Supporting Information

Exploring the role of single water molecule in the tropospheric reaction of Glycoaldehyde with OH radical: A mechanistic and kinetic study

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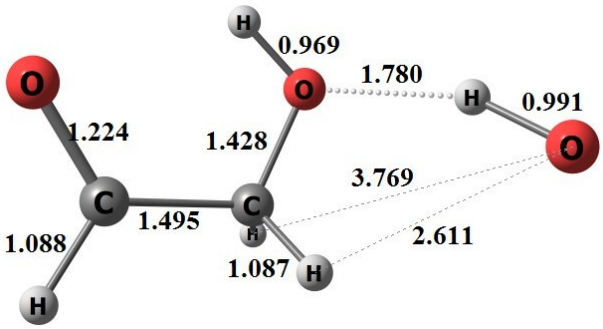


Figure S1. Structure of pre-reaction complex PRC11 located by GRRM search for the PRCs in the absence of a single-water molecule at the BHandHLYP/6-31G level of the theory.

Table S1. Relative energies (in kcal/mol) of stationary points, relative to the energy of isolated reactants R1& R2 (i.e. *trans- & cis*-isomer without water)[a] and R3 (including a single-water molecule)[a] along various pathways depicted in Figures 2-6, at the ZPE corrected M06-2X/6-311++G(d,p), BHandHLYP/6-311++G(d,p) and CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) levels of the theory. The BSSE corrected and *ZPE* scaled energies are also compared. The transition state represented as TS*n* connects the pre-reaction complex PRC*n* to the product complex PC*n*. The values in square brackets are at ROCCSD(T)/6311++G(d,p)//BHandHLYP/6-311++G(d,p) level of the theory.

Species	M06-2X /6-311++G (d,p)	BHandHLYP/ 6-311++G(d,p) +ZPE (ZPE)	CCSD(T)/6311++G(d,p)// BHandHLYP/ 6-311++G(d,p)+ZPE	CCSD(T)/6311++G(d,p)// BHandHLYP/ 6-311++G(d,p)+ZPE +(BSSE)[b]	CCSD(T)/6-311++G(d,p)// BHandHLYP/ 6-311++G(d,p)+ (ZPE x 0.9540)[d]
PRC1	–4.58	–3.45	–3.26	–1.84(1.42)	–3.33 (1.50)
PRC2	–4.39	–3.07	–2.32	–0.68 (1.64)	–2.37 (1.14)
PRC3	–8.09	–5.02	–4.08	–2.57 (1.51)	–4.18 (1.79)
PRC4	–4.39	–3.89	–3.33	–1.95 (1.38)	–3.41 (1.80)
PRC5	–5.40	–4.39	–1.00	0.87(1.87)	–1.10 (1.85)
TS1	–2.89	0.06	–2.51	2.33 (4.84)	–2.45(–1.02)
TS2	–3.45	0.00	–2.45	2.30 (4.75)	–2.45 (0.19)
TS3	–0.56	2.07	–0.19	4.64 (4.83)	–0.14 (–1.15)
TS4	–0.56	3.39	0.38	5.52 (5.15)	0.44 (–1.19)
TS5	0.69	7.09	5.02	11.95 (6.93)	5.09(–1.63)
PC1	–31.94	–25.10	–30.12	–28.28 (1.84)	–30.22 (2.27)
PC2	–35.89	–28.74	–33.63	–31.51 (2.12)	–33.74 (2.34)
PC3	–42.48	–36.77	–37.71 [23.26]	–36.52 (1.19)	–37.83 (2.26)
PC4	–41.85	–36.27	–36.21 [24.66]	–34.76 (1.44)	–36.32 (2.52)
PC5	–13.05	–11.23	–11.99	–10.13 (1.86)	–12.02 (0.59)
BC6	–2.20	–1.63	–1.88	–0.38 (1.50)	–1.98 (1.47)
BC7	–4.58	–2.76	–3.95	–1.58 (2.37)	–4.09 (2.25)
BC8	–5.15	–4.14	–4.71	–2.78 (1.93)	–4.83 (1.95)
BC9	–3.01	–3.20	–3.51	–1.45 (2.06)	–3.60 (1.29)
BC10	–2.95	–2.26	–2.38	–0.92 (1.46)	–2.48 (1.41)
PRC6	–13.49	–11.42	–11.30	–6.67 (4.63)	–11.53 (4.41)
PRC7	–14.06	–11.23	–11.04	–6.75 (4.29)	–11.27 (4.17)
PRC8	–13.55	–12.05	–10.73	–6.35 (4.38)	–10.96 (4.17)
PRC9	–11.30	–9.98	–9.66	–5.56 (4.10)	–9.87 (3.81)
PRC10	–10.92	–9.85	–8.09	–4.32 (3.77)	–8.29 (3.57)
TS6[c]	–5.84	1.82	–	–	–
TS7	–9.60	–5.46	–7.40	–0.39 (7.01)	–7.56 (2.67)
TS8	–7.72	–1.32	–6.21	1.16 (7.37)	–6.31 (1.41)
TS9	–7.03	–3.58	–4.13	3.83 (7.96)	–4.25 (1.77)
TS10	–7.97	–3.45	–4.77 [–4.89]	3.72 (8.49)	–4.84 (0.93)
PC6	–24.10	–21.90	–21.84	–17.31 (4.53)	–22.02 (3.33)
PC7	–41.60	–33.70	–37.78	–33.97(4.81)	–39.02 (4.53)
PC8	–38.28	–32.07	–37.15	–26.01(11.14)	–37.39 (4.59)
PC9	–48.95	–43.30	–43.49 [29.62]	–39.59 (3.90)	–43.70 (3.99)
PC10	–51.02	–43.05	–44.11 [28.99]	–39.58 (4.53)	–44.37 (4.83)
P1	–26.73	–21.65	–25.98	–25.98	–25.99 (0.43)
P2	–38.84	–33.89	–34.51	–34.51	–34.57 (0.89)
P3	–35.20	–31.06	–31.06	–31.06	–31.08 (0.55)
P4	–7.66	–8.09	–5.33	–5.33	–5.26 (–1.69)
P5	–10.10	–4.89	–5.46	–5.46	–5.50 (0.71)
P6	–24.03	–19.26	–23.85	–23.85	–23.86 (0.05)
P7	–25.85	–20.90	–25.16	–25.16	–25.18 (0.17)
P8	–32.51	–28.68	–28.99	–28.99	–29.01 (0.17)

[a]Total energies including (ZPE) of isolated reactants R1, at M06-2X/6-311++G(d,p), BHandHLYP/6-311++G(d,p) and CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) levels of the theory, are –304.6722 (0.0699), –304.6431(0.0715) and –304.1866,(0.0715) respectively. For R2, the corresponding values are –304.6765 (0.0707), –304.6469 (0.0721) and –304.1900 (0.0721) a.u., respectively and for R3, these are –381.0758 (0.0923), –381.0392 (0.0943) and –380.4735 (0.0943) a.u., respectively. (1 a.u.= 627.5095kcal/mol).

