3O^* , HCO^* , CH_3^* , CH_2OH , HCOO^* , and OHCO^*), all of them observed in the interstellar medium. Energy profiles proving these finding are provided as a figure set available in the Appendix, see Figure A1 in the online journal. They represent minimum energy paths computed at the M052X/6-311+G(d,p) level of theory. They were obtained by approaching the two reactants from the asymptotic region. The distance between two selected points of the two reactants, s , was defined as reaction coordinate. The remaining coordinates were allowed to be relaxed in all the geometries along the path.

2.4. Kinetic Rate Constants

The kinetic rate constants summarized in Table 3 were evaluated using the single-faceted variable-reaction-coordinate variational transition-state theory (VRC-VTST; Georgievskii & Klippenstein 2003; Bao & Truhlar 2017) implemented in POLYRATE (Zheng et al. 2017). The rate constants obey the following expression:

$$k(T, s) = \frac{\hbar^2}{2\pi} g_e \frac{\sigma_1 \sigma_2}{\sigma^\ddagger Q_1 Q_2} \left(\frac{2\pi}{\mu k_B T} \right)^{3/2} \int dE e^{-E/k_B T} dJ N(E, J, s). \quad (1)$$

In this equation, s and T denote the reaction coordinate and the temperature, respectively; g_e represents the rate between the electronic partition function of the transition state and the product of the electronic partition function of the two reactants; μ , Q_1 , and Q_2 designate the reduced mass and the rotational partition functions of the reactants. J is the angular momentum quantum number and $N(E, J, s)$ represents the number of allowed states corresponding to the E energy. σ_1 , σ_2 , and $\sigma^\ddagger$ denote the cross sections for both reactants and for the transition state.

The starting points of the rate computation were the M052X/6-311+G(d,p) energies, geometries, and harmonic fundamentals of reactants and products computed along the pathways. The s reaction coordinate was allowed to vary from 1.8 to 4.2 Å with intervals of 0.2 Å. The rates were computed at 15 different T (200, 210, 220, 230, 240, 250, 260, 280, 298, 300, 400, 500, 700, 900, and 1000 K). The number of allowed states was determined in a Monte Carlo simulation considering all the possible orientations. The rates at 200 K (middle point of the Hot Core temperature range, 100–300 K), 298 K (room temperature), and 500 K, corresponding to the 29 barrierless processes, are shown in Table 3 and they are represented in

Table 2
List of Selected Reactants (N_a = Number of Atoms)

N_a	Reactants
1	H
2	H ₂ , C-H*, OH*, CO
3	*CH ₂ , H ₂ O, H-CO*, C=C=O*
4	HO-CH*, CH ₂ O, H-C=C=O*, CH ₃ *, H-COO*, O-H-CO*
5	CH ₄ , H-COOH, CH ₂ =C=O, CH ₃ -O*, CH ₂ -OH*, C-H=C-C=O*, C=C-C-HO*
6	CH ₃ -OH, CH ₂ =C=C=O, CH=C-C-HO*, CH ₃ -C=C, CH ₂ =C=CH*, CH ₃ -CO*, CH ₂ -CHO*, CH ₂ =C-OH*, C-H=CH-OH*
7	CH ₃ -C=C-H, CH ₃ -CHO, CH ₂ =CH-OH, CH ₃ -O-CO*, CH ₂ -O-CHO*, CH ₃ -COO*, CH ₂ -COOH*, O-CH ₂ -CHO*, OH-CH ₂ -CO*, OH-CH-CHO*, CH=CH-CHO, CH ₂ =C-CHO, CH ₂ -CH=CO*
8	CH ₃ -O-CHO, CH ₃ -COOH, OH-CH ₂ -CHO, CH ₂ =CH-CHO, CH ₃ -O-CH ₂ *, CH ₂ -CH ₂ -OH*, CH ₃ -CHOH*, OH-CH ₂ -COO, O-CH ₂ -COOH*, OH-CH-COOH*, CH ₃ -O-COO*, CH ₃ -CH ₂ -O*
9	CH ₃ -O-CH ₃ , CH ₃ -CH ₂ -OH, CH ₃ -CO-CH ₂ *, OH-CH ₂ -CH ₂ -O*, CH ₃ -CH ₂ -C=O*, CH ₂ -CH ₂ -C-HO*, CH ₃ -CH-C-HO*, CH ₃ -O-CH ₂ O*, CH ₃ -O-CH-OH, CH ₂ -O-CH ₂ -OH*, HO-CH ₂ -COOH
10	CH ₃ -CO-CH ₃ , OH-CH ₂ -CH ₂ -OH, CH ₃ -CH ₂ -CHO, CH ₃ O-CH ₂ -OH, CH ₃ -O-CO-CH ₂ , CH ₃ -CH ₂ -O-CO*, CH ₃ -CHO-CHO*, CH ₂ -CH ₂ -O-CHO*, CH ₂ O-CO-CH ₃ *
11	CH ₃ -O-CO-CH ₃ , CH ₃ -CH ₂ -O-C-OH

Table 3Barrierless Processes and Rate Constants^a ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) Computed Using Conventional Canonical Variational Transition State Theory (CVT), and Microcanonical Variational Transition State Theory (μVT)^b

