Supplement of

Acid-catalyzed hydrolysis kinetics of organic hydroperoxides: Computational strategy and structure-activity relationship

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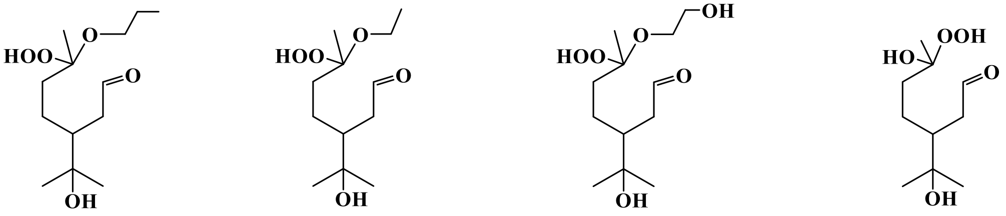
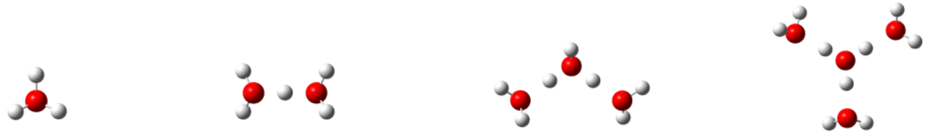


(a) C_{13} α-AH **(b) C_{12} α-$AH_{(1)}$** **(c) C_{12} α-$AH_{(2)}$** **(d) C_{10} α-HH**

Figure S1. Structures of selected four ROOHs as tested compounds. Structure **(a)** is C_{13} α-AH derived via α-terpineol derived CIs and 1-propanol, **(b)** is C_{12} α-$AH_{(1)}$ derived via α-terpineol derived CIs and ethanol, **(c)** is C_{12} α-$AH_{(2)}$ derived via α-terpineol derived CIs and ethylene glycol, and **(d)** is C_{10} α-HH derived via α-terpineol derived CIs and water.



(a) H_3O^+ **(b) $H_3O^+(H_2O)_1$** **(c) $H_3O^+(H_2O)_2$** **(d) $H_3O^+(H_2O)_3$**

Figure S2. Minimum-energy structures of H_3O^+ **(a)** and the protonated water clusters **(b)** H_3O^+ $(H_2O)_1$ (Zundel cation), **(c)** $H_3O^+(H_2O)_2$, **(d)** $H_3O^+(H_2O)_3$ (Eigen cation). The atoms in red and white represent oxygen and hydrogen atoms, respectively.

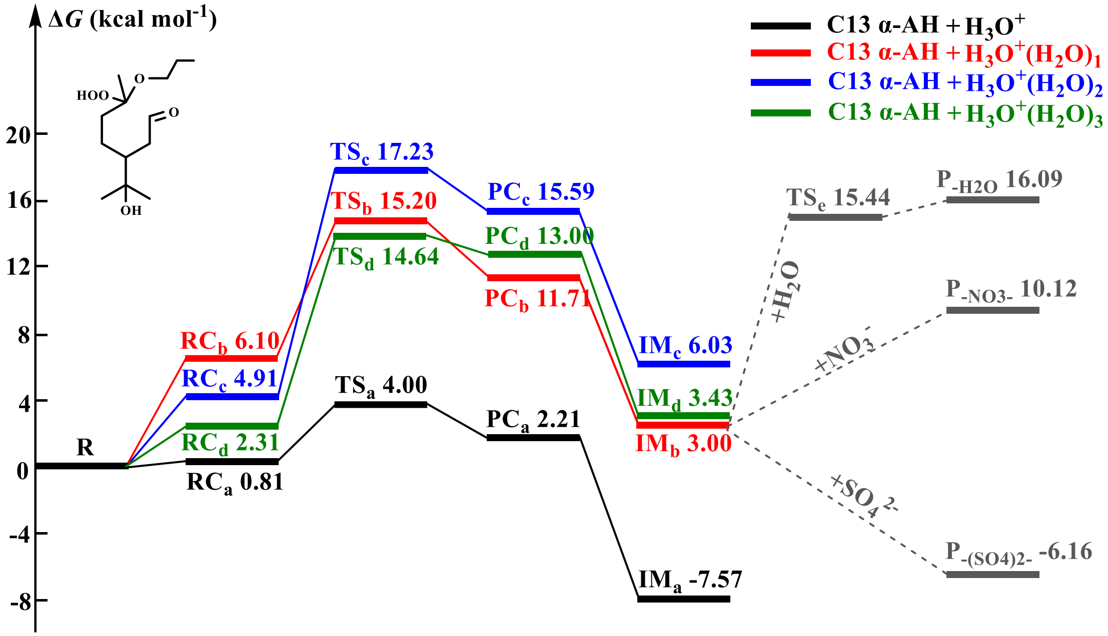


Figure S3. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of C_{13} α-AH in four different cases at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_n$ (n = 0, 1, 2, 3) are set to zero (reference state, R). RC, TS_x (x = a, b, c, d, e), PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