[b]Value of BSSE correction is given in the parenthesis,

[c] Single-point energy of TS6 could not be computed at the CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) level of the theory,

[d] Scale factor[48]

Table S2. Relative zero-point energy (ZPE) (in kcal/mol) of stationary points, relative to the ZPE of isolated reactants R1& R2 (i.e. *trans- & cis*-isomer without water)[a] and R3 (including a single-water molecule)[a] along various pathways depicted in Figures 2-6 (of the article), at the BHandHLYP/6-311++G(d,p) and M06-2X/6-311++G(d,p) levels of the theory, and relative energy[b] at the BHandHLYP/6-31G levels of the theory. The $<S^2>$ values for open-shell systems are also given at the BHandHLYP/6-31G, BHandHLYP/6-311++G(d,p) and CCSD(T)/6311++G(d,p)//BHandHLYP/6-311++G(d,p) levels of theory.

Species	ZPE		ΔE/	$<S^2>$		
	BHandHLYP/ 6-311++G(d,p)	M06-2X /6-311++G (d,p)	BHandHLYP /6-31G	BHandHLYP /6-31G	BHandHLYP/ 6-311++G(d,p)	CCSD(T)/6311++G(d,p)// BHandHLYP/6-311++G(d,p)
PRC1	1.57	1.82	7.84	0.7537	0.7530	0.7554
PRC2	1.19	1.26	–5.42	0.7527	0.7555	0.7562
PRC3	1.88	1.88	–7.72	0.7519	0.7532	0.7554
PRC4	1.88	2.07	–7.23	0.7518	0.7530	0.7554
PRC5	1.95	1.51	–9.04	0.7521	0.7537	0.7558
TS1	–1.07	–0.06	1.19	0.762	0.7645	0.779
TS2	0.19	0.50	–6.98	0.7626	0.7648	0.7718
TS3	–1.19	–0.63	2.25	0.7739	0.7733	0.7862
TS4	–1.26	–0.50	4.54	0.7706	0.7708	0.7897
TS5	–1.69	–1.63	1.69	0.7664	0.7674	0.7976
PC1	2.38	2.57	–15.44	0.7546	0.7557	0.7631
PC2	2.45	2.57	–20.41	0.7540	0.7554	0.7624
PC3	2.38	2.45	–32.63	0.7910	0.7842	0.8577
PC4	2.64	2.95	–32.58	0.7900	0.7846	0.8618
PC5	0.63	1.44	–12.11	0.7533	0.7546	0.7587
BC6	1.57	1.69	–6.15	–	–	–
BC7	2.38	2.32	–12.05	–	–	–
BC8	2.07	2.20	–8.03	–	–	–
BC9	1.38	1.57	–8.16	–	–	–
BC10	1.51	1.69	–6.84	–	–	–
PRC6	4.64	4.52	–23.59	0.7520	0.7532	0.7787
PRC7	4.39	3.83	–22.40	0.7542	0.7531	0.7557
PRC8	4.39	4.14	–22.40	0.7546	0.7530	0.7556
PRC9	3.89	3.95	–22.21	0.7842	0.7531	0.7773
PRC10	3.77	3.89	–20.65	0.7843	0.7531	0.7556
TS6	0.56	0.63	–10.35	0.7673	0.7695	–
TS7	2.82	2.95	–13.11	0.7636	0.7629	0.7653
TS8	1.51	2.26	–6.71	0.7719	0.7673	0.7837
TS9	1.88	2.32	–11.42	0.7693	0.7665	0.799
TS10	1.00	1.19	–10.35	0.7743	0.7688	0.8305
PC6	3.51	3.26	–31.06	0.7535	0.7553	0.7594
PC7	4.77	4.71	–33.01	0.7542	0.7556	0.7622
PC8	4.83	4.77	–30.69	0.7548	0.7555	0.7622
PC9	4.20	4.71	–46.50	0.7931	0.7800	0.8513
PC10	5.08	5.40	–47.75	0.7845	0.7800	0.8518

[a] The zero-point energy (ZPE) of R1, R2 and R3 at BHandHLYP/6-311++G(d,p) level of theory are 0.0715, 0.0721and 0.0943 respectively. The respective values at M06-2X/6-311++G(d,p) are 0.0699, 0.0707 and 0.0923.

[b] Total energies including (ZPE) of isolated reactants R1, R2 and R3 at BHandHLYP/6-31G level of the theory, are –304.4249 (0.0713), –304.4277 (0.0718) and –380.7503 (0.0933) a.u., respectively. (1 a.u.= 627.5095kcal/mol).

Table S3. Gibbs free-energy change (ΔG), in kcal/mol, along various pathways depicted in Figures 2–6 (of the article) at the DFT/BHandHLYP/6-311++G(d,p) level of the theory. The ΔG between the pre-reactant complexes (PRCs) and the transition states (TSs) represents free-energy of activation: $\Delta E_A = G_{TS} - G_{PRC}$. The values in parentheses correspond to net Gibbs free-energy change along the respective pathway.