Reaction	200 K μVT	CVT	298 K CVT	500 K CVT
C₂H₅-O-COOH (ethoxy formic acid)				
1 OH* + CH ₃ CH ₂ OCO* → C ₂ H ₅ -O-COOH	3.3E-10	5.8E-10	2.6E-10	2.1E-10
2 CH ₃ * + CH ₂ OCOOH → C ₂ H ₅ -O-COOH	1.6E-13	1.7E-13	6.6E-13	5.7E-12
3 HOCO* + CH ₃ CH ₂ O* → C ₂ H ₅ -O-COOH	1.1E-13	1.1E-13	5.2E-13	1.7E-12
CH₃-CHOH-COOH (lactic acid)				
4* OHCO* + CH ₃ CHOH* → CH ₃ -CHOH-COOH	...	2.3E-23	2.7E-19	8.8E-16
5* CH ₃ * + HOCHCOOH* → CH ₃ -CHOH-COOH	...	4.0E-38	2.8E-29	9.8E-22
OHCH₂-CH₂-COOH (3-hydroxypropanoic acid)				
6 OHCO* + CH ₂ CH ₂ OH* → OHCH ₂ -CH ₂ -COOH	1.2E-15	2.0E-15	3.0E-14	3.3E-13
7* CH ₂ OH* + CH ₂ COOH* → OHCH ₂ -CH ₂ -COOH	...	3.2E-42	2.6E-32	6.0E-24
CH₃-COOCH₂OH (hydroxymethyl acetate)				
8* OH* + CH ₂ OCOCH ₃ * → CH ₃ -CO-O-CH ₂ OH	...	2.5E-18	2.3E-15	2.1E-13
9 CH ₂ OH* + CH ₃ COO* → CH ₃ -CO-O-CH ₂ OH	1.3E-12	1.3E-12	3.1E-12	1.1E-11
CH₃-CHOH-OCHO (hydroxiethyl carbonyl ether)				
10† OH* + CH ₃ CHOCHO → CH ₃ -CHOH-OCHO	6.3E-06	2.7E+38	2.2E+22	4.4E+08
11 HCOO* + CH ₃ CHOH* → CH ₃ -CHOH-OCHO	8.9E-10	2.2E-08	1.2E-09	1.7E-10
CH₃O-CO-OCH₃ (dimethyl carbonate)				
12* CH ₃ * + CH ₃ OCO* → CH ₃ O-CO-OCH ₃	...	1.4E-49	1.3E-36	7.9E-26
13 CH ₃ O* + CH ₃ OCO* → CH ₃ O-CO-OCH ₃	1.6E-14	1.7E-14	2.1E-13	9.2E-13
CH₃-O-CO-CH₂OH (methyl glycolate)				
14 CH ₃ O* + OHCH ₂ CO* → CH ₃ O-CO-CH ₂ OH	6.6E-13	6.8E-13	3.2E-12	1.2E-11
15* OH* + CH ₃ OCOCH ₂ → CH ₃ O-CO-CH ₂ OH	3.4E-06	5.6E+26	1.7E+14	9.6E+03
16* CH ₂ OH* + CH ₃ OCO* → CH ₃ O-CO-CH ₂ OH	...	3.4E-21	8.6E-18	6.0E-15
cis-CH₃O-CH₂-COOH (C1-methoxy acetic acid)				
17* OHCO* + CH ₃ OCH ₂ * → CH ₃ O-CH ₂ -COOH	...	2.9E-19	4.1E-16	4.4E-14
18* CH ₃ O* + CH ₂ COOH* → CH ₃ O-CH ₂ -COOH	...	2.4E-26	1.0E-21	1.2E-17
trans-CH₃O-CH₂-COOH (T1-methoxy acetic acid)				
17** OHCO* + CH ₃ OCH ₂ * → CH ₃ O-CH ₂ -COOH	...	9.0E-12	1.3E-15	4.9E-14
19* CH ₃ * + CH ₂ OCOOH* → CH ₃ O-CH ₂ -COOH	...	7.0E-18	1.9E-15	3.4E-13
OHCH₂-CH₂-OCHO (2-hydroxyethyl formate)				
20* HCO* + OHCH ₂ CH ₂ O* → OHCH ₂ CH ₂ OCHO	...	1.1E-04	3.4E-07	3.2E-09
21 OH* + CH ₂ CH ₂ OCHO* → OHCH ₂ CH ₂ OCHO	4.4E-14	3.6E-14	2.4E-13	1.5E-12
22* CH ₂ OH* + CH ₂ OCHO* → OHCH ₂ CH ₂ OCHO	...	9.3E-27	9.8E-22	3.1E-17
OHCH₂-CO-CH₂OH (dihydroxiacetona)				
23* CH ₂ OH* + OHCH ₂ CO* → OHCH ₂ COCH ₂ OH	...	2.7E-23	3.6E-19	9.4E-16
CH₃O-CH₂-OCOH (methoxi metil formate)				
24† HCO* + CH ₃ OCH ₂ O* → CH ₃ O-CH ₂ -OCOH	1.3E-07	3.2E+03	3.8E-02	3.6E-06
25 CH ₃ O* + CH ₂ OCHO → CH ₃ O-CH ₂ -OCOH	3.8E-10	4.5E-08	1.1E-09	6.0E-11
26† HCOO* + CH ₃ OCH ₂ → CH ₃ O-CH ₂ -OCOH	3.9E-07	1.0E+10	1.5E+04	5.7E-03
OHCH₂-CHOH-CHO (glyceraldehyde)				
27* CH ₂ OH* + OHCHCHO → OHCH ₂ CHOHCHO	...	5.8E-42	9.5E-32	3.6E-23
CH₃O-C(OH)-CHOH (2-metoxi 2-ol propanal)				
28 HCO* + CH ₃ OCHOH → CH ₃ O-CHOH-CHO	1.4E-10	1.6E-10	1.4E-10	1.5E-10
OHCH₂-O-CH₂-CHO (hydroxymethyl methylcarbonyl ether)				
29 CH ₂ OH* + OCH ₂ CHO → OHCH ₂ OCH ₂ CHO	...	3.1E-61	6.4E-45	3.0E-31

Notes.^a Rate constants $> 1.0\text{E}-70 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are collected.^b * Rates(μVT) = 0; † Rates(μVT) $< < < <$ Rates(CVT).

Figure 2. Rates were computed using the canonical variational transition state theory (CVT), which is the conventional theory. However, as CVT is not recommended for very low temperatures, rates at 200 K have also been computed using microcanonical variational transition state theory (μVT) with multidimensional semiclassical approximations for tunneling and nonclassical reflection (Georgievskii & Klippenstein 2005; Löhle & Kästner 2018).

The rate constants stand out in the large range of formation probabilities of the C₃O₃H₆ isomers in the gas phase. Kinetic

rates at 200 K vary from $1.2\text{E}+38 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (corresponding to the hydroxiethyl carbonyl ether formation) to insignificant values (rates $< 1.0\text{E}-70 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Below this quantity, rates are neglected in the table. The formation in the gas phase of lactic acid, glyceraldehyde, hydroxymethyl methylcarbonyl ether, and dihydroxiacetone, the single detected isomer, is not supported by this kinetic study. However, the formation of 2-hydroxyethyl formate and methoxi methyl formate at low temperatures seems probable. The formation of the most stable isomer ethoxy formic acid is

Figure 1. Relative stability of the two most stable $C_3O_3H_6$ isomers computed using MP2/AVTZ.

reliable in gas phase at 200 K through three processes involving the OH^* , CH_3^* , and $HOCO^*$ radicals.

To avoid the high computational cost, the pressure effect on the rates has not been taken into consideration. Then, the rates might be slightly underestimated (Woon et al. 2021). Theoretical models taking into consideration the pressure imply a high computational cost given the number of systems and processes treated in the present paper. In addition, these models are recommended for processes with high energy transition states, and they are frequently neglected in studies of barrierless reactions (Xing et al. 2017).

The kinetic rates larger than $1.0E-15 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ confirm the consistency of 11 formation processes of nine isomers at 200 K for which the μVT and the CVT rates converge. Divergences are obtained for five fast processes. In some reactions, the μVT rate is obtained to be zero although the reaction viability is supported by the CVT theory. Unfortunately, it is difficult to derive more clear conclusions since kinetic studies of these kinds of molecules at low T , are not frequent. In addition, rates depend also on the relative orientation of the fragments, expressed by the s parameter, which is selected beforehand.

As was expected, rates decrease with the temperature. Faster processes at 500 K entail the OH^* hydroxyl radical. This radical, first detected in astrophysical sources in 1964 (Dieter & Ewen 1964), represents one of the main chemical species controlling the oxidizing capacity of the global Earth atmosphere (Gligorovski et al. 2015). Our computation emphasizes the role this radical can play in the interstellar chemistry and, in general, in gas phase chemistry. To a lesser degree, the HCO^* radical and the methoxy methyl radical CH_3O^* play significant roles in the $C_3O_3H_6$ formation processes.

The present work gives special attention to methoxy acetic acid (MAA; see Figure 3). According to the profiles, two low-lying conformers C1 and T1 can be formed through three addition processes involving $OHCO^*$ and $CH_3OCH_2^*$. This last unobserved radical has been proposed to be the precursor of abundant astrophysical species such as dimethyl ether and methyl formate (Herbst 2017; Yazidi et al. 2019). However, according to the conventional kinetic study CVT and in contradiction with the μVT results, only the R18 processes

leading to T1 is fast enough and assures the production of MAA at 200 K.

2.5. Structure and Spectroscopic Constants of Methoxy Acetic Acid

As far as we know, very little previous research has been devoted to the analysis of the rovibrational spectra of MAA (Lovas et al. 2010) (NIST RSD), even though it represents a fairly stable isomeric form, shows a permanent dipole moment, and can be formed from detected or at least, detectable radicals. MAA is a nonrigid molecule with eight conformers that can be interconverted by internal rotation. Their relative energies and spectroscopic properties applicable for rotational spectrum assignments (dipole moments as well as rotational and centrifugal distortion constants), are shown in Table 4. Anharmonic fundamentals computed using VPT2 are provided as supporting data in Table A2.

In Figure 4, the two low-lying conformers C1 and T1 are shown. Their CCSD(T)-F12 structural parameters are provided as supporting data in Table 5. The corresponding dipole moments were computed to be 2.299 D (C1) and 5.697 D (T1).