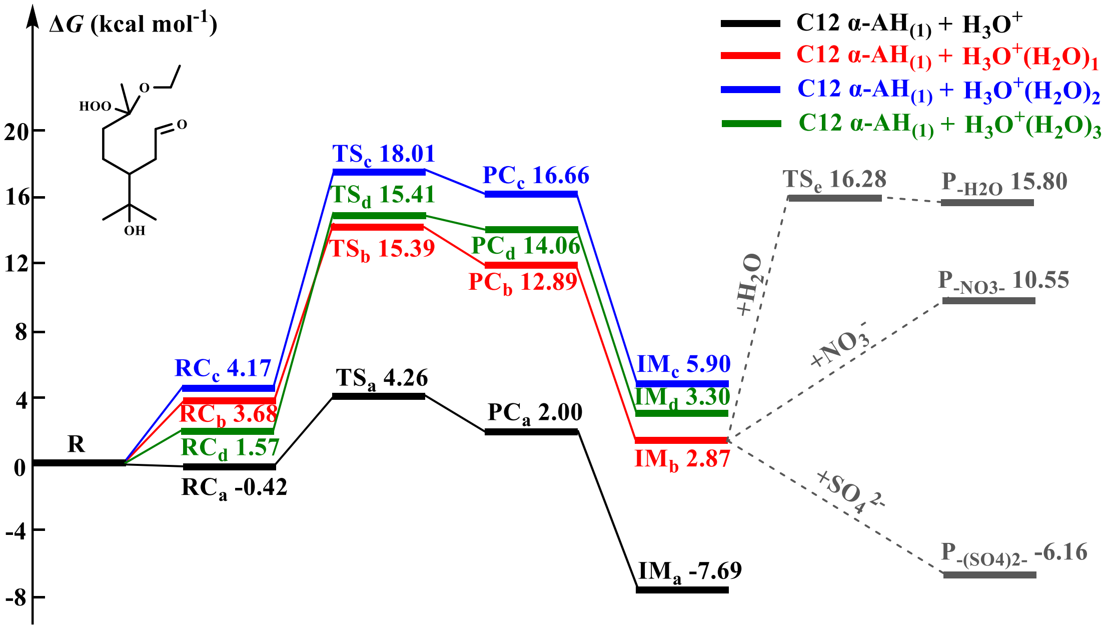


Figure S4. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of C_{12} α-$AH_{(1)}$ in four different cases at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_n$ (n = 0, 1, 2, 3) are set to zero (reference state, R). RC, TS_x (x = a, b, c, d, e), PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