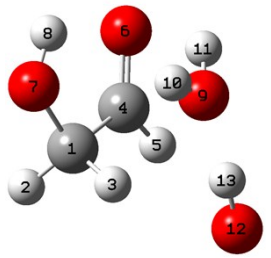
Pathway	ΔG *or* ΔE_A (in kcal/mol)				
T (K)	**10**	**100**	**200**	**298.15**	**500**
1: R1-PRC1	–3.39	–1.51	1.13	3.83	7.29
PRC1-TS1	3.51	3.64	3.89	4.08	4.52
TS1-PC1	–25.23	–25.48	–26.10	–26.86	–28.74
	(–25.11)	(–23.35)	(–21.08)	(–18.95)	(–16.93)
PRC1-PC1	–21.71	–21.84	–22.21	–22.78	–24.22
2: R1-PRC2	–3.01	–1.32	0.82	2.82	6.65
PRC2-TS2	3.07	3.58	4.52	5.71	8.47
TS2-PC2	–28.80	–29.05	–29.68	–30.56	–32.69
	(–28.74)	(–26.79)	(–24.34)	(–22.03)	(–17.57)
PRC2-PC2	–25.67	–25.48	–25.16	–24.85	–24.22
3: R2-PRC3	–4.52	–2.51	0.31	3.14	9.10
PRC3-TS3	6.65	6.71	6.67	6.59	6.34
TS3-PC3	–38.84	–39.09	–39.53	–40.10	–41.61
	(–36.71)	(–34.89)	(–32.55)	(–30.37)	(–26.17)
PRC3-PC3	–32.19	–32.38	–32.86	–33.51	–35.27
4: R1-PRC4	–3.39	–1.57	0.82	3.20	7.97
PRC4-TS4	6.84	7.09	7.66	8.28	9.60
TS4-PC4	–39.72	–39.66	–39.60	–39.53	–39.48
	(–36.27)	(–34.14)	(–31.12)	(–28.05)	(–21.91)
PRC4-PC4	–32.88	–32.57	–31.94	–31.25	–29.88
5: R2-PRC5	–1.32	0.69	3.33	3.33	11.04
PRC5-TS5	10.60	10.86	11.44	12.30	13.87
TS5-PC5	–20.46	–20.90	–21.90	–20.77	–26.23
	(–11.24)	(–9.35)	(–7.13)	(–5.15)	(–1.32)
PRC5-PC5	–9.85	–10.04	–10.46	–11.04	–12.36
6: R3-BC6	–1.57	0.38	2.89	5.15	9.60
BC6-PRC6	–6.28	–3.95	–0.94	–0.63	8.79
PRC6-TS6	9.85	10.04	10.54	13.99	12.42
TS6-PC6	–23.75	–23.97	–24.54	–25.29	–27.05
	(–21.90)	(–17.5)	(–12.05)	(–6.77)	(3.76)
PRC6-PC6	–13.93	–13.93	–13.99	–14.18	–14.62

Table 3 continued…..

Pathway	ΔG *or* ΔE_A (kcal/mol)				
T (K)	10	100	200	298.15	500
7: R3-BC7	–2.70	–0.50	2.32	5.02	10.42
BC7-PRC7	–8.41	–6.28	–3.51	–0.69	4.96
PRC7-TS7	5.84	5.85	6.11	6.40	7.22
TS7-PC7	–28.30	–28.44	–28.83	–29.42	–30.94
	(–33.70)	(–29.37)	(–23.91)	(–18.69)	(–8.34)
PRC7-PC7	–22.46	–22.59	–22.72	–23.02	–23.72
8: R3-BC8	–4.08	–2.07	0.56	3.07	8.03
BC8-PRC8	–6.59	–4.64	–2.13	–0.06	5.71
PRC8-TS8	9.54	9.98	10.67	11.92	12.86
TS8-PC8	–30.75	–31.00	–31.50	–32.19	–33.76
	(–32.06)	(–27.73)	(–22.4)	(–17.26)	(–7.16)
PRC8-PC8	–21.21	–21.02	–20.83	–21.02	–20.90
9: R3-BC9	–3.14	–1.26	0.94	2.95	6.84
BC9-PRC9	–3.45	–1.51	1.26	1.69	9.66
PRC9-TS9	3.20	3.77	4.71	8.16	8.35
TS9-PC9	–39.72	–40.10	–40.98	–42.11	–44.87
	(–43.29)	(–39.1)	(–34.07)	(–29.3)	(–20.02)
PRC9-PC9	–36.58	–36.33	–36.27	–36.27	–36.52
10: R3-BC10	–2.20	–0.25	2.20	4.46	8.85
BC10-PRC10	–8.47	–4.58	–2.20	–0.19	5.15
PRC10-TS10	9.54	6.02	7.15	8.47	11.17
TS10-PC10	–30.75	–39.72	–39.97	–40.41	–41.48
	(–43.05)	(–38.53)	(–32.82)	(–27.30)	(–16.32)
PRC10-PC10	–34.32	–33.70	–32.82	–32.00	–30.31

Table S4. . Spin density distribution, in the atomic units of electronic charge (*e*), determined from NBO analysis at each atomic centre of pre-reaction complexes and transition states involved in the hydrogen abstraction reaction of Glycoaldehyde with OH, in the presence and absence of a single-water molecule, at the BHandHLYP/6-311++G(d,p) level of theory.

Species	C1	H2	H3	C4	H5	O6	O7	H8	O9	H10	H11	O12	H13
PRC1	0.0000	0.0000	0.0000	–0.0010	0.0009	–0.0008	0.0006	–0.0001				–1.0240	0.0242
TS1	–0.0415	–0.0022	–0.0022	–0.2126	0.0545	–0.1127	–0.0007	–0.0001				–0.7009	0.0183
PRC2	–0.0040	0.0002	–0.0009	–0.0142	0.0074	–0.0191	–0.0030	0.0004				–0.9921	0.0253
TS2	–0.0411	–0.0049	–0.0003	–0.1476	0.0379	–0.1310	–0.0045	–0.0001				–0.7278	0.0194
PRC3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000				–1.0246	0.0238
TS3	–0.2699	0.0659	0.0062	0.0311	–0.0003	–0.0664	–0.0564	0.0008				–0.7303	0.0192
PRC4	–0.0022	0.0001	0.0014	0.0001	–0.0001	–0.0002	–0.0005	0.0000				–1.0228	0.0241
TS4	–0.3312	0.0118	0.0675	0.0294	–0.0096	–0.0482	–0.0578	–0.0002				–0.6797	0.0179
PRC5	0.0003	0.0001	–0.0009	0.0008	–0.0002	–0.0032	–0.0186	0.0073				–1.0097	0.0240
TS5	0.0232	–0.0013	–0.0225	–0.0019	–0.0013	–0.0099	–0.4868	0.0689				–0.5848	0.0163
PRC6	0.0000	0.0003	0.0001	0.0004	0.0000	–0.0005	–0.0161	0.0058	0.0008	–0.0001	0.0000	–1.0135	0.0228
TS6	0.0197	–0.0227	–0.0035	–0.0054	–0.0002	–0.0025	–0.4642	0.0687	0.0004	0.0000	0.0000	–0.6052	0.0149
PRC7	–0.0005	0.0000	0.0003	0.0006	0.0000	0.0000	–0.0002	0.0000	0.0009	0.0001	0.0017	–1.0267	0.0239
TS7	–0.0386	–0.0027	–0.0026	–0.1121	0.0330	–0.0957	–0.0041	–0.0001	0.0013	0.0002	0.0005	–0.8003	0.0212
PRC8	–0.0074	0.0001	0.0043	0.0007	0.0000	–0.0013	–0.0004	–0.0001	0.0007	–0.0001	0.0000	–1.0199	0.0233
TS8	–0.0381	0.0009	0.0023	–0.2288	0.0534	–0.1126	–0.0128	–0.0007	0.0002	0.0001	0.0000	–0.6814	0.0176
PRC9	–0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	–0.0110	0.0046	–0.0003	–1.0170	0.0236
TS9	–0.2275	0.0043	0.0510	0.0362	–0.0042	–0.0577	–0.0651	0.0005	0.0006	0.0004	0.0001	–0.7588	0.0201
PRC10	–0.0072	0.0003	0.0042	0.0006	–0.0002	–0.0008	–0.0011	–0.0001	0.0008	0.0000	0.0000	–1.0195	0.0232
TS10	–0.3170	0.0104	0.0756	0.0403	–0.0034	–0.0703	–0.0556	0.0002	0.0006	0.0002	0.0000	–0.6977	0.0167



Atom numbering used in spin density distribution analysis.

