Supporting Information for

Radicals Derived from Acetaldehyde and Vinyl Alcohol

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I. CARTESIAN CCSD(T)/ANO2 GEOMETRIES (IN BOHR)

TABLE I. *syn*-Vinyl Alcohol (CH_2=CHOH)

	X	Y	Z
C	−2.363 208 57	0.398 946 93	0.000 000 00
C	−0.157 867 69	−0.821 084 50	0.000 000 00
O	2.181 834 28	0.254 882 79	0.000 000 00
H	−0.023 918 44	−2.860 191 79	0.000 000 00
H	−2.469 043 64	2.443 118 27	0.000 000 00
H	−4.103 294 47	−0.663 666 12	0.000 000 00
H	1.986 986 34	2.061 884 46	0.000 000 00

TABLE II. *anti*-Vinyl Alcohol (CH_2=CHOH)

	X	Y	Z
C	−2.36627421	0.38472674	−0.00000000
C	−0.15950180	−0.82344652	0.00000000
O	2.09290336	0.44816573	0.00000000
H	−0.03561830	−2.86855272	0.00000000
H	−2.45727742	2.42520811	−0.00000000
H	−4.09664825	−0.69333181	0.00000000
H	3.44763115	−0.75227774	−0.00000000

TABLE III. 1-Hydroxyvinyl Radical (CH_2=$\dot{C}$OH)

	X	Y	Z
C	2.41650197	0.27274813	−0.02296243
C	0.14443152	−0.76795343	0.01341273
H	4.08131749	−0.88717384	0.17332040
H	2.62867163	2.29709790	−0.28414435
O	−2.13882366	0.31934158	0.07931463
H	−3.25790176	−0.58178204	−1.03425026

TABLE IV. (Z) *anti*-2-Hydroxyvinyl Radical ($\dot{C}$H=CHOH)

	X	Y	Z
O	−2.01790884	0.48603575	0.00000000
C	0.23541970	−0.82336093	0.00000000
C	2.45668825	0.29526910	0.00000000
H	−3.37315932	−0.71746202	−0.00000000
H	0.08076780	−2.86798477	−0.00000000
H	3.26360102	2.15960570	0.00000000

TABLE V. (Z) *syn*-2-Hydroxyvinyl Radical ($\dot{C}$H=CHOH)

	X	Y	Z
C	−2.44727795	0.31824363	−0.00000000
C	−0.23951871	−0.83142728	0.00000000
H	−3.24077965	2.19052593	−0.00000000
O	2.10592398	0.29549434	−0.00000000
H	−0.06597642	−2.86846460	0.00000000
H	1.87544178	2.09861891	−0.00000000

TABLE VI. (E) *anti*-2-Hydroxyvinyl Radical ($\dot{\text{C}}$H=CHOH)

	X	Y	Z
C	2.40451874	0.48850537	0.00000000
C	0.24460052	−0.74581534	−0.00000000
H	4.36779322	−0.02879450	−0.00000000
O	−2.06500244	0.42508011	0.00000000
H	−3.35233815	−0.84901044	−0.00000000
H	0.21502306	−2.80477920	−0.00000000

TABLE VII. (E) *syn*-2-Hydroxyvinyl Radical ($\dot{\text{C}}$H=CHOH)

	X	Y	Z
C	2.38644718	0.50793212	−0.00000000
C	0.24515655	−0.76203461	−0.00000000
H	4.37051102	0.07829181	−0.00000000
O	−2.13709182	0.23409161	0.00000000
H	0.19612655	−2.81431632	−0.00000000
H	−1.98349433	2.04637562	0.00000000

TABLE VIII. Acetaldehyde (CH_3CHO)

	X	Y	Z
O	−2.15910280	0.43922255	0.00000000
C	−0.23561810	−0.79580918	−0.00000000
C	2.37678464	0.31347786	0.00000000
H	−0.32930757	−2.88392840	−0.00000000
H	2.28889276	2.36673962	0.00000000
H	3.40621991	−0.35527773	1.65989715
H	3.40621991	−0.35527773	−1.65989715

TABLE IX. Acetyl Radical ($CH_3C\dot{O}$)