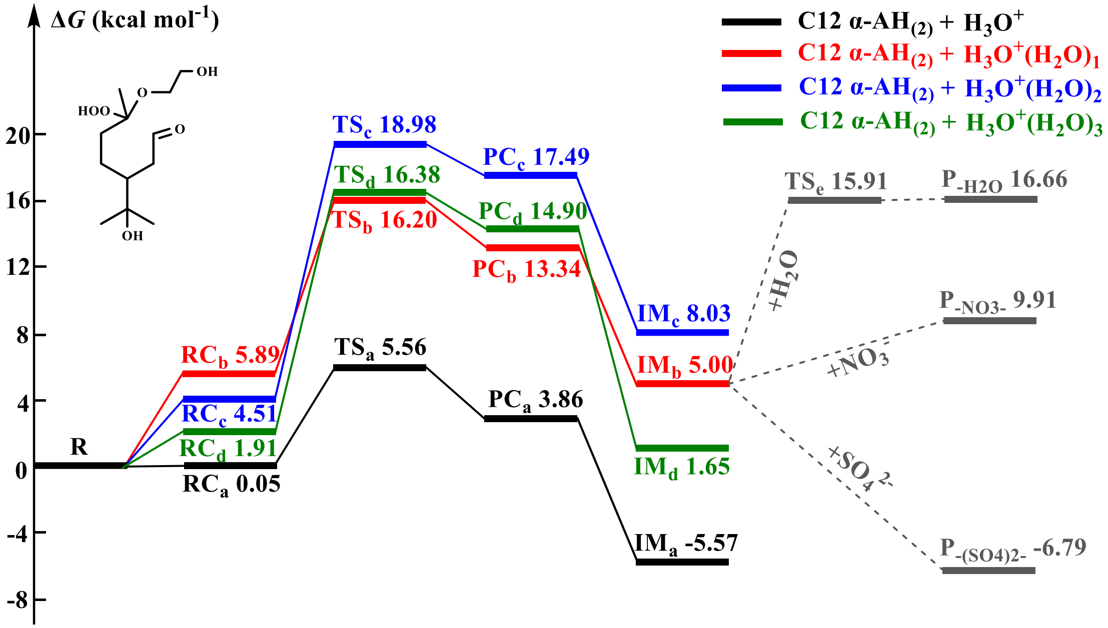


Figure S5. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of C$_{12}$ α-AH$_{(2)}$ in four different cases at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_n$ (n = 0, 1, 2, 3) are set to zero (reference state, R). RC, TS$_x$ (x = a, b, c, d, e), PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

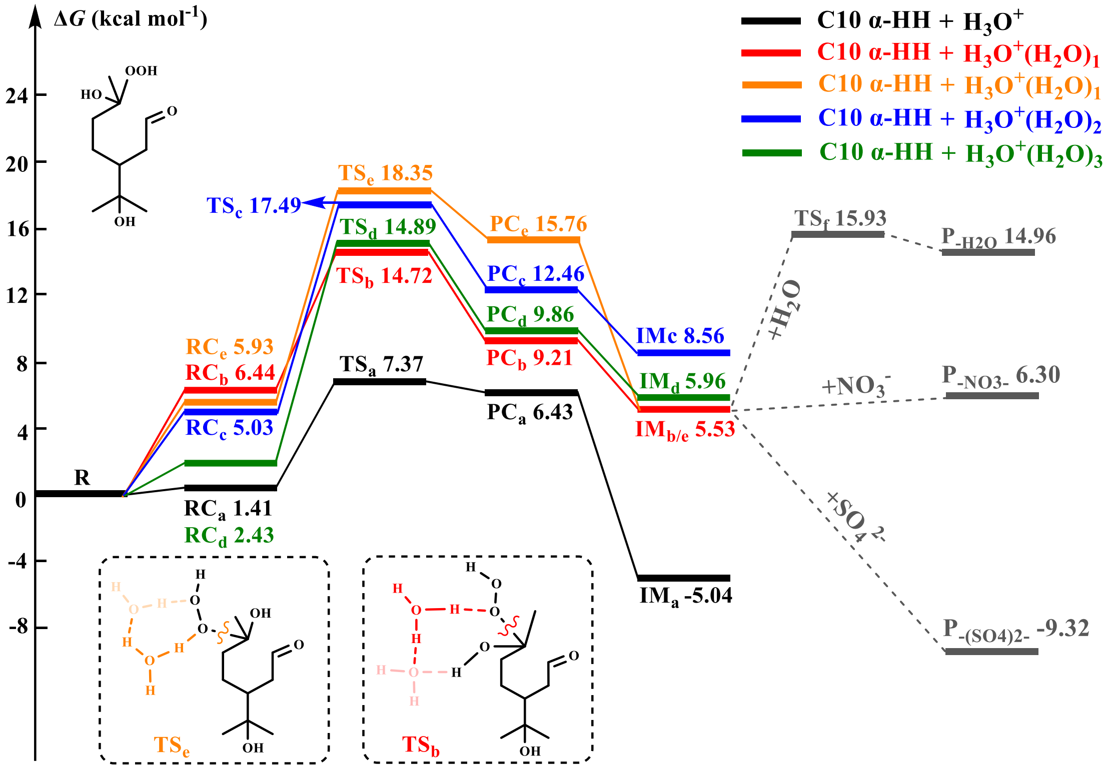


Figure S6. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of C_{10} α-HH in four different cases at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_n$ (n = 0, 1, 2, 3) are set to zero (reference state, R). RC, TS_x (x = a, b, c, d, e, f), PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