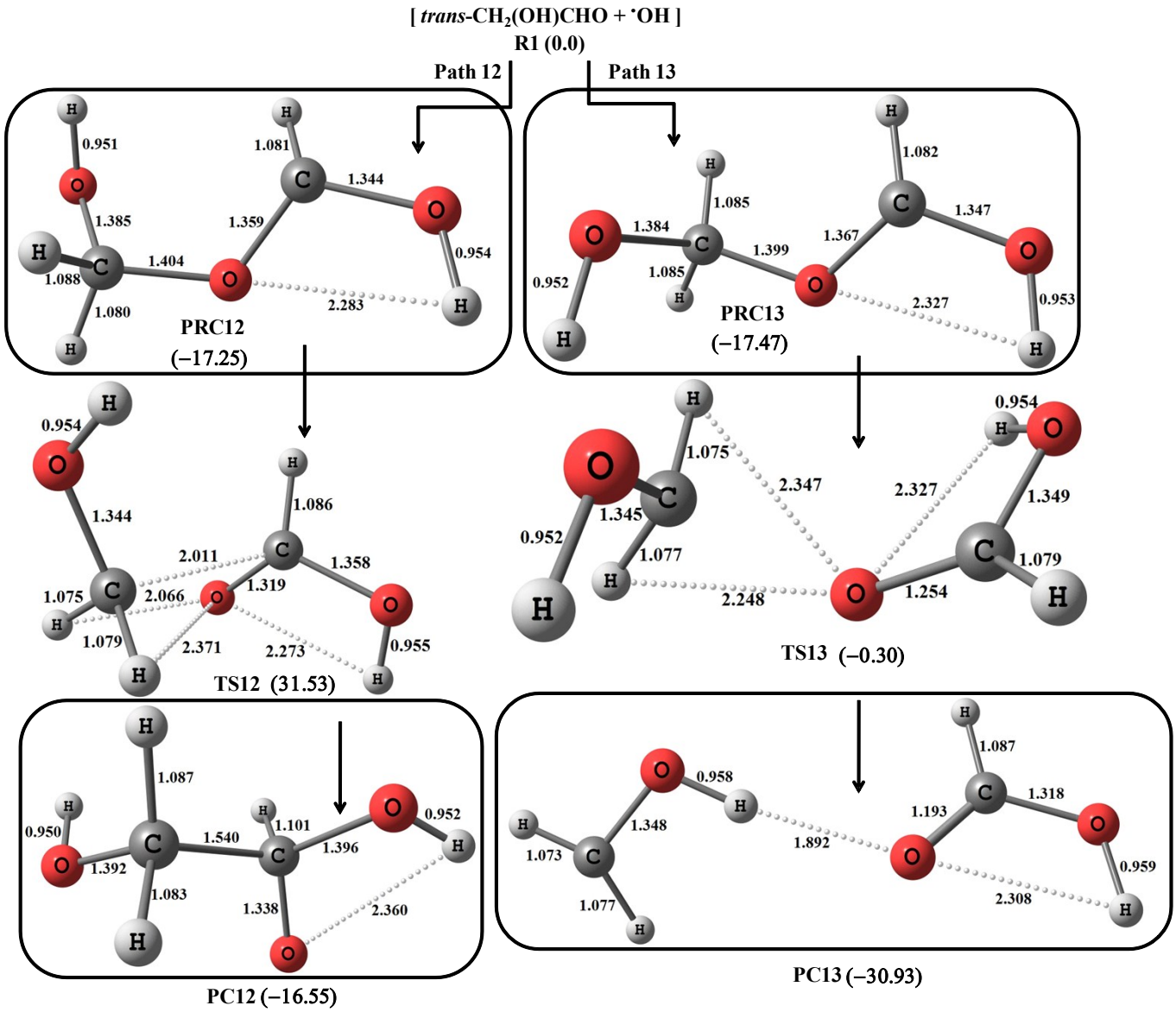
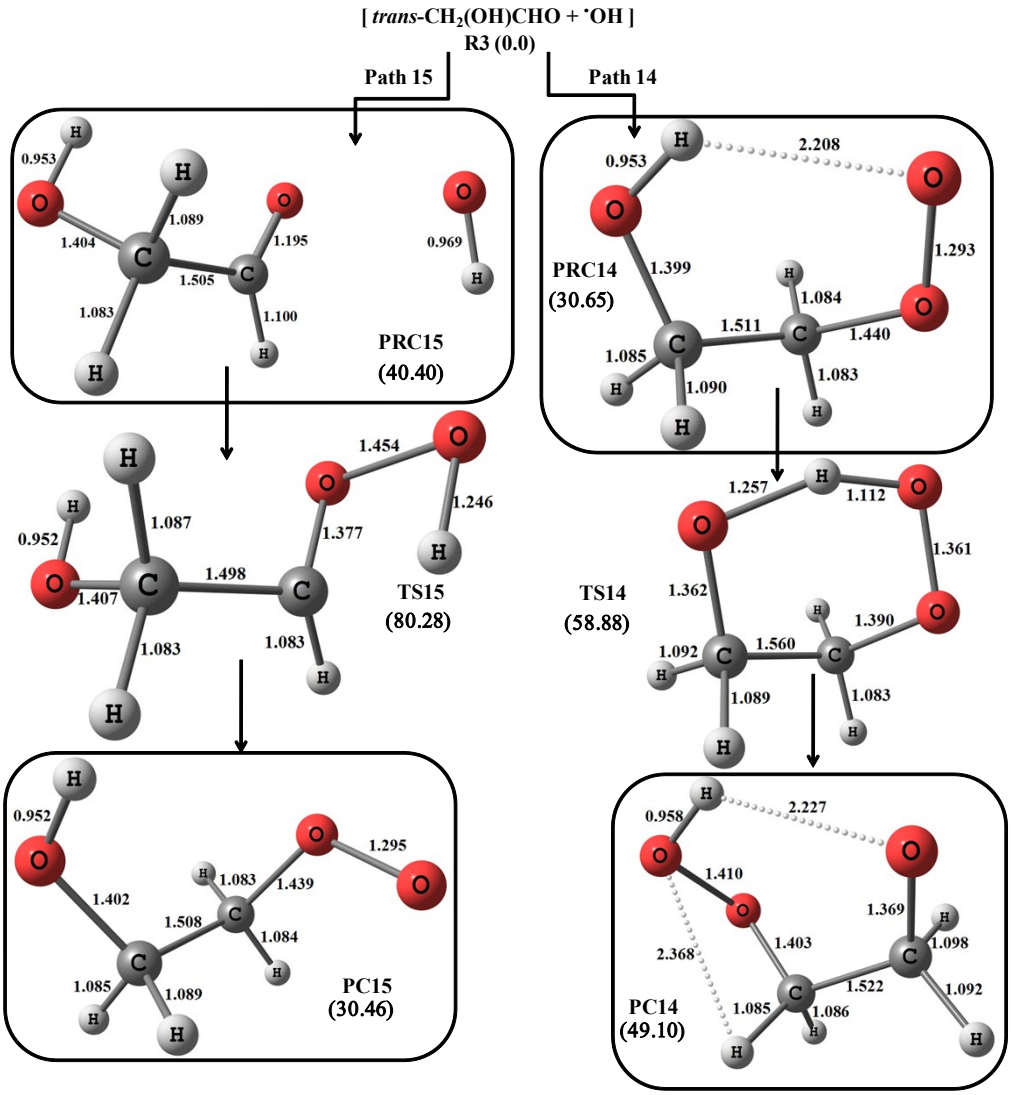