Four internal rotations are responsible for the minimum interconversion: the methyl group torsion (θ_1), the C–OCH₃ bond torsion (θ_2), the C–C bond torsion (β), and the torsion of the acid group hydroxyl. We distinguish between cis (C1, C2, C3, C4) and trans (T1, T2, T3, and T4) conformers in view of the $H_6O_4C_2O_5$ dihedral angle (dOH). Terms cis and trans refer to $dOH = \sim 0^\circ$ and $dOH = \sim 180^\circ$, respectively. The β , θ_1 , and θ_2 coordinates were defined as linear combinations of internal curvilinear coordinates:

$$\begin{aligned}\theta_1 &= (H8C7O3C1 + H9C7O3C1 + H10C7O3C1)/3 \\ \theta_2 &= C7O3C1C2 \quad \beta = O5C2C1O3.\end{aligned}\quad (2)$$

Weak intramolecular interactions play important roles in the conformer relative stability and on the dynamics at low temperatures. In general, the cis minima, where steric repulsions are minimized, represent the most stable forms, although the formation of one intramolecular hydrogen bond stabilizes T1 and T2. Then, C1 and T1 are almost isoenergetic. We cannot establish which one of the two forms represents the preferred conformer because they are so close in energy that their relative stability fluctuates with the improvement of the theoretical approximation. The zero vibrational energy alters the relative order. In absence of intramolecular hydrogen bonds, as in T3 and T4, the trans structures display relatively high energies.

For all the conformers, the centrifugal distortion constants and rotational constants are given in Table 4. They are parameters of the Watson S-reduced Hamiltonian (Watson 1968). The ground vibrational state rotational constants were computed using the CCSD(T)-F12 equilibrium rotational constants and the following equation was proposed and verified in previous studies (Dalbouha et al. 2015; Bousseffi et al. 2016; Motiyenko et al. 2018; Bousseffi & Senent 2020):

$$\begin{aligned}B_0 &= B_e(\text{CCSD}(T) - \text{F12}) \\ &+ \Delta B_e^{\text{core}}(\text{CCSD}(T)) + \Delta B^{\text{vib}}(\text{MP2}).\end{aligned}\quad (3)$$

ΔB^{vib} represents the vibrational contribution derived from the VPT2 α_i^r vibration-rotation interaction parameters (Mills 1972) determined from the MP2/VTZ cubic force field. ΔB_e^{core}

Figure 2. Synopsis of the most probable barrierless processes at low temperatures.

Figure 3. Barrierless processes forming the two favored conformers of MAA.

collects the effect of the core-electron correlation and was computed from the CCSD(T)/cc-pVCDZ rotational constants using the formula:

$$\Delta B_e^{\text{core}} = B_e(\text{CV}) - B_e(\text{V}) \quad (4)$$

where $B_e(\text{CV})$ and $B_e(\text{V})$ can be estimated correlating both core and valence electrons (CV) or just the valence electrons (V) in the post-SCF process.

Profiles of Figure 5 represent one-dimensional minimum energy pathways connecting the minima. Along the curves, the remaining coordinates including the three neglected torsions were allowed to be relaxed from their values in C1 and T1.

The profiles confirm that the interconversion is restricted by relatively low barriers and it is feasible at very low temperatures. There is one exception: the $\text{cis} \rightarrow \text{trans}$ process that implies two steps, $\text{C1} \rightarrow \text{T3}$ hindered by a barrier of $\sim 4000 \text{ cm}^{-1}$ and $\text{T3} \rightarrow \text{T1}$. On the basis of this fact, the spectra of cis - and trans -MAA are studied one by one in the present paper. Other arguments to support the separation are the values of the torsional fundamentals provided as supporting data, as detailed below. Both CH_3 barriers in cis - and trans -MAA were computed to be $\sim 600 \text{ cm}^{-1}$. This reveals that the CH_3 and OH groups are independent.

However, profiles corresponding to the $\text{C}-\text{OCH}_3$ and the $\text{C}-\text{C}$ torsional motions differ in the cis and trans regions. Whereas the $\text{C1} \rightarrow \text{C2}$ depending on the $\text{C}-\text{C}$ coordinate is low ($\sim 800 \text{ cm}^{-1}$), the $\text{T1} \rightarrow \text{T4}$ process implies a relatively high barrier ($\sim 2500 \text{ cm}^{-1}$).

As we argue in the next sections of this paper, the main attention must be given to the shape of curves depending on θ_2 ($\text{C}-\text{OCH}_3$) because they have singular consequences in the distribution of the torsional energies. The trans -MAA minimum is planar, whereas cis -MAA displays a double minimum. The corresponding barrier is higher in cis -MAA than in trans -MAA.

2.6. Three-dimensional Variational Procedure

A variational procedure implemented in the ENEDIM Fortran code (Senent 1998a, 1998b, 2001b) that takes into consideration the minimum interconversion is applied to

Table 4
Relative Energies (E_r , E_r^{ZPVE} , in cm^{-1}) and Spectroscopic Parameters of Methoxy Acetic Acid^a

	C1 (C_1)	T1 (C_s)	T2 (C_1)	C2 (C_1)	C3 (C_s)	C4 (C_s)	T3 (C_1)	T4 (C_s)
$\theta_1(\text{o})$	177.4	180	178.5	177.6	180	180	182.4	180
$\theta_2(\text{o})$	74.2	180	-83.7	73.3	180	180	73.0	180
$\beta(\text{o})$	179.2	0	-16.9	16.3	180	0	179.8	180
dOH ^b	0.4	180	179.2	-0.1	0.0	0	179.8	180
E_r	0.0 ^c	-32.3	207.8	313.7	529.3	622.4	1835.3	2503.4
E_r^{ZPVE}	0.0	9.0	312.7	341.8	482.4	598.9	1775.0	2355.1
$\mu(\text{D})$	2.299	5.697	4.458	1.550	3.250	2.142	4.452	6.048
Ground vibrational state rotational constants (in MHz)								
A_0	7635.1	9414.4	7167.1	7078.1	9576.7	9316.8	7540.8	9412.6
B_0	2382.4	2090.6	2424.6	2448.4	2009.2	2054.5	2385.8	2010.4
C_0	2027.5	1751.1	2150.9	2139.7	1697.3	1731.0	2029.0	1693.1
Centrifugal distortion constants (in $\text{MHz} \times 10^3$, S reduction, I ^r representation)								
Δ_J	0.680944	0.158804	1.128143	1.275317	0.113885	0.314222	0.666903	0.118027
Δ_{JK}	-0.615388	1.840566	-5.019966	-2.403220	4.351757	6.919442	-0.648733	4.066747
Δ_K	15.750789	4.933838	23.443960	31.473540	32.615532	22.205094	14.476446	30.476724
d_1	-0.006549	-0.026783	0.055317	0.267178	-0.005681	-0.006759	-0.008330	-0.007242
d_2	-0.022018	-0.001419	0.000127	-0.085321	-0.004545	0.089884	-0.019038	-0.004523
H_J	0.000471	0.000073	-0.000291	0.005859	-0.000032	-0.005102	0.000421	-0.000032
H_K	0.018075	0.027715	0.030253	0.341963	0.139382	-19.55634	0.047063	0.159148
H_{JK}	-0.005353	-0.007316	0.002972	-0.032009	0.000137	-0.597664	-0.005270	0.000199
H_{KJ}	-0.117998	-0.007544	-0.109209	-0.552656	0.020113	-11.46257	-0.088080	0.014168
h_1	-0.000708	0.000003	-0.000344	-0.004103	-0.000006	-0.004762	-0.000578	-0.000006
h_2	0.000200	-0.000037	0.000148	0.000994	0.000004	-0.001717	0.000154	0.000005
h_3	0.000016	0.000000	-0.000002	0.000022	0.000003	0.000507	0.000015	0.000003

Notes.

^a Rotational constants are computed using Eg (3); CCSD(T)/F12 relative energies and geometries; centrifugal distortion constants and anharmonic corrections are computed at the MP2/AVTZ level of theory.

^b dOH = $\text{H}_6\text{O}_4\text{C}_2\text{O}_5$ dihedral angle.

^c $E = -343.221035$ au.

Figure 4. The most stable conformers C1 and T1 of MAA; atom labeling and torsional coordinates.

explore the far-infrared region. The molecule is treated using a three-dimensional model depending on the θ_1 , θ_2 , and β coordinates. The work regards cis- and trans-MAA as two different molecules on the basis of the following arguments:

- (1) The barrier between cis- and trans-MAA is relatively high ($<4000 \text{ cm}^{-1}$), hindering the interconversion at low temperatures.
- (2) The band center positions are predicted with VPT2: the OH-torsional fundamentals (513 cm^{-1} (C1); 654 cm^{-1} (T1)) were predicted to lie at higher frequencies than the remaining torsional fundamentals θ_1 , θ_2 , and β (175 cm^{-1} , 129 cm^{-1} , 69 cm^{-1} (C1); 217 cm^{-1} , 116 cm^{-1} , and 48 cm^{-1} (T1), making the separability possible. In structures such as T1 and T2, where the OH hydrogen is involved in a hydrogen bond, the separation is more remarkable.