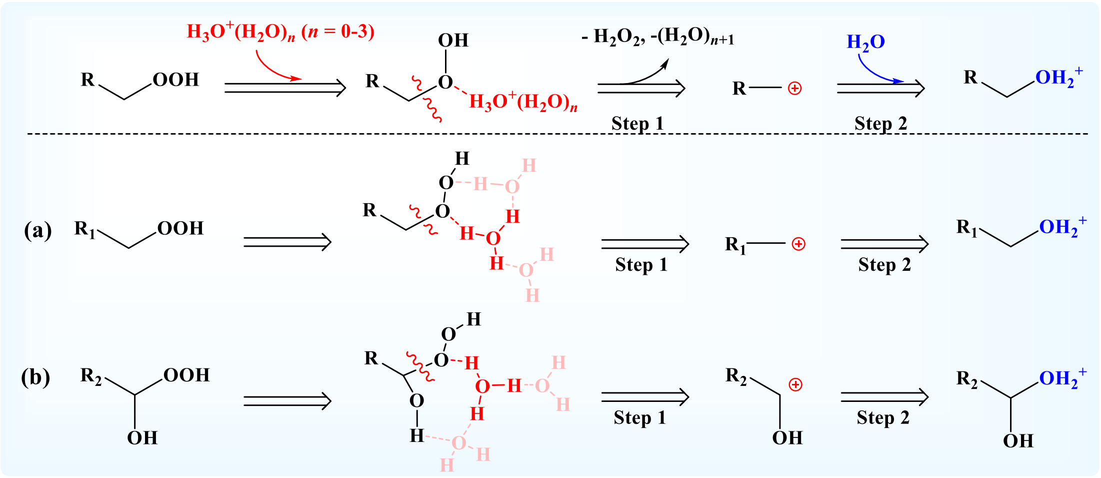


Figure S7. Two-step acid-catalyzed hydrolysis pathway for four tested ROOHs. The reaction pathways **(a)** for C_{13} α-AH, C_{12} α-AH$_{(1)}$, and C_{12} α-AH$_{(2)}$, and **(b)** for C_{10} α-HH.