	X	Y	Z
O	−2.18483227	0.33515626	0.00000000
C	−0.25825721	−0.80117117	0.00000000
C	2.40215001	0.24121760	0.00000000
H	2.38232507	2.30068452	0.00000000
H	3.38279208	−0.47629315	1.66292407
H	3.38279208	−0.47629315	−1.66292407

TABLE X. Vinyl Radical ($CH_2{=}\dot{C}H$)

	X	Y	Z
C	1.17056527	0.04344375	0.00000000
C	−1.30355350	−0.16017932	0.00000000
H	2.39499755	−1.59940034	0.00000000
H	2.09110324	1.88553562	−0.00000000
H	−2.90263271	1.10381515	0.00000000

TABLE XI. Vinoxy Radical ($\dot{C}H_2CH{=}O$)

	X	Y	Z
C	2.33952604	0.35058494	−0.00000000
C	−0.10201988	−0.80716171	0.00000000
H	4.03882359	−0.78354085	0.00000000
H	2.47172569	2.38919910	−0.00000000
O	−2.07853640	0.42323079	−0.00000000
H	−0.16427074	−2.88625656	0.00000000

II. FOCAL POINT APPROACH

CCSDT(Q) computations with a restricted open-shell Hartree-Fock (ROHF) reference may be performed in Kállay's MRCC code using one of two variants (M. Kállay and J. Gauss, *J. Chem. Phys.*, 2008, **129**, 144101). While standard closed-shell CCSDT(Q) computations employing a restricted Hartree-Fock (RHF) reference do not need to distinguish between these two, internal consistency in this project requires that variant B RHF CCSDT(Q) computations also be employed. In this work, all CCSDT(Q) computations employed variant B. For use with an ROHF reference, this corresponds to solving the equations

$$\Delta E^{\mathrm{ROHF/B}}_{\mathrm{CCSDT(Q)}} = \langle 0 \big| \big(\hat{T}_2^\dagger \hat{V}_2 + \big[\hat{T}_3^\dagger + \hat{R}_3^\dagger \big(\hat{T}_1^\dagger \hat{V}_2 + \hat{T}_2^\dagger \hat{F}^{1a} \big) \big] \hat{V} \big) \hat{T}_4^{\{3\}} \big| 0 \rangle$$

An RHF reference employs the corresponding equations

$$\Delta E^{\mathrm{B}}_{\mathrm{CCSDT(Q)}} = \langle 0 \big| \big(\hat{T}_2^\dagger \hat{V}_2 + \big[\hat{T}_3^\dagger + \hat{R}_3^\dagger \big(\hat{T}_1^\dagger \hat{V}_2 \big) \big] \hat{V} \big) \hat{T}_4^{\{3\}} \big| 0 \rangle$$

To each electronic energy difference computed here using focal point analysis, we add a zero-point vibrational energy (ZPVE) correction (Δ_{ZPVE}) computed by adding CCSD(T)/ANO1 anharmonic ZPVE terms to a CCSD(T)/ANO2 harmonic ZPVE. Furthermore, we a CCSD(T)/PCVTZ core correction (Δ_{core}), a HF/PVTZ diagonal Born-Oppenheimer correction (Δ_{DBOC}), and a CCSD/PVTZ relativistic correction (ΔE_{rel}).

TABLE XII. *syn*→ *anti* Conversion

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+2.11	+0.20	−0.26	+0.05	−0.01	+0.01	[+2.09]
cc-PVTZ	+1.60	+0.08	−0.18	+0.04	−0.01	+0.01	[+1.54]
cc-PVQZ	+1.44	+0.05	−0.14	+0.03	[−0.01]	[+0.01]	[+1.38]
cc-PV5Z	+1.37	+0.03	−0.13	+0.03	[−0.01]	[+0.01]	[+1.31]
CBS	[+1.34]	[+0.00]	[−0.11]	[+0.02]	[−0.01]	[+0.01]	[+1.26]

$$\Delta E_{\text{final}} = \Delta\text{E[CCSDT(Q)/CBS]} + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 1.26 - 0.17 - 0.01 + 0.00 + 0.00 = \textbf{1.08 kcal mol}^{-1}$$

TABLE XIII. acetaldehyde → *syn*-vinyl alcohol (Reaction 1)