If it is assumed that the torsional modes can be separated from the remaining vibrational modes, the low-lying rovibrational

energies for $J = 0$ can be calculated by solving variationally the torsional Hamiltonian (Senent 1998a, 1998b, 2001b):

$$H(\theta, \theta_1, \theta_2) = -\sum_{i=1}^3 \sum_{j=1}^3 \left(\frac{\partial}{\partial q_i} \right) B_{q_i q_j}(\theta_1, \theta_2, \beta) \left(\frac{\partial}{\partial q_j} \right) + V^{\text{eff}}(\theta_1, \theta_2, \beta) \quad (5)$$

$B_{q_i q_j}$ represents the kinetic energy parameters. A $V(\theta_1, \theta_2, \beta)$ surface computed using ab initio theory allows us to build the vibrationally corrected effective potential:

$$V^{\text{eff}}(\theta_1, \theta_2, \beta) = V(\theta_1, \theta_2, \beta) + V'(\theta_1, \theta_2, \beta) + V^{\text{ZPVE}}(\theta_1, \theta_2, \beta). \quad (6)$$

Here, $V'(\theta_1, \theta_2, \beta)$ and $V^{\text{ZPVE}}(\theta_1, \theta_2, \beta)$ represent the Podolsky pseudopotential and the zero-point vibrational energy corrections, respectively (Senent 1998b).

Two potential energy surfaces $V(\theta_1, \theta_2, \beta)$ were computed for both cis- and trans-MAA. Each one was built from the MP2/AVTZ electronic energies of 160 selected geometries corresponding to different values of the H8C7O3C1 , C7C3C1C2 , and O5C2C1O3 dihedral angles that were chosen every 45° covering all the space. The remaining 27 internal coordinates were allowed to be relaxed in all the structures.

To specify the potential, the energies were fitted to a triple Fourier series of 132 terms ($\sigma = 0.11$, $R^2 = 1$) taking into consideration the symmetry requirements. MAA can be classified as the molecular symmetry group G_6 , which contains three irreducible representations, two nondegenerate (A_1 , A_2) and one twofold-degenerate (E) (Yazidi et al. 2019). The

Figure 5. One-dimensional cuts of the ground electronic state potential energy surface computed at the MP2/AVTZ level of theory.

Table 5

CCSD(T)-F12 Structural Parameters of the Most Stable Cis (C1) and Trans (T1) Conformers of Methoxy Acetic Acid (Distances in Å, Angles in Degrees)

	C1	T1		C1	T1		C1	T1
θ_1	177.4	178.5	θ_2	74.2	-83.7	β	179.2	-16.9
C2C1	1.5188	1.5272	O3C1C2	113.4	112.2	O5C2C1O4	...	...
O3C1	1.3906	1.4217	O4C2C1	110.1	113.8	H6O4C2O5	0.4	179.2
O4C2	1.3496	1.3426	O5C2C1	126.3	123.2	H8C7O3C1	-63.5	-62.3
O5C2	1.2006	1.1978	H6O4C2	107.3	106.2	H9C7O3C1	177.2	178.6
H6O4	0.9655	0.9695	C7O3C1	112.6	117.7	H10C7O3C1	58.6	59.1
C7O3	1.4164	1.4217	H8C7O3	111.4	110.5	H11C1C2O4	-55.7	-141.4
H8C7	1.0913	1.0927	H9C7O3	106.8	107.1	H11C1C2O4	59.9	101.4
H9C7	1.0867	1.0867	H10C7O3	110.6	111.3	...	...	...
H10C7	1.0959	1.0947	H11C1C2	107.8	108.5	H6-O3	...	1.9867
H11C1	1.0908	1.0920	H12C1C2	107.5	107.6	...	...	...
H12C1	1.0971	1.0904	...	...	...	...	...	...

analytical expression of the potential must be totally symmetric:

$$\begin{aligned}
 V^{\text{eff}}(\theta_1, \theta_2) = & \sum \sum \sum (A_{nml} \cos 3n\theta_1 \cos m\theta_2 \cos l\beta \\
 & + A_{-n-m-l} \sin 3n\theta_1 \sin m\theta_2 \cos l\beta \\
 & + A_{n-m-l} \cos 3n\theta_1 \sin m\theta_2 \sin l\beta \\
 & + A_{-nm-l} \sin 3n\theta_1 \cos m\theta_2 \sin l\beta). \quad (7)
 \end{aligned}$$

The expansion coefficients are provided in a machine-readable version of Table A3. The parameters $B_{\text{qiq}}(\theta_1, \theta_2, \beta)$, $V'(\theta_1, \theta_2, \beta)$ and $V^{\text{ZPVE}}(\theta_1, \theta_2, \beta)$ were computed for all the geometries and later on, they were fitted to analytical expressions formally identical to Equation (4) (Senent 1998a). $V^{\text{ZPVE}}(\theta, \theta_1, \theta_2)$ was constructed within the harmonic

Table 6
 A_{000} Coefficients of the Kinetic Energy Parameters (in cm^{-1})

cis-MAA				trans-MAA			
B_θ	6.1801	$B_{\theta\beta_1}$	-0.9377	B_θ	6.2012	$B_{\theta\beta_1}$	-0.9605
B_{β_1}	1.7464	$B_{\theta\beta_2}$	-0.0063	B_{β_1}	1.7682	$B_{\theta\beta_2}$	-0.0035
B_{β_2}	1.1136	$B_{\beta_1\beta_2}$	-0.5032	B_{β_2}	1.0922	$B_{\beta_1\beta_2}$	-0.4989

approximation. The independent coefficients A_{000} of the kinetic energy surfaces are summarized in Table 6.

The Hamiltonian of Equation (4) was solved variationally using symmetry adapted triple Fourier series as trial functions. A Hamiltonian matrix of 196911×196911 elements is needed

Table 7
Torsional Energies (E , in cm^{-1}) of Methoxy Acetic Acid Localized in the C1, T1, and T2 Minima of the MP2/AVTZ Potential Energy Surface

Cis-MAA					Trans-MAA				
$\nu_{01}\nu_{02}\nu_{\beta}$	E (minimum)				$\nu_{01}\nu_{02}\nu_{\beta}$ (minimum)	E			
0 0 0	A_1	0	E	0.001	0 0 0	A_1	0	E	0
(C1)	A_2	0	E	0.001	(T1)				
0 0 1	A_1	63.397	E	63.398	0 0 1	A_2	77.556	E	77.555
(C1)	A_2	63.399	E	63.4	(T1)				
0 1 0	A_1	92.65	E	92.644	0 1 0	A_2	106.056	E	106.056
(C1)	A_2	92.658	E	92.641	(T1)				
0 0 2	A_1	125.049	E	125.049	0 0 0	A_1	111.727	E	111.726
(C1)	A_2	125.049	E	125.05	(T2)	A_2	111.726	E	111.726
0 1 1	A_1	156.431	E	156.426	0 0 2	A_1	155.231	E	155.231
(C1)	A_2	156.419	E	156.414	(T1)	E			
1 0 0	A_1	177.346	E	177.3	0 1 1	A_1	179.925	E	179.924
(C1)	A_2	177.332	E	177.285	(T1)	E			
0 0 3	A_1	185.172	E	185.172	0 0 3	A_1	207.358	E	207.358
(C1)	A_2	185.171	E	185.171	(T1)				
0 2 0	A_1	190.018	E	190.023	0 0 1	A_1	215.866	E	215.865
(C1)	A_2	189.999	E	190.003	(T2)	A_2	215.867	E	215.865
0 1 2	A_1	218.45	E	218.477	1 0 0	A_2	218.907	E	218.893
(C1)	A_2	218.46	E	218.456	(T1)				
1 0 1	A_1	241.017	E	240.98	0 1 0	A_1	230.741	E	230.741
(C1)	A_2	241.029	E	240.991	(T2)	A_2	230.742	E	230.746
ZPVE		120.5							
									209.2

to obtain convergent levels up to 300 cm^{-1} . The symmetry factorizes it into four submatrices, two corresponding to the nondegenerate representations, A_1 , and A_2 , and two corresponding to the two components of the twofold-degenerate, E . To reduce dimensionality, contracted functions depending on the β coordinate were employed following the procedure of Boussessi & Senent (2020). Probability integrals allow localization of the torsional levels in the minima using the torsional wave functions (Boussessi & Senent 2020).