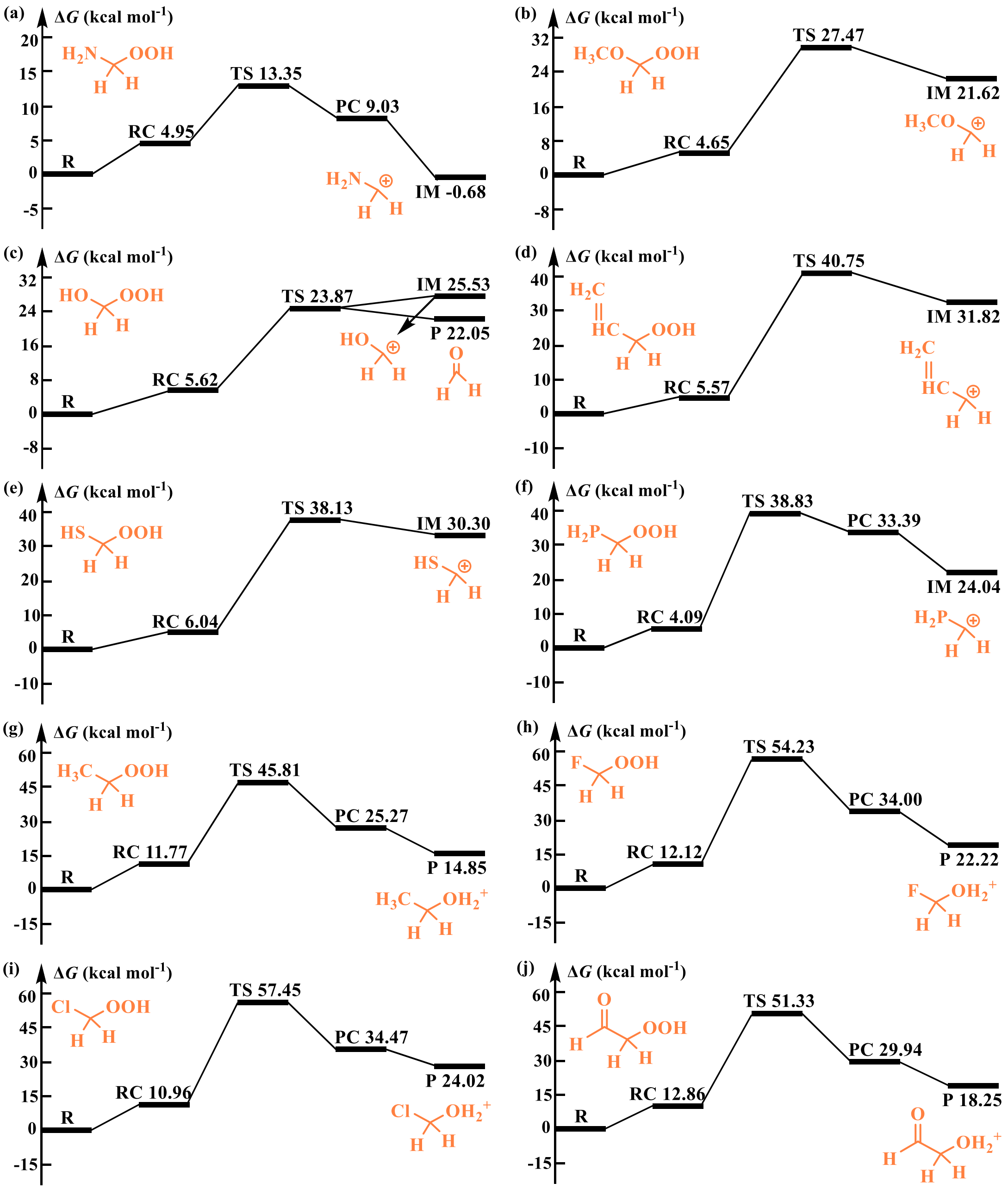


Figure S8. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of $CH_2(X)OOH$ (X = NH_2, OCH_3, OH, $CH{=}CH_2$, SH, PH_2, CH_3, F, Cl and CHO) at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state, R). RC, TS, PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