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+12.99	+0.25	−0.34	+0.10	+0.01	−0.03	[+12.98]
cc-PVTZ	+11.81	−1.49	−0.16	−0.19	+0.03	−0.05	[+9.96]
cc-PVQZ	+11.77	−1.89	−0.10	−0.24	[+0.03]	[−0.05]	[+9.52]
cc-PV5Z	+11.66	−2.02	−0.05	−0.26	[+0.03]	[−0.05]	[+9.32]
CBS	[+11.58]	[−2.16]	[+0.00]	[−0.27]	[+0.03]	[−0.05]	[+9.14]

$$\Delta E_{\text{final}} = \Delta\text{E[CCSDT(Q)/CBS]} + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 9.14 + 0.65 - 0.03 - 0.06 + 0.00 = \textbf{9.70 kcal mol}^{-1}$$

A. Relative Energies of Radicals

TABLE XIV. $CH_3CHO \rightarrow CH_3\dot{C}O + H$ (Reaction 2)

Basis Set	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-pVDZ	+77.03	+11.02	+2.95	−0.40	−0.10	−0.00	[+90.51]
cc-pVTZ	+77.75	+14.62	+2.40	−0.33	−0.07	−0.02	[+94.35]
cc-pVQZ	+77.68	+15.57	+2.17	−0.31	[−0.07]	[−0.02]	[+95.01]
cc-pV5Z	+77.68	+15.85	+2.05	−0.32	[−0.07]	[−0.02]	[+95.17]
CBS LIMIT	[+77.69]	[+16.15]	[+1.93]	[−0.33]	[−0.07]	[−0.02]	[+95.35]

$$\Delta E_{\text{final}} = \Delta\text{E[CCSDT(Q)/CBS]} + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 95.35 - 7.63 - 0.00 - 0.15 - 0.07 = \textbf{87.50 kcal mol}^{-1}$$

TABLE XV. *syn*-$CH_2CHOH \rightarrow CH_2{=}\dot{C}OH + H$ (Reaction 3)

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+94.40	+16.90	−0.06	+0.17	−0.16	+0.03	[+111.29]
cc-PVTZ	+94.95	+20.43	−0.52	+0.35	−0.18	[+0.03]	[+115.06]
cc-PVQZ	+94.94	+21.45	−0.77	+0.38	[−0.18]	[+0.03]	[+115.85]
cc-PV5Z	+94.97	+21.78	−0.91	+0.38	[−0.18]	[+0.03]	[+116.07]
CBS	[+95.00]	[+22.13]	[−1.05]	[+0.38]	[−0.18]	[+0.03]	[+116.30]

$$\Delta E_{\text{final}} = \Delta E\text{[CCSDT(Q)/CBS]} + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 116.30 - 8.68 + 0.17 - 0.14 - 0.03 = \textbf{107.63 kcal mol}^{-1}$$

TABLE XVI. *syn*-CH_2=CHOH → (Z) *syn*-$H\dot{C}$=CHOH + $\dot{H}$ (Reaction 4)

basis set	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	NET
cc-pVDZ	+98.28	+18.63	−0.61	+0.36	−0.17	+0.01	[+116.51]
cc-pVTZ	+99.18	+21.74	−1.00	+0.58	−0.20	+0.01	[+120.31]
cc-pVQZ	+99.23	+22.65	−1.21	+0.62	[−0.20]	[+0.01]	[+121.10]
cc-pV5Z	+99.27	+22.95	−1.33	+0.62	[−0.20]	[+0.01]	[+121.32]
CBS	[+99.29]	[+23.27]	[−1.46]	[+0.63]	[−0.20]	[+0.01]	[**+121.53**]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 121.53 - 8.54 + 0.21 - 0.14 - 0.03 = \textbf{113.03 kcal mol}^{-1}$$

TABLE XVII. *syn*-CH_2=CHOH → (E) *syn*-$H\dot{C}$=CHOH + $\dot{H}$ (Reaction 5)