Energy levels are shown in Table 7. The three-fold CH_3 barrier splits the levels into three sublevels, one nondegenerate A_i ($i = 1$ or 2) and the twofold-degenerate E . The profiles (see Figure 5) can help us to understand their distribution. The energies provide evidence of the relevance of the interactions between θ_2 and β , and the differences between the shapes of the curves depending on θ_2 in the cis and trans regions. The trans-MAA absolute minimum lies at 180° , whereas cis-MAA displays an absolute double-well. Then, the trans-MAA levels split into three components, whereas the number of splittings is double in cis-MAA due to of the double-well absolute minimum effect.

For the cis-conformer, C1, the fundamentals' frequencies were localized at 177.3 cm^{-1} (CH_3 torsion, ν_{28}), 92.6 cm^{-1} ($\text{C}-\text{OCH}_3$ torsion, ν_{29}), and 63.4 cm^{-1} ($\text{C}-\text{C}$ torsion, ν_{30}). The fundamentals of T1 were found to be 218.9 cm^{-1} (CH_3 torsion, ν_{28}), 106.1 cm^{-1} ($\text{C}-\text{OCH}_3$ torsion, ν_{29}), and 77.6 cm^{-1} ($\text{C}-\text{C}$ torsion, ν_{30}). Strong disagreements with the VPT2 frequencies, provided as supporting data, are not observed in spite of VPT2 not being the proper theory for the torsional motions. This theory cannot derive torsional splitting components.

3. Conclusions

A preliminary search for all the possible $\text{C}_3\text{O}_3\text{H}_6$ isomeric structures performed using a standardized computing tool

provides 102 structures of a reasonable stability. Our methodology points to the ethoxy formic acid, ($\text{C}_2\text{H}_5\text{O}-\text{COOH}$, ISO1), as the most stable form lying 1019 cm^{-1} ($2.9 \text{ Kcal mol}^{-1}$) below the lactic acid proposed as the most stable form in previous works.

Profiles corresponding to the minimum energy pathways reveal that the preferred conformers of the 14 low-lying isomers can be formed in the gas phase through these 29 one-step barrier-less processes involving the $^{\circ}\text{OH}$, $\text{CH}_3\text{O}^{\bullet}$, HCO , $\text{CH}_3^{\bullet}$, CH_2OH , $\text{HCOO}^{\bullet}$, and OHCO interstellar observed radicals. The kinetic rates larger than $1.0\text{E}-15 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ confirm the consistency of 11 formation processes of nine isomers at 200 K, and underline five more processes as possible reactions. The formation in the gas phase of lactic acid, glyceraldehyde, hydroxymethyl methylcarbonyl ether, and dihydroxiacetona, the single detected isomer, is not supported by this kinetic study. However, the formation of 2-hydroxyethyl formate and methoxy methyl formate at low temperatures seems probable. The formation of the most stable isomer ethoxy formic acid is reliable in gas phase at 200 K through three processes involving the $^{\bullet}\text{OH}$, $^{\bullet}\text{CH}_3$, and HOCO radicals.

A final effort has been dedicated to the characterization of methoxy acetic acid. This species was listed (but no characterized) in previous works devoted to astrochemistry, even though it represents a fairly stable isomeric form, shows a permanent dipole moment, and can be formed from detected or at least, detectable radicals. It displays eight conformers that can be interconverted by internal rotation. Internal rotation barriers, low-lying states, and their splittings are provided.

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Appendix

This appendix contains supporting data in the form of Table A1 (127 exergonic processes are derived from STAR), Table A2 (Anharmonic fundamentals computed using VPT2), and Table A3 (expansion coefficients of the 3D-potential energy surfaces). Figure A1 is a 14 element figure set displaying energy profiles.

Table A1
Exergonic Formation Processes of the $C_3O_3H_6$ Isomers

	Formation Processes	$\Delta G < 0$	MNES
$C_2H_5-O-COOH$ (Ethoxy formic acid)			
1	$OH + CH_3CH_2OCO \rightarrow C_2H_5-O-COOH$	-101.5	1
2	$CH_3 + CH_2OCOOH \rightarrow C_2H_5-O-COOH$	-93.0	1
3	$HOCO + CH_3CH_2O \rightarrow C_2H_5-O-COOH$	-89.6	1
4	$CH_3CH_2OH + \bullet OCH_2OCOOH \rightarrow C_2H_5-O-COOH + \bullet CH_2OH$	-17.4	4
5	$\bullet OH + CH_3CH_2OCHO \rightarrow C_2H_5-O-COOH + \bullet H$	-10.3	2
	step 1: $\bullet OH + CH_3CH_2OCHO \rightarrow CH_3CH_2OCHO-OH$	-0.6	
	step 2: $CH_3CH_2OCHO-OH \rightarrow C_2H_5-O-COOH + \bullet H$	-12.7	
6	$CH_3CH_2OH + \bullet CH_2OCOOH \rightarrow C_2H_5-O-COOH + CH_3O\bullet$	-8.8	4
7	$HCOOH + CH_3CH_2OH \rightarrow C_2H_5-O-COOH + H_2$	-1.5	4
8	$OHCO + CH_3CH_2OCHO \rightarrow C_2H_5-O-COOH + HCO$	-1.3	4
$CH_3-CHOH-COOH$ (Lactic acid)			
9	$HCOO\bullet + CH_3CHOH \rightarrow CH_3-CHOH-COOH$	-91.3	3
10	$OHCO + CH_3CHOH \rightarrow CH_3-CHOH-COOH$	-77.6	1
11	$\bullet CH_3 + HOCHCOOH \rightarrow CH_3-CHOH-COOH$	-65.2	1
12	$CH_3CHOH + HOCHCOOH \rightarrow CH_3-CHOH-COOH + CH_2O$	-54.7	4
13	$CH_3CHCHO + HOCHCOOH \rightarrow CH_3-CHOH-COOH + CH_2CO$	-44.8	4
14	$HCOO\bullet + CH_3CH_2OH \rightarrow CH_3-CHOH-COOH + H$	-4.4	4
15	$CH_3CHOH + HOCHCOOH \rightarrow CH_3-CHOH-COOH + HOCH$	-1.8	3
$OHCH_2-CH_2-COOH$ (3-hydroxypropanoic acid)			
16	$HCOO\bullet + \bullet CH_2CH_2OH \rightarrow OHCH_2-CH_2-COOH$	-92.2	3
17	$^3CH_2 + OHCH_2COOH \rightarrow OHCH_2-CH_2-COOH$	-85.4	3
18	$OHCO + \bullet CH_2CH_2OH \rightarrow OHCH_2-CH_2-COOH$	-78.4	1
19	$\bullet CH_2OH + CH_2COOH \rightarrow OHCH_2-CH_2-COOH$	-68.7	1
$CH_3-CO-O-CH_2OH$ (Hydroxymethyl acetate)			
20	$\bullet OH + \bullet CH_2OCOCH_3 \rightarrow CH_3-CO-O-CH_2OH$	-89.8	1
21	$\bullet CH_2OH + CH_3COO\bullet \rightarrow CH_3-CO-O-CH_2OH$	-80.6	1
$CH_3-CHOH-OCHO$ (Hydroxiethyl carbonyl ether)			
22	$\bullet OH + \bullet CH_2CH_2OCHO \rightarrow CH_3-CHOH-OCHO$	-91.1	4
23	$\bullet OH + CH_3CHOCHO \rightarrow CH_3-CHOH-OCHO$	-86.6	1
24	$HCOO\bullet + CH_3CHOH \rightarrow CH_3-CHOH-OCHO$	-80.7	1
25	$OHCO + CH_3CHOH \rightarrow CH_3-CHOH-OCHO$	-67.0	3
$CH_3O-CO-OCH_3$ (Dimethyl carbonate)			
26	$\bullet CH_3 + CH_3OCO\bullet \rightarrow CH_3O-CO-OCH_3$	-77.1	1
27	$CH_3O\bullet + CH_2OCHO \rightarrow CH_3O-CO-OCH_3$	-91.3	3
28	$CH_3O\bullet + CH_3OCO \rightarrow CH_3O-CO-OCH_3$	-91.2	1
29	$\bullet CH_2OH + \bullet CH_2OCHO \rightarrow CH_3O-CO-OCH_3$	-82.7	5
30	$\bullet CH_2OH + CH_3OCO \rightarrow CH_3O-CO-OCH_3$	-82.6	3
31	$CH_3OCO\bullet + CH_3OCOCH_2 \rightarrow CH_3O-CO-OCH_3 + CH_2CO$	-56.9	4
$CH_3O-CO-CH_2OH$ (Methyl glycolate)			
32	$CH_3O\bullet + \bullet OHCH_2CO \rightarrow CH_3O-CO-CH_2OH$	-90.9	1
33	$CH_3O\bullet + CH_3OCO\bullet \rightarrow CH_3O-CO-CH_2OH$	-88.4	3
34	$CH_3OCO\bullet + \bullet OHCH_2CO \rightarrow CH_3O-CO-CH_2OH + CO$	-88.0	2
	step 1: $CH_3OCO \rightarrow CH_3O\bullet + CO$	16.0	
35	$\bullet OH + CH_3OCOCH_2 \rightarrow CH_3O-CO-CH_2OH$	-81.8	1
36	$\bullet CH_2OH + CH_3OCO\bullet \rightarrow CH_3O-CO-CH_2OH$	-79.8	1
37	$CH_3OCO\bullet + \bullet CH_2OCH_2OH \rightarrow CH_3O-CO-CH_2OH + CH_2O$	-79.4	2
	step 1: $CH_2OCH_2OH \rightarrow CH_2O + \bullet CH_2OH$	10.8	
38	$CH_3OCO\bullet + CH_3OCOCH_2 \rightarrow CH_3O-CO-CH_2OH + \bullet CH_2OH$	-54.1	4
39	$CH_3OCHO + CH_2OHCOO \rightarrow CH_3O-CO-CH_2OH + OHCO$	-16.5	3
40	$OHCH_2CO\bullet + CH_3OCH_2OH \rightarrow CH_3O-CO-CH_2OH + \bullet CH_2OH$	-14.8	2
	step 1: $OHCH_2CO\bullet \rightarrow CH_2OH + CO$	5.0	
41	$CH_3OCO\bullet + CH_3OCH_2OH \rightarrow CH_3O-CO-CH_2OH + CH_2OH$	-12.4	4

