Electronic supplementary information for: Electron-Induced Origins of Prebiotic Building Blocks of Sugars: Mechanism of Self-Reactions of a Methanol Anion Dimer

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This file contains information about the orbital stabilization method, molecular and natural transition orbitals of excited states, additional potential energy surfaces, and cartesian coordinates of important geometries.

1. Orbital stabilization method for resonances of methanol

The energies and widths for methanol are obtained using an orbital stabilization method. Stabilization curves for methanol are shown in Figure S1. The top curve is used to obtain the shape resonances using the ground singlet state as reference in EOM-EA-CCSD. The bottom curve is used to obtain the lowest Feshbach resonance using the lowest triplet state as reference in EOM-EA-CCSD. α is the parameter scaling the exponent of the diffuse functions in the basis set. Analytic continuation is applied to avoided crossings to obtain the position and widths of related resonances. Analytic Continuation can be used with the orbital stabilization method where the complex stationary points and energies are located using various forms of the Generalized Padé Approximation (GPA). [1-3] GPA has been used here in the following form:

$$E^2 P + E\,Q + R = 0$$

The quantities, P, Q and R are themselves polynomial expansions of the scaling parameter (α) with coefficients p_i, r_k, q_j respectively. These expansions are commonly denoted as the (*i, j, k*) General Padé Approximations. We have used the (*3,3,3*), (*4,4,4*) and (*5,5,5*) approximations here. Using more than one version checks the viability of the results. The results reported in the main manuscript are an average of the three values. Once P, R, Q are obtained (by fitting to the ab initio data), the location of the complex stationary points (α^*) is determined. More details of how we use the GPA approximation can be found in our previous publications.[4,5]

Table S1: Shape Resonance of Methanol Monomer

GPA	E_r (Γ) [eV]
(3,3,3)	1.6472 (0.8958)
(4,4,4)	1.6633 (0.9374)
(5,5,5)	1.6971 (0.9990)

Table S2: Feshbach Resonance of Methanol Monomer

GPA	E_r (Γ) [eV]	E_r (Γ) [eV]/shifted
(3,3,3)	0.0588 (0.0056)	6.6270 (0.0056)
(4,4,4)	0.0515 (0.0638)	6.6197 (0.0638)
(5,5,5)	0.0760 (0.1416)	6.6442 (0.1416)

The Feshbach resonance is shifted using the energy gap between the singlet and triplet reference states, which is 6.568 eV. Only the lowest Feshbach resonance associated with the lowest triplet state can be calculated using this approach.