Figure S2. Addition pathways for the reaction of Glycolaldehyde with OH radical in the absence of water, Path 12: resulting in the formation of the oxy radical PC12; Path 13: leading to the formic acid and the hydroxyl methyl radical (PC13). The geometries, with bond lengths depicted in angstroms, are optimized at the level of BHandHLYP/6-311++G(d,p) level of the theory. The numerical values, in parentheses, respectively represent the relative energy change, in kcal/mol, with respect to the isolated reactants R1, at BHandHLYP/6-311++G(d,p) level of the theory, Path 14: leading to the peroxy radical (PC15), and path 14 leading to the oxy radical species containing peroxy linkage (PC15).

Figure S2 continued…….



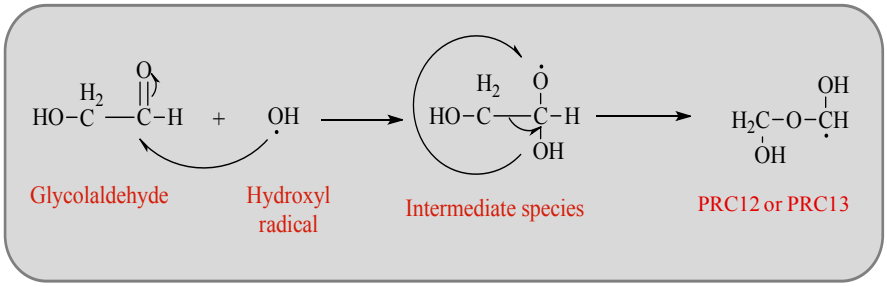


Figure S3. A schematic mechanism for the formation of species of type PRC12 or PRC13 by the reaction of Glycolaldehde with hydroxyl radical via the oxy radical intermediate species.

Table S5. Calculated rate constants (in cm^3 $molecule^{-1}$ s^{-1}), without taking tunneling corrections into account for water-free pathway 2 in the temperature range 200K-500K at the CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) (BSSE uncorrected) level of the theory and comparison with k_{lit} reported in Ref. 12.

Temperature(K)	k_2	k_{lit}	Temperature(K)	k_2	k_{lit}
200	7.28×10^{-11}	2.56×10^{-11}	340	5.34×10^{-12}	2.12×10^{-12}
220	3.99×10^{-11}	1.47×10^{-11}	350	4.85×10^{-12}	1.92×10^{-12}
240	2.44×10^{-11}	9.24×10^{-11}	360	4.44×10^{-12}	1.76×10^{-12}
260	1.61×10^{-11}	6.25×10^{-12}	370	4.09×10^{-12}	1.60×10^{-12}
270	1.34×10^{-11}	5.26×10^{-12}	380	3.77×10^{-12}	1.49×10^{-12}
280	1.14×10^{-11}	4.48×10^{-12}	390	2.80×10^{-12}	1.38×10^{-12}
290	9.79×10^{-12}	3.87×10^{-12}	400	3.28×10^{-12}	1.28×10^{-12}
298.15	8.70×10^{-12}	3.46×10^{-12}	420	2.91×10^{-12}	1.12×10^{-12}
300	8.48×10^{-12}	3.37×10^{-12}	440	2.61×10^{-12}	1.00×10^{-12}
310	7.48×10^{-12}	2.97×10^{-12}	460	2.38×10^{-12}	9.01×10^{-13}
320	6.63×10^{-12}	2.64×10^{-12}	480	2.19×10^{-12}	8.19×10^{-13}
330	5.93×10^{-12}	2.35×10^{-12}	500	2.05×10^{-12}	7.51×10^{-13}

Table S6. Calculated rate constant (in cm^3 $molecule^{-1}$ s^{-1}), without taking tunneling corrections into account for water-free pathway 5 in the temperature range 200K-500K at the CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) (BSSE uncorrected) level of the theory and comparison with k_{lit} reported in Ref. 12.

Temperature(K)	k_5	k_{lit}	Temperature(K)	k_5	k_{lit}
200	3.84×10^{-19}	1.5×10^{-18}	340	7.27×10^{-17}	1.63×10^{-16}
220	1.19×10^{-18}	4.13×10^{-18}	350	9.08×10^{-17}	1.99×10^{-16}
240	3.09×10^{-18}	9.65×10^{-18}	360	1.12×10^{-16}	2.42×10^{-16}
260	6.96×10^{-18}	2.00×10^{-17}	370	1.39×10^{-16}	2.91×10^{-16}
270	1.01×10^{-17}	2.75×10^{-17}	380	1.68×10^{-16}	3.44×10^{-16}
280	1.40×10^{-17}	3.73×10^{-17}	390	2.03×10^{-16}	4.08×10^{-16}
290	1.93×10^{-17}	4.95×10^{-17}	400	2.41×10^{-16}	4.80×10^{-16}
298.15	2.47×10^{-17}	6.18×10^{-17}	420	3.37×10^{-16}	6.47×10^{-16}
300	2.60×10^{-17}	6.46×10^{-17}	440	4.58×10^{-16}	8.56×10^{-16}
310	3.43×10^{-17}	8.33×10^{-17}	460	6.08×10^{-16}	1.11×10^{-15}
320	4.48×10^{-17}	1.05×10^{-16}	480	1.68×10^{-15}	1.40×10^{-15}
330	5.75×10^{-17}	1.31×10^{-16}	500	2.26×10^{-15}	1.76×10^{-15}

Table S7. Enthalpy (ΔH) and entropy (ΔS) change in terms of ΔH and −TΔS respectively, in kcal/mol, at temperature (T) 298K, at the BHandHLYP/6-311++G(d,p) level of the theory for various pathways obtained.