Table A1
(Continued)

	Formation Processes	$\Delta G < 0$	MNES
42	$\text{CH}_3\text{OCO}\cdot + \text{CH}_3\text{OCH}_2\text{OH} \rightarrow \text{CH}_3\text{O}-\text{CO}-\text{CH}_2\text{OH} + \text{CH}_3\text{O}\cdot$	-3.8	2
	step 1: $\text{CH}_3\text{OCH}_2\text{OH} \rightarrow \text{CH}_3\text{O}\cdot + \cdot\text{CH}_2\text{OH}$	87.5	
43	$\text{CH}_3\text{OH} + \text{CH}_3\text{OCOCH}_3 \rightarrow \text{CH}_3\text{O}-\text{CO}-\text{CH}_2\text{OH} + \text{CH}_4$	-3.4	4
44	$\text{CH}_3\text{OCHO} + \text{CH}_2\text{OHCOO} \rightarrow \text{CH}_3\text{O}-\text{CO}-\text{CH}_2\text{OH} + \text{HCOO}$	-2.8	3
45	$\text{OHCH}_2\text{CO}\cdot + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}-\text{CO}-\text{CH}_2\text{OH} + {}^3\text{CH}_2$	-2.6	2
	step 1: $\text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}\cdot + {}^3\text{CH}_2$	97.8	
46	$\text{CH}_3\text{OCHO} + \text{OHCH}_2\text{CO} \rightarrow \text{CH}_3\text{O}-\text{CO}-\text{CH}_2\text{OH} + \text{HCO}$	-1.6	2
	step 1: $\text{CH}_3\text{OCHO} \rightarrow \text{CH}_3\text{O}\cdot + \text{HCO}$	100.4	
	cis-CH₃-O-CH₂-COOH (C1-Methoxy acetic acid)		
47	$\text{HCOO}\cdot + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-88.5	3
48	$\text{CH}_3\text{OCH}_2 + \cdot\text{CH}_2\text{OCOOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH} + \text{CH}_2\text{O}$	-76.6	3
49	${}^3\text{CH}_2 + \text{OHCH}_2\text{COOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-76.0	3
50	$\text{OHCO} + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-74.8	1
51	$\cdot\text{CH}_3 + \cdot\text{CH}_2\text{OCOOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-74.6	1
52	$\text{CH}_3\text{O}\cdot + \cdot\text{CH}_2\text{COOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-68.0	1
53	$\text{CH}_3\text{OCH}_2 + \cdot\text{CH}_2\text{OCOOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH} + \text{HOC}\cdot\text{H}$	-23.7	3
54	$\text{CH}_3\text{OH} + \text{OHCH}_2\text{COOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH} + \text{H}_2\text{O}$	-1.1	4
	trans-CH₃-O-CH₂-COOH (T1-Methoxy acetic acid)		
47'	$\text{HCOO}\cdot + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-100.8	3
48'	$\text{CH}_3\text{OCH}_2 + \text{CH}_2\text{OCOOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH} + \text{CH}_2\text{O}$	-78.4	3
49'	${}^3\text{CH}_2 + \text{OHCH}_2\text{COOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-86.3	3
50'	$\text{OHCO} + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-87.0	1
51'	$\cdot\text{CH}_3 + \cdot\text{CH}_2\text{OCOOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-85.5	1
52'	$\text{CH}_3\text{O}\cdot + \cdot\text{CH}_2\text{COOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH}$	-79.8	1
53'	$\text{CH}_3\text{OCH}_2 + \cdot\text{CH}_2\text{OCOOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH} + \text{HOC}\cdot\text{H}$	-0.1	3
54'	$\text{CH}_3\text{OH} + \text{OHCH}_2\text{COOH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{COOH} + \text{H}_2\text{O}$	-3.1	4
	OHCH₂-CH₂-OCHO (2-hydroxyethyl formate)		
55	$\text{HCO} + \text{OHCH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO}$	-87.9	1
56	$\cdot\text{OH} + \cdot\text{CH}_2\text{CH}_2\text{OCHO} \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO}$	-83.9	1
57	$\cdot\text{CH}_2\text{OH} + \cdot\text{CH}_2\text{OCHO} \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO}$	-74.0	1
58	$\text{HOCH} + \text{OHCH}_2\text{CH}_2\text{OH} \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO} + \text{H}_2$	-60.0	4
59	$\text{HOCH} + \text{OHCH}_2\text{CH}_2\text{O} \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO} + \cdot\text{H}$	-59.9	2
	step 1: $\text{HOCH} + \text{OHCH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{OHCH}_2\text{CH}_2\text{OCHOH}$	-72.6	
	step 2: $\text{OHCH}_2\text{CH}_2\text{OCHOH} \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO} + \cdot\text{H}$	7.4	
60	$\text{CH}_2\text{O} + \text{OHCH}_2\text{CH}_2\text{OH} \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO} + \text{H}_2$	-7.1	3
61	$\text{CH}_2\text{O} + \text{OHCH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{OHCH}_2-\text{CH}_2-\text{OCHO} + \text{H}$	-7.0	2
	step 1: $\text{OHCH}_2\text{CH}_2\text{O}\cdot + \text{CH}_2\text{O} \rightarrow \text{OHCH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{O}$	-13.5	
	CH₃-C(OH)₂-CHO (3-metil 2,2-diol propanal)		
62	$\text{HOC}\cdot\text{H} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3-\text{C}(\text{OH})_2\text{CHO}$	-39.3	3
	OHCH₂-CO-CH₂OH (Dihydroxyacetone)		
63	$\cdot\text{CH}_2\text{OH} + \cdot\text{OCH}_2\text{CHO} \rightarrow \text{OHCH}_2-\text{CO}-\text{CH}_2\text{OH}$	-89.1	3
64	$\cdot\text{CH}_2\text{OH} + \cdot\text{OHCH}_2\text{CO} \rightarrow \text{OHCH}_2-\text{CO}-\text{CH}_2\text{OH}$	-71.4	1
65	${}^3\text{CH}_2 + \text{CH}_2\text{OHCOOH} \rightarrow \text{OHCH}_2-\text{CO}-\text{CH}_2\text{OH}$	-68.6	3
66	$\text{OHCH}_2\text{CHO} + \cdot\text{OCH}_2\text{CHO} \rightarrow \text{OHCH}_2-\text{CO}-\text{CH}_2\text{OH} + \text{HCO}$	-19.1	3
67	$\text{OHCH}_2\text{CHO} + \text{OHCH}_2\text{COO} \rightarrow \text{OHCH}_2-\text{CO}-\text{CH}_2\text{OH} + \text{OHCO}$	-16.3	3
68	$\text{CH}_2\text{O} + \text{OHCH}_2\text{CHO} \rightarrow \text{OHCH}_2-\text{CO}-\text{CH}_2\text{OH}$	-9.8	3
69	$\text{OHCH}_2\text{CHO} + \text{OHCH}_2\text{CO} \rightarrow \text{OHCH}_2-\text{CO}-\text{CH}_2\text{OH} + \text{HCO}$	-1.4	2
	step 1: $\text{OHCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{O} + \text{HCO}$	81.3	
	CH₃O-CH₂-OCO₂H (Methoxy metil formate)		
70	$\text{CH}_3\text{O}\cdot + \text{CH}_3\text{OCH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H} + \text{H}_2$	-91.1	4
71	$\text{HCO} + \text{CH}_3\text{OCH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H}$	-87.0	1
72	$\text{HCOO}\cdot + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H}$	-80.7	1
73	$\text{CH}_3\text{O}\cdot + \cdot\text{CH}_2\text{OCHO} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H}$	-77.3	1
74	$\cdot\text{CH}_2\text{OCHO} + \text{CH}_3\text{OCH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H} + \text{CH}_2\text{O}$	-76.3	2
	step 1: $\text{CH}_2\text{OCHO} \rightarrow \text{CH}_2\text{O} + \text{CHO}$	20.6	
75	$\text{OHCO} + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H}$	-67.0	3
76	$\cdot\text{CH}_2\text{OCHO} + \text{CH}_3\text{OCH}_2\text{O} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H} + \text{HOC}\cdot\text{H}$	-23.4	4
77	$\text{CH}_2\text{O} + \text{CH}_3\text{OCH}_2\text{OH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H} + \text{H}_2$	-7.5	4
78	$\text{CH}_2\text{O} + \text{CH}_3\text{OCH}_2\text{O} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H} + \cdot\text{H}$	-6.1	2
	step 1: $\text{CH}_3\text{OCH}_2\text{O} + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCH}_2\text{O}$	-12.6	
79	$\cdot\text{CH}_2\text{OCHO} + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H} + \cdot\text{CH}_3$	-4.5	4
80	$\cdot\text{CH}_2\text{OCHO} + \text{CH}_3\text{OCH}_2\text{OH} \rightarrow \text{CH}_3\text{O}-\text{CH}_2-\text{OCO}_2\text{H} + \cdot\text{CH}_2\text{OH}$	-1.3	3
	OHCH₂-CHOH-CHO (Gliceraldehyde)		
81	$\cdot\text{CH}_2\text{OH} + \cdot\text{OCH}_2\text{CHO} \rightarrow \text{OHCH}_2-\text{CHOH}-\text{CHO}$	-86.5	3