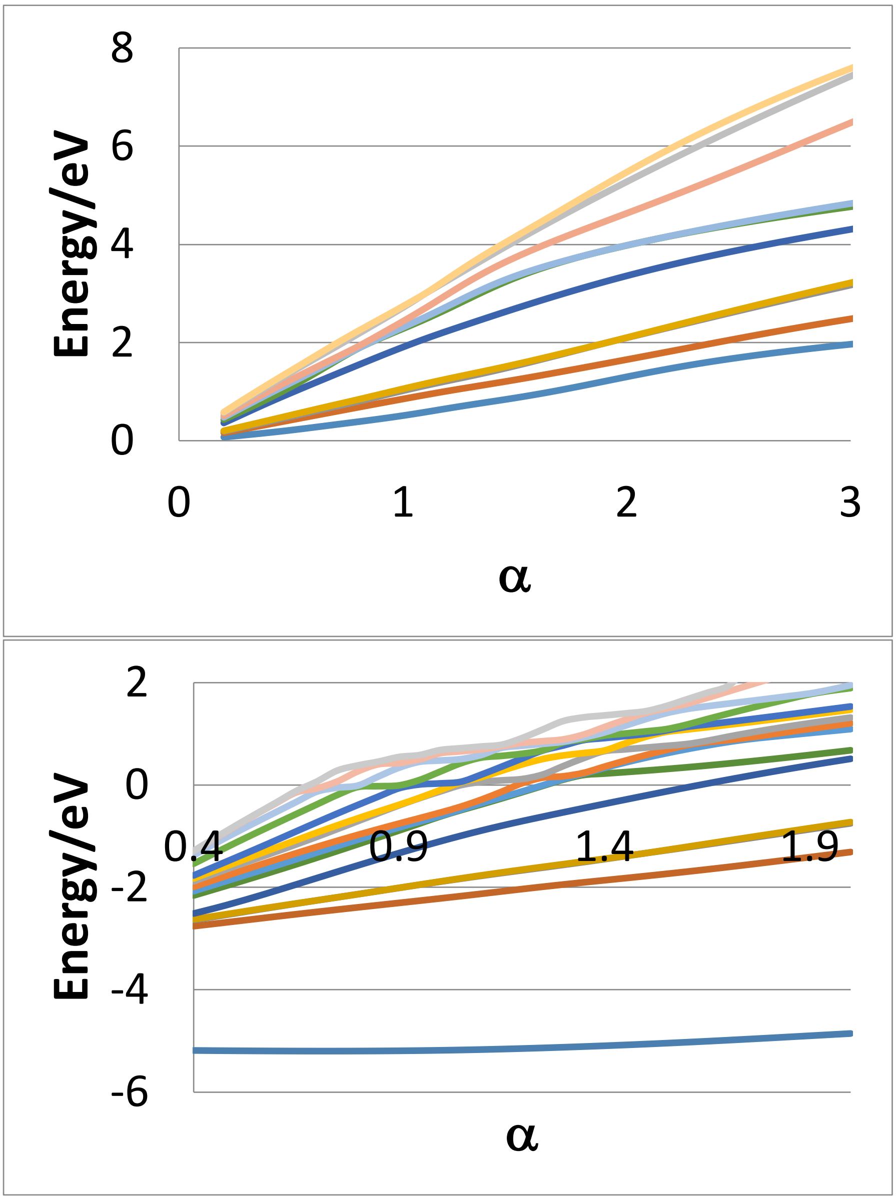

Figure S1: Orbital stabilization curves derived from EOM-EA-CCSD/aug-cc-pVDZ+1s,1p,1d for methanol monomer. Top plot uses the singlet ground state as reference while bottom plot uses the lower triplet state.

2. Orbitals and natural transition orbitals of methanol and methanol dimer

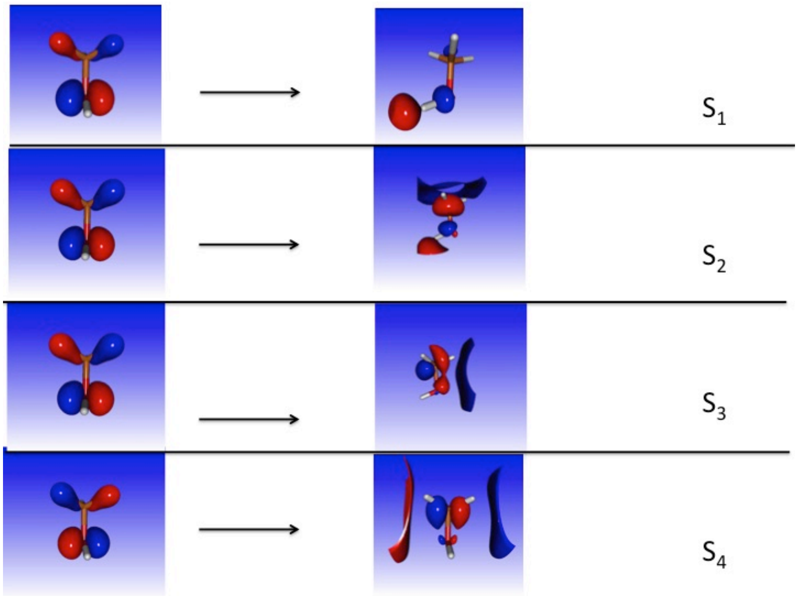

Figure S2: Natural transition orbitals at the EOM-EE-CCSD/aug-cc-pVDZ level for the first 4 excited states of methanol

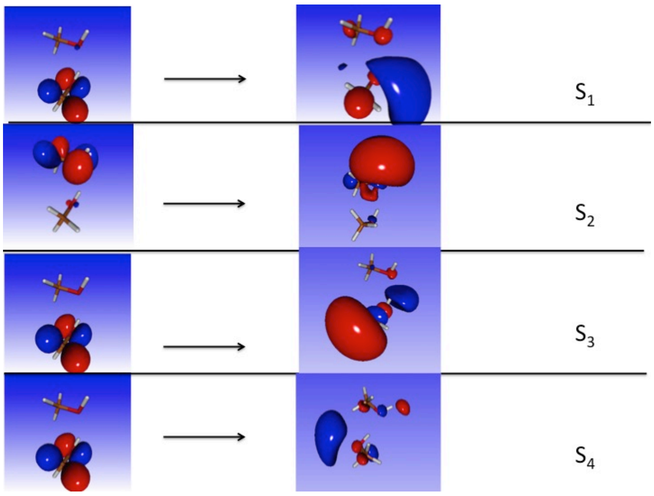

Figure S3: Natural transition orbitals at the EOM-EE-CCSD/aug-cc-pVDZ level for the first 4 singlet excited states of methanol dimer

