Supporting Information

Bottom-Up Synthesis of 1,1-Ethenediol ($H_2CC(OH)_2$) - the Simplest Unsaturated Geminal Diol - in Interstellar Analogue Ices

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Table S1. Assignments of new infrared peaks after irradiation in the CO_2:CH_4 ice

Band position (cm^{-1})	Assignment	Characterization
821	ν_{12} C_2H_6	CH_3 rock
958	ν_7 C_2H_4	CH_2 wag
1022	ν_{15} CH_3OH	CO stretch
1051	ν_{15} t-CH_3COOH	CH_3 rocking
1078	ν_4 t-HOCO	CO stretch
1091	ν_2 HCO	HCO bending
1157	ν_8 t-CH_3COOH	CHO rocking
1195	ν_8 t-CH_3COOH	CHO rocking
1352	ν_7 CH_3CHO	CH_3 deformation
1373	ν_6 C_2H_6	CH_3 symm. def.
1465	ν_{11} C_2H_6	CH_3 d-def.
1499	ν_3 H_2CO	CH_2 scissor
1610	ν_5 H_2C=CHOH	C=C stretch
1640 br	ν_5 H_2C=CHOH	C=C stretch
1722	ν_4 t-CH_3COOH B	CO stretch
1736 br	ν (CO) RCHO	CO stretch
1756	ν_4 t-CH_3COOH A	CO stretch
1783	ν_4 t-CH_3COOH M	CO stretch
1823	ν_2 t-HOCO	CO stretch
1842	ν_2 t-HOCO	CO stretch
1853	ν_2 t-HOCO/ν_3 HCO	CO stretch
2093	ν_1 ^{13}CO	CO stretch
2140	ν_1 CO	CO stretch
2742	ν(CH) RCHO	CH stretch
2844	ν_2 + ν_4+ ν_{12} C_2H_6	combination
2884	ν_5 C_2H_6	CH_3 symm str.
2924	methylacetelyne/propene	CH_3 symm str.
2945	ν_3 CH_3COOH	CH_3 symm str.
2962	ν_1 C_2H_6	CH_3 symm str.
2977	ν_{10} C_2H_6	CH_3 deg. str.
3097	ν_9 C_2H_4	CH_2 asymm. str.
3147	ν_3 CH_3	CH stretch
3259	ν_3 C_2H_2	CH stretch
3500 br	ν(OH)	OH stretch

Table S2. Error analysis of computed ionization energies for COMs containing oxygen atoms; adiabatic ionization energies were computed at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory + zero-point vibrational energy.

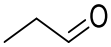
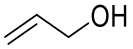
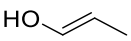
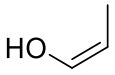
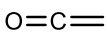
Structure	Name	Experimental adiabatic ionization energy in eV	Lowest Computed adiabatic ionization energy in eV	Difference to lower bound	Difference to upper bound
	Acetone	9.703 ± 0.006 [1]	9.71	−0.013	−0.001
	Propanal	9.96 ± 0.01 [1]	9.97	-0.02	0.00
	Propylene oxide	10.22 ± 0.02 [2]	10.24	−0.04	0.00
	Prop-1-en-2-ol	8.67 ± 0.05 [3]	8.71	−0.09	0.01
	2-Propen-1-ol	9.67 ± 0.03 [1]	9.65	−0.01	0.05
	(*E*)-1-Propenol	8.64 ± 0.02 [4]	8.61	0.01	0.05
	(*Z*)-1-Propenol	8.70 ± 0.03 [4]	8.63	0.04	0.10
	Methanol	10.84 ± 0.01	10.86	−0.03	−0.01
	Propadienone	9.12 ± 0.05	9.15	−0.08	0.02
	Formaldehyde	10.88 ± 0.01	10.89	−0.02	0.00
	Ketene	9.617 ± 0.003	9.58	0.034	0.040
	Acetaldehyde	10.229 ± 0.0007	10.24	−0.0117	−0.0103
			Average difference	−0.019	0.021
			Std. deviation	0.039	0.033
			Error bounds	−0.06	0.05

Table S3. Data used to calculate irradiation doses of methane and carbon dioxide

irradiation current, I (nA)	50 ± 5	
initial kinetic energy of the electrons, E_{init}	5 keV	
total number of electrons	$(1.1 \pm 0.1)\times10^{15}$	
average penetration depth, l^* (nm)	360 ± 30	
density of the ice, ρ (g cm^{-3})	0.87 ± 0.09	
average kinetic energy of transmitted electrons, E_{trans}^* (keV)	0.8 ± 0.1	
average kinetic energy of backscattered electrons, E_{bs}^* (keV)	3.4 ± 0.3	
fraction of transmitted electrons, f_{trans}^*	0	
fraction of backscattered electrons, f_{bs}^*	0.37 ± 0.04	
irradiated area, A (cm^2)	1.0 ± 0.1	
dose per molecule (eV)	CO_2	CH_4
	9.9 ± 1.6	3.6 ± 0.6

Notes: *CASINO output values

References

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(2) Watanabe, K.; Nakayama, T.; Mottl, J. Ionization Potentials of Some Molecules. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2* (4), 369-382

(3) Iraqi, M.; Pri-Bar, I.; Lifshitz, C. Electron Impact Ionization of Unstable Enols: H_2C=CHOH, H_2C=C(OH)-CH_3 and H_2C=C(OH)-C_2H_5. *Org. Mass Spectrom.* **1986**, *21* (10), 661-664

(4) Tureček, F. (E)- and (Z)-Prop-1-en-1-ol: Gas-Phase Generation and Determination of Heats of Formation by Mass Spectrometry. *J. Chem. Soc., Chem. Commun.* **1984**, (20), 1374-1375