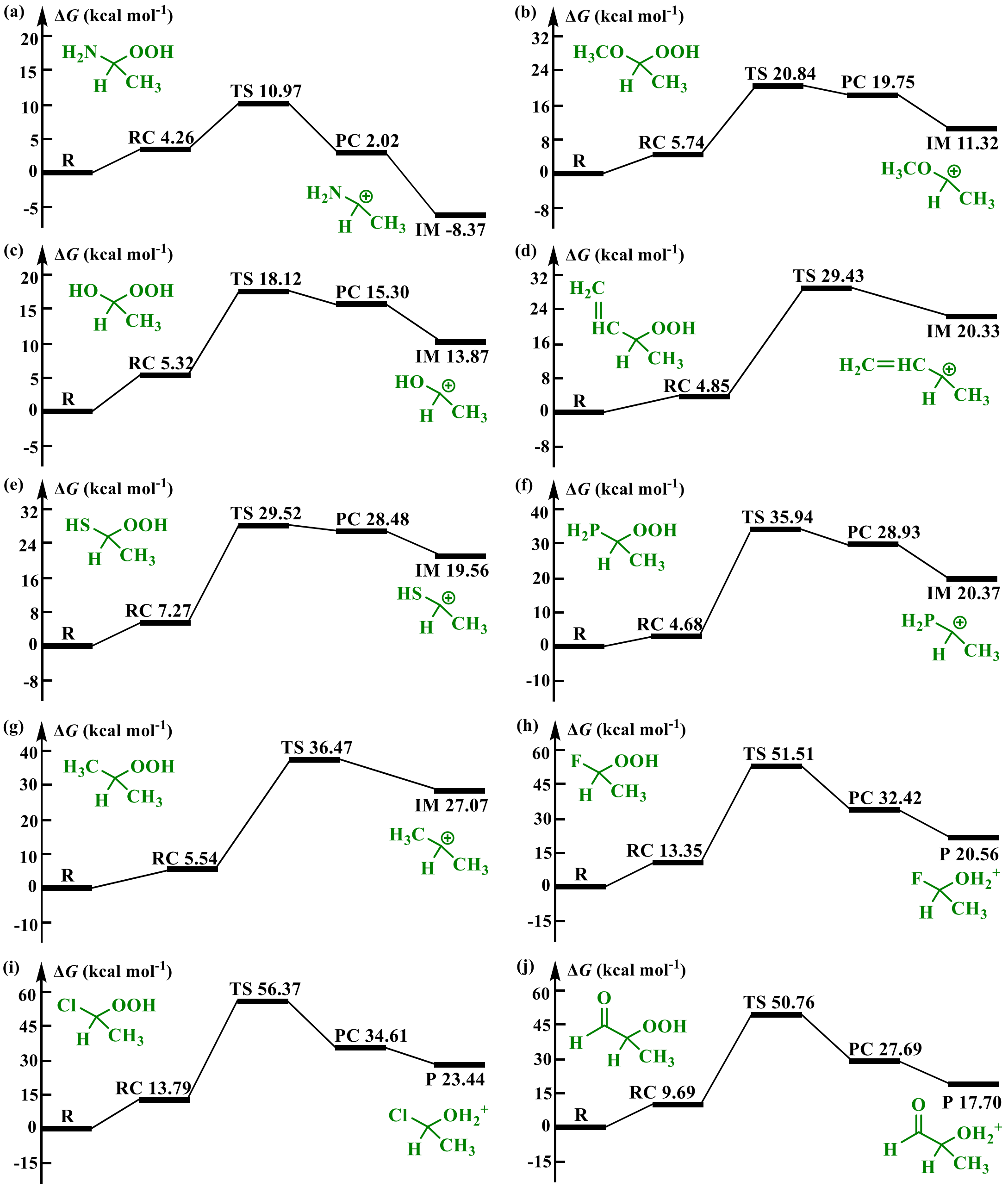


Figure S9. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of $CH(CH_3)(X)OOH$ (X = NH_2, OCH_3, OH, $CH{=}CH_2$, SH, PH_2, CH_3, F, Cl and CHO) at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state, R). RC, TS, PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