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	NET
cc-pVDZ	+96.76	+18.76	−0.54	+0.42	−0.16	+0.01	[+115.26]
cc-pVTZ	+97.59	+21.92	−0.99	+0.66	−0.19	+0.01	[+119.00]
cc-pVQZ	+97.62	+22.83	−1.22	+0.69	[−0.19]	[+0.01]	[+119.74]
cc-pV5Z	+97.63	+23.13	−1.34	+0.70	[−0.19]	[+0.01]	[+119.94]
CBS	[+97.65]	[+23.45]	[−1.48]	[+0.70]	[−0.19]	[+0.01]	[+120.14]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 120.14 - 8.53 + 0.19 - 0.13 - 0.03 = \textbf{111.64 kcal mol}^{-1}$$

TABLE XVIII. *syn*-CH_2=CHOH $\rightarrow$ $\dot{C}H_2CH$=O (Reaction 6)

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	NET
cc-pVDZ	+69.35	+15.31	+0.51	+0.09	−0.17	−0.02	[+85.05]
cc-pVTZ	+71.12	+19.69	+0.04	+0.53	−0.20	−0.02	[+91.16]
cc-pVQZ	+71.20	+20.88	−0.13	+0.59	[−0.20]	[−0.02]	[+92.31]
cc-pV5Z	+71.28	+21.26	−0.26	+0.60	[−0.20]	[−0.02]	[+92.65]
CBS	[+71.33]	[+21.66]	[−0.40]	[+0.60]	[−0.20]	[−0.02]	[**+92.98**]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 92.98 - 8.68 + 0.24 - 0.06 - 0.10 = \textbf{84.38 kcal mol}^{-1}$$

TABLE XIX. *syn*-CH_2CHOH $\rightarrow$ CH_2=$\dot{C}H$ + $\dot{O}H$ (Reaction 7)

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+80.13	+36.79	−10.28	+2.31	−0.25	+0.26	[+108.96]
cc-PVTZ	+81.18	+40.13	−11.60	+3.25	−0.45	+0.24	[+112.74]
cc-PV5Z	+81.15	+41.62	−11.83	+3.37	[−0.45]	[+0.24]	[+114.10]
cc-PVQZ	+81.11	+42.19	−11.93	+3.40	[−0.45]	[+0.24]	[+114.56]
CBS	[+81.08]	[+42.79]	[−12.04]	[+3.43]	[−0.45]	[+0.24]	[+115.04]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 115.04 - 7.10 + 0.38 + 0.09 - 0.23 = \textbf{108.18 kcal mol}^{-1}$$

TABLE XX. Focal point analysis of 1-hydroxyvinyl radical ($H_2C{=}\dot{C}OH$) energy compared to that of acetyl radical ($CH_3C{=}\dot{O}$).

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+30.36	+6.13	−3.35	+0.67	−0.06	+0.00	[+33.76]
cc-PVTZ	+29.02	+4.32	−3.08	+0.49	−0.08	[+0.00]	[+30.67]
cc-PVQZ	+29.03	+3.99	−3.03	+0.45	[−0.08]	[+0.00]	[+30.37]
cc-PV5Z	+28.96	+3.91	−3.01	+0.44	[−0.08]	[+0.00]	[+30.23]
CBS	[+28.90]	[+3.82]	[−2.98]	[+0.43]	[−0.08]	[+0.00]	[+30.10]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 30.10 - 0.17 - 0.08 - 0.04 + 0.12 = \mathbf{29.93\ kcal\ mol^{-1}}$$

TABLE XXI. Focal point analysis of (Z) *anti*-2-hydroxyvinyl radical ($H\dot{C}{=}CHOH$) energy compared to that of acetyl radical ($CH_3C{=}\dot{O}$).

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+36.25	+8.50	−4.16	+0.99	−0.07	−0.01	[+41.49]
cc-PVTZ	+34.73	+6.18	−3.76	+0.86	−0.10	−0.01	[+37.90]
cc-PVQZ	+34.67	+5.74	−3.65	+0.82	[−0.10]	[−0.01]	[+37.47]
cc-PV5Z	+34.54	+5.61	−3.59	+0.82	[−0.10]	[−0.01]	[+37.26]
CBS	[+34.44]	[+5.47]	[−3.53]	[+0.81]	[−0.10]	[−0.01]	[+37.08]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 37.08 + 0.56 - 0.05 - 0.04 + 0.13 = \mathbf{37.68\ kcal\ mol^{-1}}$$

TABLE XXII. Focal point analysis of (Z) *syn*-2-hydroxyvinyl radical ($\dot{\text{H}}$C=CHOH) energy compared to that of acetyl radical ($CH_3C{=}\dot{O}$).