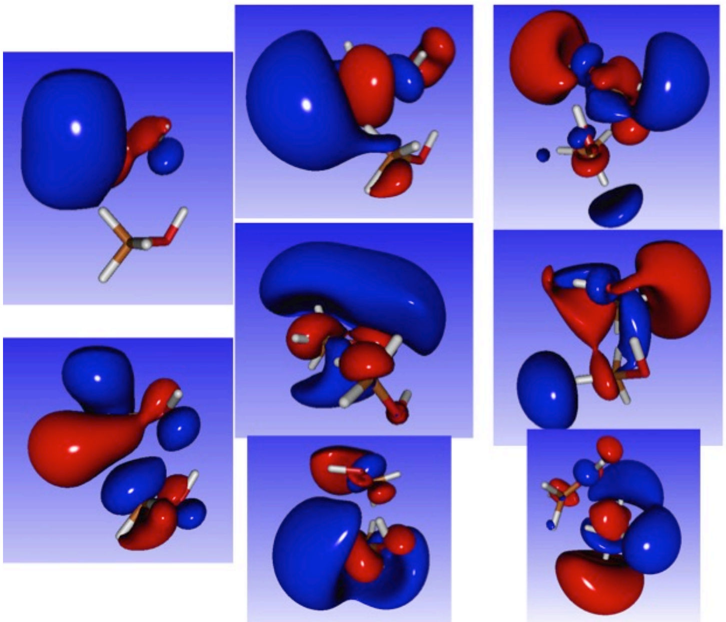

Figure S4: Orbitals in the active space for CASSCF and CASPT2 calculations for $(CH_3OH)_2$ anion close to equilibrium.

3. Additional potential energy surfaces for neutral and anionic pathways

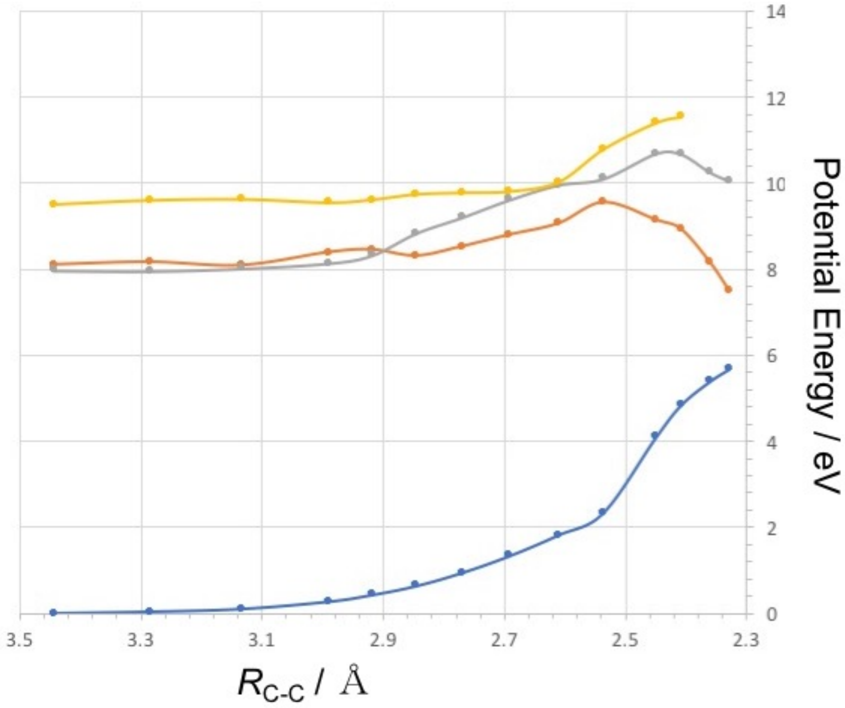

Figure S5: Ground and excited state energies of methanol dimer along the MEP profile between reactant and the transition state calculated at the CASPT2/cc-pVDZ level.