Pathway	**ΔH**	**–TΔS**	**Pathway**	**ΔH**	**–TΔS**
R1/PRC1	–4.27	8.10	**PC1/P1**	3.70	–6.97
R1/PRC2	–3.07	5.89	**PC2/P1**	7.34	–7.58
R2/PRC3	–5.46	6.31	**PC3/P2**	2.89	–6.88
R1/PRC4	–4.39	7.40	**PC4/P3**	6.15	–9.22
R2/PRC5	–5.02	8.32	**PC5/P4**	3.01	–6.70
R3/BC6+OH	–1.69	6.80	**PC6/P5**	17.95	–17.04
R3/BC7+OH	–3.14	8.11	**PC7/P6**	15.50	–17.15
R3/BC8+OH	–4.52	7.54	**PC8/P7**	11.74	–15.97
R3/BC9+OH	–3.01	5.93	**PC9/P8**	15.06	–14.99
R3/BC10+OH	–2.32	6.72	**PC10/P8**	15.44	–17.37

Table S8. Effect of basis set in the CCSD(T) calculations, employing cc-pVTZ and 6-311G(d,p) basis sets, for the relative energy of species explored along path 2, w.r.t the isolated reactants R1.

Species	CCSD(T)/ cc-pVTZ// BHandHLYP/ 6-311++G(d,p)+ZPE	CCSD(T)/ 6-311++G(d,p)// BHandHLYP/ 6-311++G(d,p)+ZPE	CCSD(T)/cc-pVTZ// BHandHLYP/ 6-311++G(d,p)+ ZPE+(BSSE)	CCSD(T)/ 6311++G(d,p)// BHandHLYP/ 6-311++G(d,p)+ZPE +(BSSE)
PRC2	–2.57	–2.32	–0.76(1.81)	–0.68(1.64)
TS2	–3.78	–2.45	1.70(5.47)	2.30(4.74)
PC2	–33.13	–33.63	–31.03(2.10)	–31.51(2.12)

[a]Total energies including (ZPE) of isolated reactants R1, CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) and CCSD(T)/cc-pVTZ//BHandHLYP/6-311++G(d,p) levels of the theory, are –304.1866(0.0715) and –304.4107(0.0715) respectively.

Table S9. Rate constants (in cm^3 $molecule^{-1}$ s^{-1}) of water-free pathways for hydrogen abstraction in Glycolaldehyde with hydroxyl radical, in the temperature range 200-500K, at the CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) level of the theory. The subscript on the rate constant *k* depicts the respective pathway depicted in main text Figures 2, 3 and 4 (of the main article).

T(K)	k_1	k_2	k_3	k_4	k_5
200	3.90×10^{-8}	1.27×10^{-10}	4.25×10^{-11}	1.17×10^{-10}	2.18×10^{-12}
220	1.07×10^{-8}	6.32×10^{-11}	2.03×10^{-11}	3.91×10^{-11}	6.39×10^{-13}
240	3.76×10^{-9}	3.58×10^{-11}	1.21×10^{-11}	1.71×10^{-11}	2.44×10^{-13}
260	1.59×10^{-9}	2.24×10^{-11}	8.37×10^{-12}	9.09×10^{-12}	1.14×10^{-13}
270	1.09×10^{-9}	1.82×10^{-11}	7.27×10^{-12}	7.06×10^{-12}	8.30×10^{-14}
280	7.81×10^{-10}	1.51×10^{-11}	6.41×10^{-12}	5.64×10^{-12}	6.22×10^{-14}
290	5.71×10^{-10}	1.27×10^{-11}	5.76×10^{-12}	4.64×10^{-12}	4.83×10^{-14}
298.15	4.59×10^{-10}	1.13×10^{-11}	5.44×10^{-12}	4.14×10^{-12}	4.07×10^{-14}
300	4.30×10^{-10}	1.08×10^{-11}	5.29×10^{-12}	3.92×10^{-12}	3.88×10^{-14}
310	3.31×10^{-10}	9.41×10^{-12}	4.88×10^{-12}	3.38×10^{-12}	3.18×10^{-14}
320	2.60×10^{-10}	8.22×10^{-12}	4.59×10^{-12}	2.97×10^{-12}	2.69×10^{-14}
330	2.08×10^{-10}	7.67×10^{-12}	4.33×10^{-12}	2.65×10^{-12}	2.31×10^{-14}
340	1.69×10^{-10}	6.46×10^{-12}	4.13×10^{-12}	2.40×10^{-12}	2.02×10^{-14}
350	1.41×10^{-10}	5.80×10^{-12}	3.95×10^{-12}	2.20×10^{-12}	1.80×10^{-14}
360	1.18×10^{-10}	5.26×10^{-12}	3.82×10^{-12}	2.04×10^{-12}	1.63×10^{-14}
370	1.00×10^{-10}	4.80×10^{-12}	3.73×10^{-12}	1.91×10^{-12}	1.51×10^{-14}
380	8.63×10^{-11}	4.39×10^{-12}	3.63×10^{-12}	1.81×10^{-12}	1.41×10^{-14}
390	7.53×10^{-11}	3.25×10^{-12}	3.57×10^{-12}	1.72×10^{-12}	1.32×10^{-14}
400	6.56×10^{-11}	3.76×10^{-12}	3.49×10^{-12}	1.64×10^{-12}	1.26×10^{-14}
420	5.21×10^{-11}	3.30×10^{-12}	3.42×10^{-12}	1.54×10^{-12}	1.17×10^{-14}
440	4.23×10^{-11}	2.93×10^{-12}	3.37×10^{-12}	1.46×10^{-12}	1.13×10^{-14}
460	3.55×10^{-11}	2.65×10^{-12}	3.36×10^{-12}	1.41×10^{-12}	1.12×10^{-14}
480	3.02×10^{-11}	2.41×10^{-12}	3.37×10^{-12}	1.37×10^{-12}	1.13×10^{-14}
500	2.65×10^{-11}	2.24×10^{-12}	3.42×10^{-12}	1.36×10^{-12}	1.16×10^{-14}

Table S10. Rate constants (in cm^3 $molecule^{-1}$ s^{-1}) of water-assisted pathways for the hydrogen abstraction in Glycolaldehyde with hydroxyl radical, in the temperature range 240-500K, at the CCSD(T)/-311++G(d,p)//BHandHLYP/6-311++G(d,p) (BSSE uncorrected) level of the theory. The subscript on the rate constant k depicts the respective pathway depicted in Figures 4-6 (of the main article).