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+34.24	+7.87	−3.90	+0.86	−0.07	−0.02	[+38.99]
cc-PVTZ	+33.24	+5.63	−3.56	+0.73	−0.09	−0.03	[+35.92]
cc-PVQZ	+33.33	+5.19	−3.48	+0.69	[−0.09]	[−0.03]	[+35.61]
cc-PV5Z	+33.25	+5.08	−3.43	+0.69	[−0.09]	[−0.03]	[+35.47]
CBS	[+33.19]	[+4.96]	[−3.38]	[+0.68]	[−0.09]	[−0.03]	[+35.33]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 35.33 - 0.26 - 0.04 - 0.04 + 0.12 = \mathbf{35.11\ kcal\ mol^{-1}}$$

TABLE XXIII. Focal point analysis of (E) *anti*-2-hydroxyvinyl radical ($\dot{\text{H}}$C=CHOH) energy compared to that of acetyl radical ($CH_3C{=}\dot{O}$).

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+36.02	+8.45	−4.23	+0.97	−0.07	−0.01	[+41.13]
cc-PVTZ	+34.34	+6.16	−3.84	+0.84	−0.10	−0.01	[+37.37]
cc-PVQZ	+34.18	+5.69	−3.74	+0.80	[−0.10]	[−0.01]	[+36.82]
cc-PV5Z	+34.01	+5.56	−3.68	+0.80	[−0.10]	[−0.01]	[+36.57]
CBS	[+33.90]	[+5.42]	[−3.62]	[+0.79]	[−0.10]	[−0.01]	[+36.37]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 36.37 - 0.47 - 0.05 - 0.03 + 0.13 = \mathbf{35.95\ kcal\ mol^{-1}}$$

TABLE XXIV. Focal point analysis of (E) *syn*-2-hydroxyvinyl radical ($H\dot{C}$=CHOH) energy compared to that of acetyl radical (CH_3C=$\dot{O}$).

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+32.72	+8.00	−3.83	+0.92	−0.06	−0.02	[+37.73]
cc-PVTZ	+31.66	+5.81	−3.55	+0.80	−0.09	−0.02	[+34.61]
cc-PVQZ	+31.71	+5.37	−3.48	+0.77	[−0.09]	[−0.02]	[+34.26]
cc-PV5Z	+31.62	+5.26	−3.44	+0.76	[−0.09]	[−0.02]	[+34.09]
CBS	[+31.55]	[+5.14]	[−3.40]	[+0.76]	[−0.09]	[−0.02]	[+33.93]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 33.93 - 0.25 - 0.06 - 0.04 + 0.13 = \mathbf{33.71\ kcal\ mol^{-1}}$$

TABLE XXV. Focal point analysis of vinoxy radical ($\dot{C}H_2CH$=O) energy compared to that of acetyl radical (CH_3C=$\dot{O}$).

Method	HF	δMP2	δCCSD	δCCSD(T)	δCCSDT	δCCSDT(Q)	[Net]
cc-PVDZ	+5.30	+4.54	−2.79	+0.59	−0.07	−0.05	[+7.52]
cc-PVTZ	+5.19	+3.58	−2.52	+0.67	−0.09	−0.05	[+6.77]
cc-PVQZ	+5.29	+3.42	−2.40	+0.66	[−0.09]	[−0.05]	[+6.83]
cc-PV5Z	+5.26	+3.39	−2.36	+0.66	[−0.09]	[−0.05]	[+6.80]
CBS	[+5.23]	[+3.35]	[−2.32]	[+0.66]	[−0.09]	[−0.05]	[+6.77]

$$\Delta E_{\text{final}} = \Delta E[\text{CCSDT(Q)/CBS}] + \Delta_{\text{ZPVE}} + \Delta_{\text{core}} + \Delta_{\text{DBOC}} + \Delta E_{\text{rel}}$$

$$\Delta E_{\text{final}} = 6.77 - 0.40 - 0.01 + 0.03 + 0.05 = \mathbf{6.44\ kcal\ mol^{-1}}$$