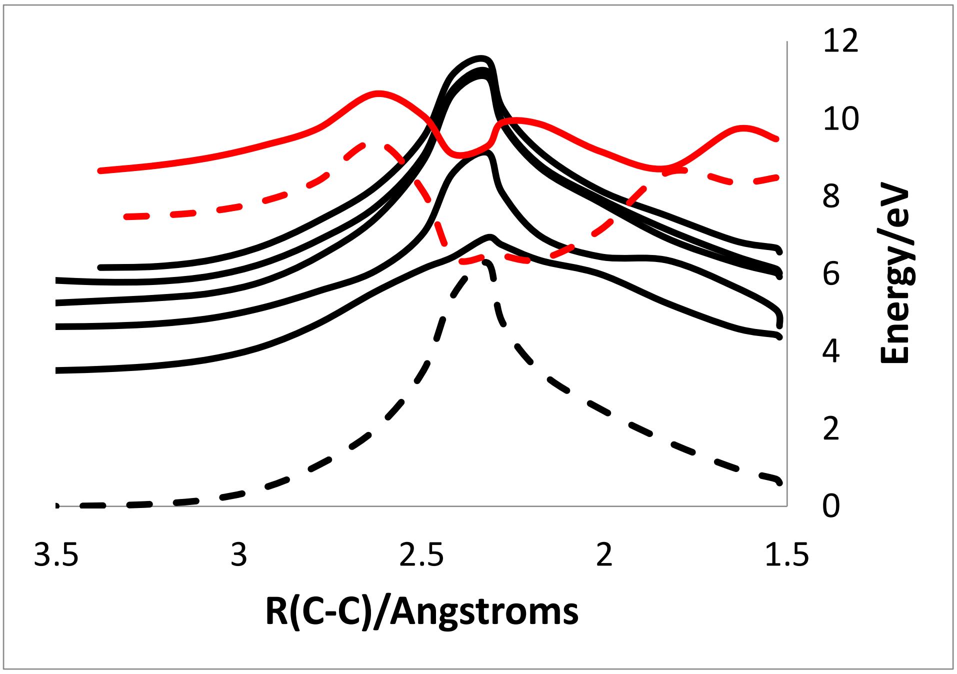

Figure S6: Potential energy profiles associated with the anionic dimer along the minimum energy profile of the $(CH_3OH)_2 \rightarrow C_2H_6O_2 + H_2$ reaction, calculated using EOM-EA-CCSD/cc-pVDZ . Black dashed curve represents the neutral S_0 MEP path, while the black solid curves represent the shape resonances originating by attaching an electron to the ground state. Red dashed line is the first excited triplet state while the red solid curve represents the core-excited Feshbach resonance originating by attaching an electron to the triplet state.

4. Cartesian coordinates

Cartesian coordinates (in Angstroms) of the ground state minimum energy geometry of $(CH_3OH)_2$

C	-1.88321304	0.28713000	0.42135099
H	-2.76734090	0.84409302	0.07623300
H	-1.21817303	1.00278497	0.94458503
H	-2.22716999	-0.45681900	1.16693199
O	-1.27773905	-0.30115300	-0.69948202
H	-0.46608600	-0.72748798	-0.38245600
O	1.27913904	-0.67116600	0.25721401
H	1.86754501	-1.03120899	0.92717898
C	1.75409806	0.59964001	-0.15016600
H	2.72707009	0.53256702	-0.66753697
H	1.00369501	0.99070603	-0.85003102
H	1.84395599	1.30330205	0.69613099

Cartesian coordinates (in Angstroms) of the first point used in the MEP paths shown in Figures 5 and 6 of the main manuscript

C	-1.571131000000	0.555319000000	0.305811000000
H	-2.641515000000	0.794126000000	0.397092000000
H	-1.087979000000	1.407819000000	-0.214146000000
H	-1.152535000000	0.512112000000	1.332517000000
O	-1.450138000000	-0.654692000000	-0.387864000000
H	-0.507798000000	-0.880842000000	-0.344688000000
O	1.258063000000	-0.572724000000	0.202895000000
H	1.372700000000	-0.667852000000	1.154389000000
C	1.705997000000	0.715731000000	-0.177945000000
H	2.800216000000	0.816431000000	-0.073597000000
H	1.443308000000	0.844037000000	-1.236360000000
H	1.215704000000	1.519239000000	0.397998000000

Cartesian coordinates (in Angstroms) of the neutral TS associated with the $(CH_3OH)_2$ → $C_2H_6O_2 + H_2$ reaction

C	-1.09907305	0.52492398	0.28012201
H	-1.66517305	1.38998497	-0.10141700
H	-0.00347700	1.19502401	-0.00552100
H	-1.03773105	0.47252199	1.38331997
O	-1.38958704	-0.61530799	-0.38108900
H	-0.73592401	-1.27275395	-0.09700500
O	1.20426297	-0.66726297	0.18147400
H	1.42955005	-0.75527501	1.11607003
C	1.19763398	0.70251602	-0.12898999
H	1.86619794	1.27284300	0.51243198
H	1.35957801	0.83204103	-1.19848096
H	0.55461502	2.60589194	-0.24083599
H	0.55461502	2.60589194	-0.24083599

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[2] K. D. Jordan, J. Mol. Spectrosc., 1975, **56**, 329–331.

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[4] M. A. Fennimore, S. Matsika, Phys. Chem. Chem. Phys. 2016, **18**, 30536-30545

[5] M. A. Fennimore, T. N. V. Karsili, S. Matsika, Phys. Chem. Chem. Phys. 2017, **19**, 17233-17241