Table A1
(Continued)

	Formation Processes	$\Delta G < 0$	MNES
82	$\bullet\text{OCH}_2\text{CHO} + \text{OHCHCHO} \rightarrow \text{OHCH}_2\text{-CHOH-CHO} + \text{CO}$	-79.1	4
83	$\bullet\text{CH}_2\text{OH} + \text{OHCH}_2\text{CO? OHCH}_2\text{-CHOH-CHO}$	-68.8	4
84	$\text{OHCH}_2\text{CO} + \text{OHCHCHO} \rightarrow \text{OHCH}_2\text{-CHOH-CHO} + \text{CO}$	-61.4	2
	step 1: $\text{OHCH}_2\text{CO} \rightarrow \text{CH}_2\text{OH} + \text{CO}$	5.0	
85	$\text{HOCH} + \text{OHCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{-CHOH-CHO}$	-60.1	3
86	$\bullet\text{CH}_2\text{OH} + \text{OHCHCHO} \rightarrow \text{OHCH}_2\text{-CHOH-CHO}$	-57.2	1
87	$\text{OHCH}_2\text{CHO} + \bullet\text{OCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{-CHOH-CHO} + \text{HCO}$	-16.5	3
88	$\text{CH}_2\text{O} + \text{OHCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{-CHOH-CHO}$	-7.2	3
	$\text{OHCH}_2\text{-CH=C(OH)}_2$ (1-propen 1,1-diol 3-ol)		
89	$\text{CH}_2\text{O} + \text{OHCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{CHC(OH)}_2$	-3.1	7
	$\text{CH}_3\text{O-CHOH-CHO}$ (3-methoxy 2-ol propanal)		
90	$\text{HCO} + \text{CH}_3\text{OCH}_2\text{O} \rightarrow \text{CH}_3\text{O-CHOH-CHO}$	-79.1	3
91	$\text{CH}_3\text{O}\bullet + \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{O-CHOH-CHO} + \text{H}_2$	-74.5	4
92	$\text{HCO} + \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{O-CHOH-CHO}$	-70.4	1
93	$\text{CH}_3\text{O}\bullet + \text{CH}_3\text{OCO} \rightarrow \text{CH}_3\text{O-CHOH-CHO}$	-69.3	5
94	$\text{HOCH} + \text{CH}_3\text{OCH}_2\text{OH} \rightarrow \text{CH}_3\text{O-CHOH-CHO} + \text{H}_2$	-52.5	5
95	$\text{HOCH} + \text{CH}_3\text{OCH}_2\text{O} \rightarrow \text{CH}_3\text{O-CHOH-CHO} + \bullet\text{H}$	-51.1	4
96	$\text{HOCH} + \text{CH}_3\text{OCHO} \rightarrow \text{CH}_3\text{O-CHOH-CHO}$	-43.8	3
97	$\text{HOCH} + \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{O-CHOH-CHO} + \bullet\text{H}$	-42.4	2
	step 1: $\text{CH}_3\text{OCHOH} + \text{HOC}^*\text{H} \rightarrow \text{CH}_3\text{O-CHOH-CHOH}$	-76.6	
	$\text{OHCH}_2\text{-COH-CHOH}$ (1,2,3 propene triol)		
98	$\bullet\text{CH}_2\text{OH} + \text{OHCH}_2\text{CO}\bullet \rightarrow \text{OHCH}_2\text{-COH-CHOH}$	-60.7	3
99	$\text{HOCH} + \text{OHCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{-COH-CHOH}$	-52.0	3
100	$\text{HOCH} + \text{OHCH}_2\text{CH}_2\text{OH} \rightarrow \text{OHCH}_2\text{-COH-CHOH} + \text{H}_2$	-44.4	4
101	$\text{HOCH} + \text{OHCH}_2\text{CH}_2\text{O}\bullet \rightarrow \text{OHCH}_2\text{-COH-CHOH} + \bullet\text{H}$	-44.2	4
102	$\bullet\text{CH}_2\text{COH} + \text{OHCH}_2\text{CH}_2\text{O}\bullet \rightarrow \text{OHCH}_2\text{-COH-CHOH} + {}^3\text{CH}_2$	-6.6	6
103	$\text{OHCH}_2\text{CHO} + \text{OHCH}_2\text{CH}_2\text{O} \rightarrow \text{OHCH}_2\text{-COH-CHOH} + \bullet\text{CH}_2\text{OH}$	-2.2	7
	$\text{OHCH}_2\text{-O-CH}_2\text{-CHO}$ (Hydroxymethyl methylcarbonyl ether)		
104	$\bullet\text{CH}_2\text{OCHO} + \bullet\text{OCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{-O-CH}_2\text{CHO} + \text{CO}$	-79.2	4
105	$\bullet\text{CH}_2\text{OH} + \bullet\text{OCH}_2\text{CHO} \rightarrow \text{OHCH}_2\text{-O-CH}_2\text{CHO}$	-77.4	1
106	$\text{OHCH}_2\text{CHO} + \text{OHCH}_2\text{CH}_2\text{O} \rightarrow \text{OHCH}_2\text{-O-CH}_2\text{CHO} + \bullet\text{CH}_2\text{OH}$	-1.2	3
	$\text{OHCH=CH-O-CH}_2\text{OH}$ (methoxy 1,1 ethylene diol)		
107	$\bullet\text{CH}_2\text{OH} + \bullet\text{OCH}_2\text{CHO} \rightarrow \text{OHCH=CH-O-CH}_2\text{OH}$	-68.8	3
	$\text{CH}_3\text{O-CH=C(OH)}_2$ (2-methoxy 1,1-ethylene diol)		
108	$\text{HCOO}\bullet + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{O-CH=C(OH)}_2$	-64.6	3
109	$\text{HOCH} + \text{CH}_3\text{OCHO} \rightarrow \text{CH}_3\text{O-CH=C(OH)}_2$	-35.5	5
110	$\text{HOCH} + \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{O-CH=C(OH)}_2 + \text{H}$	-34.1	4
	$\text{CH}_3\text{O-COH=CHOH}$ (2-methoxy 1,2-ethylene diol)		
111	$\text{CH}_3\text{OCH}_2\text{O}\bullet + \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CH}_3\text{OH}$	-75.2	6
112	$\text{HCOO}\bullet + \text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3\text{-O-COH-CHOH}$	-62.5	7
113	$\text{CH}_3\text{O}\bullet + \text{CH}_3\text{OCO}\bullet \rightarrow \text{CH}_3\text{-O-COH-CHOH}$	-59.0	5