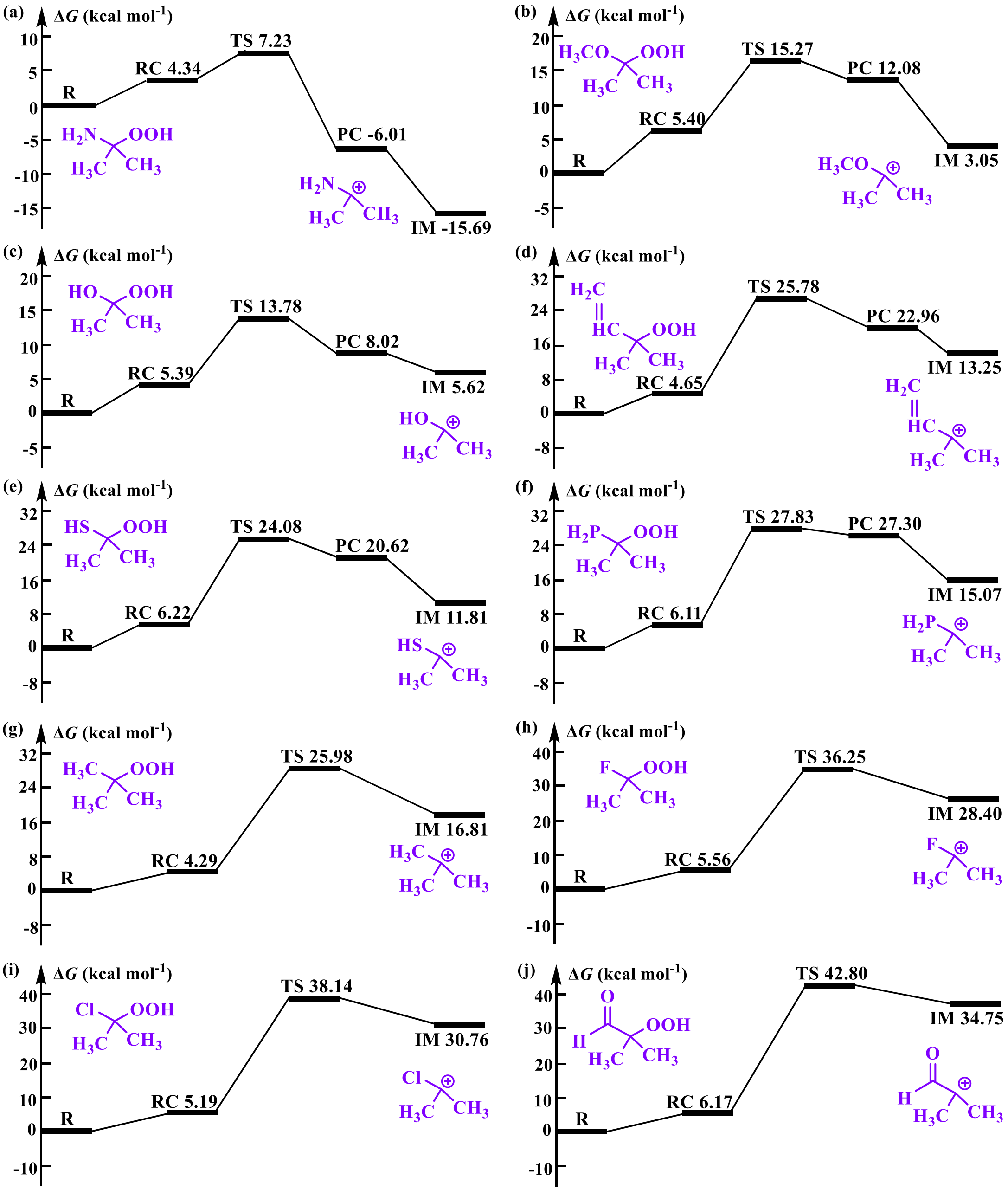


Figure S10. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of (C(CH$_3$)$_2$(X)OOH) (X = NH$_2$, OCH$_3$, OH, CH=CH$_2$, SH, PH$_2$, CH$_3$, F, Cl and CHO) at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and H$_3$O$^+$(H$_2$O)$_1$ are set to zero (reference state, R). RC, TS, PC and IM represent pre-reactive complexes, transition states, post-reactive complexes and intermediates, respectively.