III. VIBRATIONAL FREQUENCIES

TABLE XXVI. *syn*-CH_2=CHOH analytic harmonic CCSD(T)/ANO2 frequencies (cm^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a}'$		
ν_1	3827.3434	39.8280
ν_2	3264.0957	5.3852
ν_3	3213.2498	3.6315
ν_4	3156.3377	4.0373
ν_5	1697.2711	142.5704
ν_6	1450.9122	15.5311
ν_7	1356.0386	3.1599
ν_8	1329.5014	4.7910
ν_9	1121.7452	173.7217
ν_{10}	959.1410	12.7241
ν_{11}	485.0625	12.7377
$\mathbf{a}''$		
ν_{12}	989.6173	31.7522
ν_{13}	824.9139	53.7972
ν_{14}	710.5164	1.1103
ν_{15}	440.4104	94.4942

TABLE XXVII. *anti*-vinyl alcohol (CH_2=CHOH) analytic harmonic CCSD(T)/ANO2 frequencies (cm^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a}'$		
ν_1	3886.2863	85.4140
ν_2	3275.9869	3.1269
ν_3	3181.6788	4.0960
ν_4	3165.5074	7.9674
ν_5	1722.1627	88.9951
ν_6	1441.6047	0.1353
ν_7	1346.7142	10.7425
ν_8	1298.4251	187.2271
ν_9	1143.3232	15.1927
ν_{10}	957.3000	49.2618
ν_{11}	475.2633	3.6399
$\mathbf{a}''$		
ν_{12}	965.5866	23.3523
ν_{13}	845.8884	48.1163
ν_{14}	710.4500	17.9293
ν_{15}	262.9711	95.9766

TABLE XXVIII. $H_2C=\dot{C}OH$ CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a}'$		
ν_1	3828.9885	124.6249
ν_2	3253.3360	0.2969
ν_3	3123.2061	0.9892
ν_4	1699.0797	117.2215
ν_5	1410.5374	2.5190
ν_6	1245.6584	184.3302
ν_7	1132.3552	8.1966
ν_8	960.6732	40.6743
ν_9	816.5536	51.5530
ν_{10}	631.6073	10.1765
ν_{11}	443.0085	9.4938
ν_{12}	317.4504	140.4823

TABLE XXIX. (Z) *anti*-$\dot{\text{H}}$C=CHOH CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a}'$		
ν_1	3866.2121	72.3312
ν_2	3296.1474	6.9231
ν_3	3157.5914	6.8506
ν_4	1676.9719	63.1310
ν_5	1329.8020	23.3192
ν_6	1259.1428	141.6660
ν_7	1082.7215	98.9791
ν_8	831.6447	4.3546
ν_9	439.8339	17.7720
$\mathbf{a}''$		
ν_{10}	864.5366	49.2466
ν_{11}	609.2159	46.2836
ν_{12}	221.9100	92.7140

TABLE XXX. (Z) *syn*-HĊ=CHOH CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a'}$		
ν_1	3826.1845	43.3835
ν_2	3284.3600	4.6632
ν_3	3202.0900	2.4698
ν_4	1641.9694	109.2278
ν_5	1363.8048	1.5115
ν_6	1255.3314	9.6348
ν_7	1064.7693	179.4312
ν_8	813.7519	37.7797
ν_9	443.0631	8.0764
$\mathbf{a''}$		
ν_{10}	901.3034	47.4751
ν_{11}	584.2249	49.0318
ν_{12}	418.6500	89.0746

TABLE XXXI. (E) *anti*-HĊ=CHOH CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a}'$		
ν_1	3878.2613	80.6273
ν_2	3302.4876	7.1152
ν_3	3095.6602	11.0037
ν_4	1694.2897	71.7197
ν_5	1317.2654	65.6149
ν_6	1276.4951	108.9439
ν_7	1120.6148	41.8550
ν_8	794.4399	60.1067
ν_9	488.1687	3.9749
$\mathbf{a}''$		
ν_{10}	791.4086	9.3295
ν_{11}	609.4423	71.1695
ν_{12}	255.9994	66.8588