114	$\text{CH}_3\text{OCO}\bullet + \text{CH}_3\text{OCH}_2\text{O}\bullet \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CH}_2\text{O}$	-57.9	6
115	$\text{CH}_3\text{OCO}\bullet + \text{OHCH}_2\text{CO} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CO}$	-54.5	4
116	$\text{CH}_3\text{OCO}\bullet + \text{OHCH}_2\text{CH}_2\text{O} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CH}_2\text{O}$	-53.5	4
117	$\bullet\text{OH} + \text{CH}_3\text{OCOCH}_2 \rightarrow \text{CH}_3\text{-O-COH-CHOH}$	-52.3	3
118	$\text{CH}_3\text{OCO}\bullet + \text{CH}_2\text{OCHO} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CO}$	-52.2	6
119	$\bullet\text{CH}_2\text{OH} + \text{CH}_3\text{OCO}\bullet \rightarrow \text{CH}_3\text{-O-COH-CHOH}$	-50.4	3
120	$\text{CH}_3\text{OCO}\bullet + \text{CH}_2\text{OCH}_2\text{OH} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CH}_2\text{O}$	-50.0	4
121	$\text{CH}_3\text{OCO}\bullet + \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CH}_2\text{O}$	-49.2	4
122	$\text{CH}_3\text{OCO}\bullet + \text{OHCHCHO} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{CO}$	-42.9	4
123	$\text{HOCH} + \text{CH}_3\text{OCH}_2\text{OH} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{H}_2$	-42.2	4
124	$\text{HOCH} + \text{CH}_3\text{OCH}_2\text{O} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \bullet\text{H}$	-40.8	4
125	$\text{HOCH} + \text{CH}_3\text{OCHO} \rightarrow \text{CH}_3\text{-O-COH-CHOH}$	-33.4	3
126	$\text{HOCH} + \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \bullet\text{H}$	-32.0	2
	step 1: $\text{CH}_3\text{OCHOH} + \text{HOC}^*\text{H} \rightarrow \text{CH}_3\text{-O-CHOH-CHOH}$	-69.9	
	step 2: $\text{CH}_3\text{-O-CHOH-CHOH} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \bullet\text{H}$	32.4	
127	$\text{CH}_3\text{OCO}\bullet + \text{OHCH}_2\text{CH}_2\text{O} \rightarrow \text{CH}_3\text{-O-COH-CHOH} + \text{HOCH}$	-0.7	4

Note. The barrierless processes for which MNES < 3 (MNES = Maximum number of Necessary Elementary Steps, MNES) are shown in italics.

Table A2
Anharmonic Vibrational Frequencies^a of the MAA Conformers (in cm⁻¹) Computed Using MP2/cc-pVTZ

	C ₁ Symmetry					C _s Symmetry			
	C1	C2	T2	T3		T1	C3	C4	T4
ν_1	3588	3576	3473	3640	A'	3497	3594	3577	3646
ν_2	3057	3056	3060	3061		3061	3037	3056	3059
ν_3	3007	3003	3017	3016		2907	2843	2906	2920
ν_4	3009	2990	2996	2982		2845	2876	2867	2866
ν_5	2865	2943	2975	2856		1818	1825	1797	1843
ν_6	2924	2981	2950	2874		1490	1492	1488	1489
ν_7	1810	1794	1838	1832		1470	1466	1466	1466
ν_8	1491	1484	1485	1493		1450	1451	1448	1447
ν_9	1465	1470	1474	1461		1383	1417	1410	1399
ν_{10}	1460	1457	1460	1493		1346	1308	1361	1259
ν_{11}	1429	1437	1444	1428		1222	1224	1214	1218
ν_{12}	1396	1384	1343	1373		1173	1160	1166	1157
ν_{13}	1332	1354	1329	1306		1134	1113	1138	1122
ν_{14}	1259	1288	1274	1259		994	1008	1007	1006
ν_{15}	1215	1209	1191	1212		881	890	878	889
ν_{16}	1165	1159	1180	1166		628	637	619	646
ν_{17}	1162	1166	1167	1161		479	448	462	452
ν_{18}	1105	1137	1108	1111		383	371	366	369
ν_{19}	1024	1024	1020	1020		210	194	170	193
ν_{20}	959	957	935	958	A''	3013	2934	2968	2969
ν_{21}	849	840	857	853		2944	2923	2926	2895
ν_{22}	689	668	690	665		1470	1474	1470	1470
ν_{23}	585	612	648	566		1227	1242	1249	1258
ν_{24}	<i>513</i>	<i>515</i>	548	505		1168	1240	1169	1167
ν_{25}	474	505	509	<i>415</i>		1021	1024	1020	1020
ν_{26}	376	385	400	371		<i>654</i>	630	674	579
ν_{27}	280	280	301	281		568	<i>513</i>	<i>516</i>	<i>415</i>
ν_{28}	<i>175</i>	<i>172</i>	<i>178</i>	<i>178</i>		217	253	227	228
ν_{29}	<i>129</i>	<i>135</i>	<i>132</i>	<i>131</i>		<i>116</i>	<i>104</i>	94	<i>101</i>
ν_{30}	<i>69</i>	<i>49</i>	83	74		48	<i>102</i>	<i>127</i>	71

Note.

^a Effects of Fermi resonances have been considered. Torsional frequencies are emphasized in italics.

Table A3

Expansion Coefficients of the 3D-potential Energy Surfaces (in cm⁻¹)

cis-MAA	trans-MAA	<i>n</i>	<i>m</i>	1
1575.637	3451.485	0	0	0
393.356	391.269	3	0	0

(This table is available in its entirety in machine-readable form.)

Figure A1. Barrierless energy profiles for the production of the $\text{C}_2\text{H}_5\text{-O-COOH}$ isomer.

(The complete figure set (14 images) is available.)

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