T(K)	$[H_2O]$[a]	$k_6^b[H_2O]$	$k_7[H_2O]$	$k_8[H_2O]$	$k_9[H_2O]$	$k_{10}[H_2O]$
240	1.14×10^{16}	9.57×10^{-19}	1.29×10^{-15}	1.37×10^{-14}	2.28×10^{-18}	3.11×10^{-16}
280	2.56×10^{17}	1.23×10^{-18}	3.00×10^{-15}	8.85×10^{-15}	1.31×10^{-17}	5.12×10^{-16}
290	4.79×10^{17}	1.31×10^{-18}	3.53×10^{-15}	8.44×10^{-15}	1.86×10^{-17}	5.74×10^{-16}
298.15	7.69×10^{17}	1.41×10^{-18}	4.05×10^{-15}	8.30×10^{-15}	2.46×10^{-17}	6.36×10^{-16}
300	8.53×10^{17}	1.42×10^{-18}	4.13×10^{-15}	8.29×10^{-15}	2.60×10^{-17}	6.49×10^{-16}
310	1.45×10^{18}	1.54×10^{-18}	4.76×10^{-15}	8.19×10^{-15}	3.53×10^{-17}	7.25×10^{-16}
320	2.39×10^{18}	1.67×10^{-18}	5.41×10^{-15}	8.18×10^{-15}	4.69×10^{-17}	8.07×10^{-16}
330	3.78×10^{18}	1.81×10^{-18}	6.10×10^{-15}	8.25×10^{-15}	6.11×10^{-17}	8.98×10^{-16}
340	5.79×10^{18}	1.97×10^{-18}	6.83×10^{-15}	8.43×10^{-15}	7.87×10^{-17}	9.99×10^{-16}
350	8.62×10^{18}	2.16×10^{-18}	7.59×10^{-15}	8.62×10^{-15}	9.97×10^{-17}	1.11×10^{-15}
360	1.25×10^{19}	2.37×10^{-18}	8.36×10^{-15}	8.88×10^{-15}	1.24×10^{-16}	1.22×10^{-15}
370	1.77×10^{19}	2.61×10^{-18}	9.19×10^{-15}	9.25×10^{-15}	1.54×10^{-16}	1.36×10^{-15}
380	2.45×10^{19}	2.87×10^{-18}	1.00×10^{-14}	9.57×10^{-15}	1.87×10^{-16}	1.49×10^{-15}
390	3.33×10^{19}	3.20×10^{-18}	1.09×10^{-14}	9.99×10^{-15}	2.27×10^{-16}	1.64×10^{-15}
400	4.45×10^{19}	3.52×10^{-18}	1.17×10^{-14}	1.04×10^{-14}	2.69×10^{-16}	1.78×10^{-15}
420	7.54×10^{19}	4.35×10^{-18}	1.35×10^{-14}	1.13×10^{-14}	3.75×10^{-16}	2.12×10^{-15}
440	1.21×10^{20}	5.41×10^{-18}	1.55×10^{-14}	1.24×10^{-14}	5.06×10^{-16}	2.52×10^{-15}
460	1.84×10^{20}	6.80×10^{-18}	1.75×10^{-14}	1.37×10^{-14}	6.75×10^{-16}	2.96×10^{-15}
480	2.70×10^{20}	8.46×10^{-18}	1.97×10^{-14}	1.50×10^{-14}	8.72×10^{-16}	3.45×10^{-15}
500	3.82×10^{20}	1.07×10^{-17}	2.19×10^{-14}	1.66×10^{-14}	1.12×10^{-15}	4.04×10^{-15}

[a] water concentration values in molecules cm^{-3} at 100% relative humidity. Calculated using formula; $c = p/RT$; c: concentration; p: vapour pressure in atm; R: universal gas constant & T is temperature in Kelvin.[58,59]

[b] The energy values used for calculating rate constant for path 6 are at the BHandHLYP/6-311++G(d,p) level of the theory since TS6 could not be refined at the CCSD(T) single-point level.

Table S11. Comparison of the rate constants (in cm^3 $molecule^{-1}$ s^{-1}), without tunneling correction, for water-free and water-assisted pathways for hydrogen abstraction in Glycolaldehyde with hydroxyl radical, at 298K, at the BHandHLYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and CCSD(T)/-311++G(d,p)//BHandHLYP/6-311++G(d,p) (BSSE uncorrected) levels of the theory.

Pathway	**BH&HLYP/6-311++G(d,p)**	**M06-2X/6-311++G(d,p)**	**CCSD(T)/6-311++G(d,p)// BHandHLYP/6-311++G(d,p)**
1	3.87×10^{-13}	2.73×10^{-11}	2.70×10^{-11}
2	1.41×10^{-13}	1.03×10^{-10}	8.86×10^{-12}
3	1.71×10^{-14}	1.34×10^{-12}	7.18×10^{-13}
4	9.66×10^{-16}	3.48×10^{-13}	1.41×10^{-13}
5	8.44×10^{-19}	4.09×10^{-14}	2.48×10^{-17}
Overall (water-free)	**1.49×10^{-13}**	**3.97×10^{-12}**	**1.42×10^{-12}**
6	2.04×10^{-22}	4.04×10^{-17}	2.04×10^{-22}
7	1.08×10^{-16}	3.42×10^{-14}	3.76×10^{-15}
8	9.49×10^{-20}	1.98×10^{-15}	4.37×10^{-16}
9	6.16×10^{-18}	1.23×10^{-14}	9.56×10^{-18}
10	4.06×10^{-18}	8.28×10^{-14}	2.13×10^{-17}
Overall (water-assisted)	**1.13×10^{-16}**	**4.65×10^{-14}**	**4.23×10^{-15}**

Table S12. Relative energies and ZPE (in kcal/mol) of the stationary points obtained for the addition of hydroxyl radical to glycolaldehyde depicted in Figure S2 at the BHandHLYP/6-311++G(d,p) level of theory. The values are relative to the isolated reactants R1 depicted in Figure S2.