TABLE XXXII. (E) *syn*-HĊ=CHOH CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a'}$		
ν_1	3818.8288	46.4070
ν_2	3303.9364	8.2818
ν_3	3143.3313	4.9836
ν_4	1659.3398	117.4245
ν_5	1365.2612	3.0920
ν_6	1253.6293	11.5298
ν_7	1108.4644	159.4694
ν_8	796.1797	29.9523
ν_9	475.4202	21.6992
$\mathbf{a''}$		
ν_{10}	827.2868	14.3887
ν_{11}	587.7108	14.4126
ν_{12}	452.4406	147.0078

TABLE XXXIII. Acetaldehyde (CH_3CHO) analytic harmonic CCSD(T)/ANO2 frequencies (cm^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a}'$		
ν_1	3160.1971	6.8409
ν_2	3038.3749	2.3949
ν_3	2929.9536	92.3746
ν_4	1788.4434	140.0144
ν_5	1469.2812	20.1357
ν_6	1427.0570	10.3466
ν_7	1385.7376	15.6245
ν_8	1137.0701	22.4522
ν_9	896.8112	6.5570
ν_{10}	505.1960	13.6432
$\mathbf{a}''$		
ν_{11}	3108.6133	5.9853
ν_{12}	1479.5747	9.0805
ν_{13}	1131.9367	0.0310
ν_{14}	774.7900	1.2845
ν_{15}	156.2357	1.5818

TABLE XXXIV. Acetyl radical ($CH_3C\dot{O}$) CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a'}$		
ν_1	3144.0879	6.1062
ν_2	3042.9155	3.5204
ν_3	1899.9421	113.2228
ν_4	1467.8763	19.8807
ν_5	1361.7352	8.5087
ν_6	1057.3571	15.7811
ν_7	868.8217	3.9766
ν_8	468.0069	5.7713
$\mathbf{a''}$		
ν_9	3139.7400	1.1779
ν_{10}	1465.1562	10.8420
ν_{11}	959.3705	0.0659
ν_{12}	110.5517	0.5017

TABLE XXXV. Vinyl radical (CH_2=$\dot{C}$H) CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a}'$		
ν_1	3251.5171	0.7881
ν_2	3181.3473	1.8927
ν_3	3075.4205	2.3059
ν_4	1617.0775	2.0158
ν_5	1392.2662	6.9440
ν_6	1069.4841	7.2039
ν_7	723.0675	17.1388
$\mathbf{a}''$		
ν_8	914.2962	67.7760
ν_9	812.2229	9.2054

TABLE XXXVI. $\dot{O}$H CCSD(T)/ANO2 finite difference harmonic frequency (cm^{-1}) and intensity (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
ν	3738.8115	11.3794

TABLE XXXVII. Vinoxy radical ($\dot{C}H_2CH{=}O$) CCSD(T)/ANO2 finite difference harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}).

Mode	ω_{ANO2}	I_{ANO2}
$\mathbf{a'}$		
ν_1	3278.5804	1.4074
ν_2	3157.4222	1.7931
ν_3	2989.3865	65.3343
ν_4	1576.5452	41.1700
ν_5	1476.5052	11.0784
ν_6	1403.1173	8.6787
ν_7	1161.8551	27.3955
ν_8	972.1529	2.3972
ν_9	500.1228	12.4563
$\mathbf{a''}$		
ν_{10}	975.0825	0.1450
ν_{11}	735.4489	37.8106
ν_{12}	431.7117	0.2355

TABLE XXXVIII. ZPVE values (kcal mol^{-1}) for the species studied.

	ANO2 Harmonic	Correction	Anharmonic
acetaldehyde	34.8295	−0.5005	34.329
syn-vinyl alcohol	35.4826	−0.5061	34.9765
anti-vinyl alcohol	35.2806	−0.4785	34.8021
acetyl radical	27.0925	−0.3929	26.6996
vinyl radical	22.9373	−0.3507	22.5866
vinoxy radical	26.6502	−0.3515	26.2987
1-hydroxyvinyl radical	26.9652	−0.4343	26.5309
(Z) *anti* 2-hydroxyvinyl radical	27.6703	−0.4094	27.2609
(Z) *syn* 2-hydroxyvinyl radical	26.8797	−0.4394	26.4403
(E) *anti* 2-hydroxyvinyl radical	26.6176	−0.3919	26.2257
(E) *syn* 2-hydroxyvinyl radical	26.8674	−0.4163	26.4511