Species	ZPE	BHandHLYP/ 6-311++G(d,p)+ZPE
PRC12	4.52	-17.25
PRC 13	5.33	-17.47
PRC 14	5.39	30.65
PRC 15	1.96	40.40
TS12	3.76	31.53
TS13	2.83	-0.30
TS14	1.14	58.88
TS15	1.02	80.28
PC12	5.52	-16.55
PC13	2.49	-30.93
PC14	4.23	49.10
PC15	5.26	30.46

Optimized Cartesian Coordinates (X,Y,Z), in angstroms, for the pre-reactant complexes (PRCs), at the BHandHLYP/6-311++G(d,p) level of theory:

PRC1

C	0.72944500	0.93689200	0.00482500
H	-2.12001900	-0.20323800	0.00000500
H	1.16872400	1.38340000	0.89460900
C	1.07679900	-0.52968200	-0.00426000
H	-0.92192400	1.98481400	-0.00216700
O	2.20018900	-0.91981100	0.00155000
O	-0.67374600	1.06728800	-0.00544400
H	0.22023000	-1.21878300	-0.01676600
O	-2.82234400	-0.87083100	0.00284600
H	1.18273500	1.39737700	-0.87068800

PRC2

C	0.73956061	-0.90949436	-0.45824334
H	-0.32530301	0.93586202	0.12580711
H	-0.31822072	1.42738493	2.61701754
C	-0.32342765	0.15336120	-0.64714146
H	1.21027245	-1.10741230	-1.41736657
O	1.73239872	-0.51152049	0.43799281
H	0.23463304	-1.82736640	-0.14143523
O	-0.31975152	0.52254258	2.29829402
H	1.34599636	-0.38776906	1.30044722
O	-1.11946489	0.15278504	-1.53824592

PRC3

C	0.35739600	-0.78484000	-0.00024900
H	0.18040400	-1.40717500	-0.87771700
H	0.17965800	-1.40711200	0.87710500
C	1.79707200	-0.36656700	0.00031100
H	2.54095300	-1.17236600	0.00074500
O	2.11603800	0.78342100	0.00025400
O	-0.49235300	0.32016500	-0.00063100
H	0.04566600	1.11294700	-0.00071900
O	-3.31351700	0.08937200	0.00040400
H	-2.35482800	0.23848800	-0.00000300

PRC4

C	0.88767800	-0.42343100	0.32161800
H	0.90809900	-0.50242900	1.40659800
H	0.18232100	-1.16553300	-0.04380400
C	0.38252200	0.95725700	-0.00941700
H	1.16357300	1.69999400	-0.22153200
O	-0.77609800	1.25556000	-0.02993600
O	2.19614600	-0.62479100	-0.13432600
H	2.18654800	-0.91496400	-1.03911200
O	-2.65424700	-0.91283000	-0.07947300
H	-2.18815200	-0.06353700	-0.02547700

PRC5

C	-1.01970100	0.88942400	0.07343900
H	0.59429400	-1.15486900	0.05131200
H	-2.17971900	-0.81262300	-0.34550900
C	-1.26272500	-0.58539000	0.19430100
H	1.78990300	0.59054700	-0.14011000
O	0.02418400	1.39435300	-0.22224300
O	2.34747100	-0.14009700	0.17402600
H	-1.89025900	1.51681300	0.31402600
O	-0.26338800	-1.40438000	-0.29429700
H	-1.48579600	-0.76308100	1.25395500

PRC6

C	-1.31664400	0.00597800	0.65404700
H	-1.80926300	-1.14226000	-1.16393400
H	1.67257200	1.13696100	-0.15858800
C	-1.05452900	-1.06661700	-0.37079000
H	3.10543300	-0.86401000	0.30288000
O	1.13558600	1.90884000	-0.42838000
O	-1.64558700	1.20746800	0.02339500
H	1.58820500	-1.13897000	0.20913900
O	-0.09657600	-1.78813500	-0.37053300
H	-2.17585000	-0.30525800	1.24541700
H	-0.45991300	0.09379100	1.31727800
O	2.24855300	-0.45964500	0.37440800
H	-0.82995100	1.63535700	-0.24286000

PRC7

C	-1.37176500	-0.04928200	0.63120700
H	1.67915300	1.09330900	-0.10399700
H	-0.81659900	1.57364300	-0.21779900
C	-0.99146700	-1.09534100	-0.38328800
H	-2.27723400	-0.38540500	1.13321800
O	2.43919700	-0.62534900	0.35264800
O	1.05332800	1.79445500	-0.30481400
H	-0.58238500	0.04282200	1.37381200
O	-1.65623900	1.15581400	-0.00972600
H	-1.67771300	-1.18450400	-1.23471700
H	1.68403500	-1.22661100	0.22044000
O	-0.00861700	-1.78059000	-0.32086000
H	1.54877500	2.59984000	-0.39645500

PRC8

C	0.72922300	0.24317900	0.70692700
H	-2.51379900	0.72686600	-0.25366600
H	-1.41411300	-1.27827700	-0.04340800
C	1.98741600	0.64771500	0.00437400
H	-2.87016100	-1.79493800	0.02677600
O	-2.32945600	1.68002700	-0.16397800
O	-2.32780000	-1.07373800	-0.26910900
H	1.05076800	-1.41928800	-0.19955400
O	2.57572000	-0.10375500	-0.71423700
H	-0.06488600	0.94009200	0.44035300
H	0.89555700	0.33148400	1.78124800
O	0.36570400	-1.06747500	0.37146500
H	2.34345500	1.66823200	0.18732700

PRC9

C	-2.14323800	0.06096300	-0.38459500
H	-1.06499100	0.07588000	1.45145000
H	1.87229200	-1.26218300	-0.13985700
C	-1.03804100	-0.45867000	0.50473100
H	0.60126000	0.48976300	-0.04228800
O	-3.25495600	0.25080000	-0.00273300
O	2.12857500	1.53509500	0.12246600
H	-1.84784400	0.24338100	-1.42968800
O	2.84672300	-1.24799600	-0.13791900
H	2.77100400	0.82980200	0.02818900
H	-1.25020300	-1.50363200	0.71400300
O	0.21663900	-0.38922900	-0.11405100
H	2.51031100	2.32387200	-0.24471800

PRC10

C	-1.12532000	-1.03300200	-0.24484800
H	-0.95303400	0.31777600	1.36272400
H	3.14937400	-1.23803300	0.22899300
C	-1.19469700	0.36235400	0.29963200
H	-2.51982500	1.78108100	0.22005800
O	-0.13133700	-1.70168200	-0.23224200
O	1.83011200	1.96714700	-0.32852700
H	-2.06238600	-1.41814500	-0.66484600
O	2.41034200	-0.64814000	0.31925300
H	-0.42852900	0.96455300	-0.18579800
H	1.60922200	-1.15774200	0.16318900
O	-2.49229600	0.84327700	0.07277600
H	2.19070800	1.08958000	-0.10309400