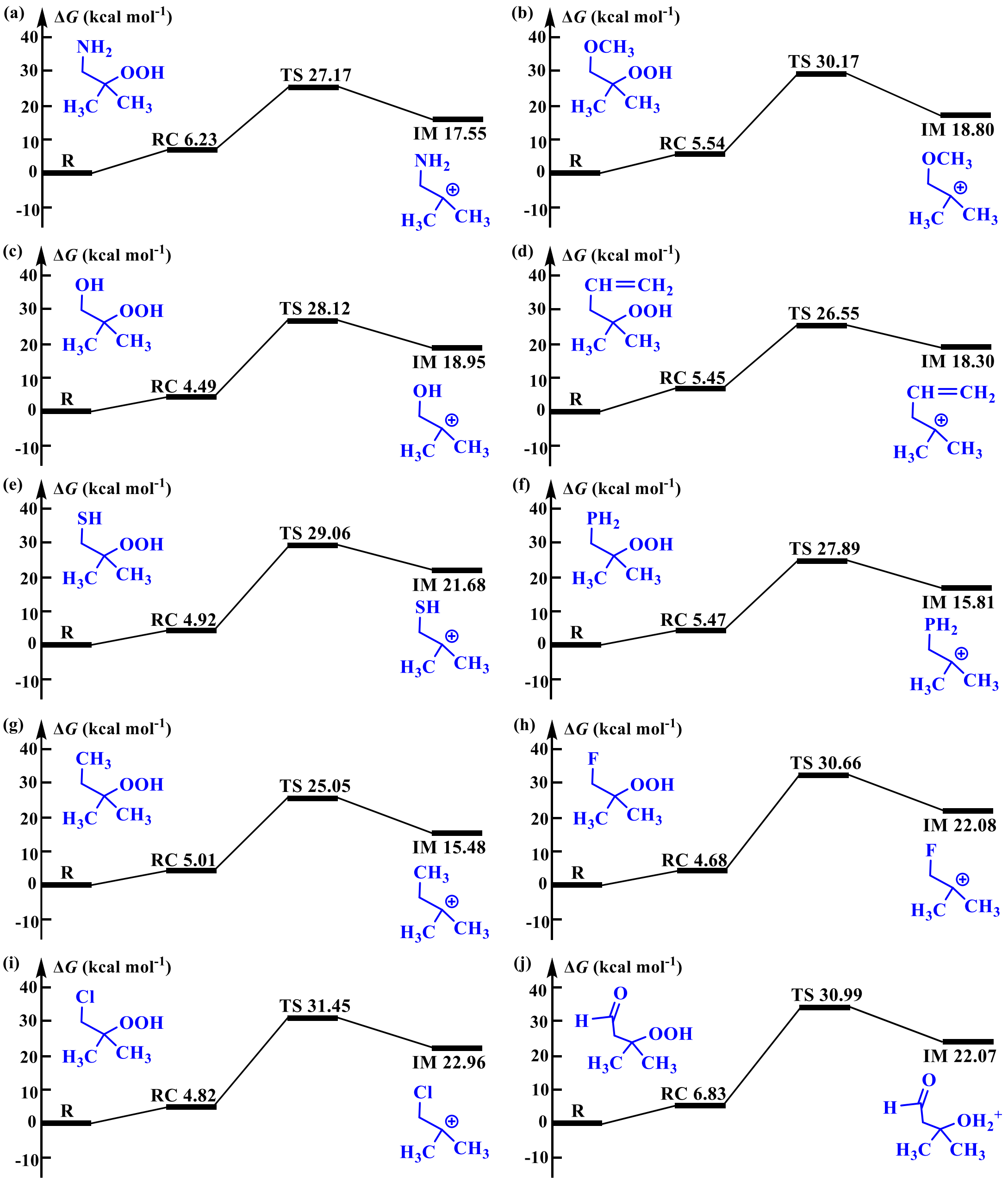


Figure S11. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of $C(CH_3)_2(CH_2(X))OOH$ (X = NH_2, OCH_3, OH, $CH{=}CH_2$, SH, PH_2, CH_3, F, Cl and CHO) at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state, R). RC, TS and IM represent pre-reactive complexes, transition states and intermediates, respectively.

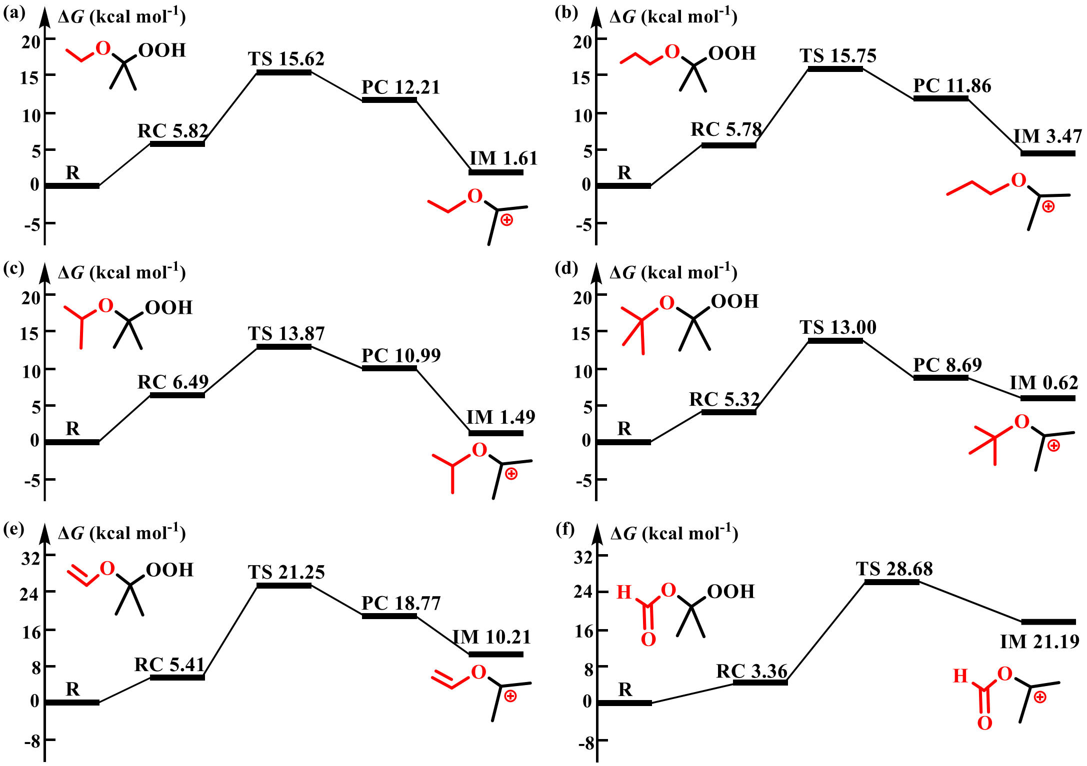


Figure S12. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of $C(CH_3)_2(OY)OOH$ (Y = CH_2CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$, $C(CH_3)_3$, $CH=CH_2$, and CHO) at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state, R). RC, TS, PC and IM represent pre-reactive complexes, transition states, post-reactive complexes and intermediates, respectively.

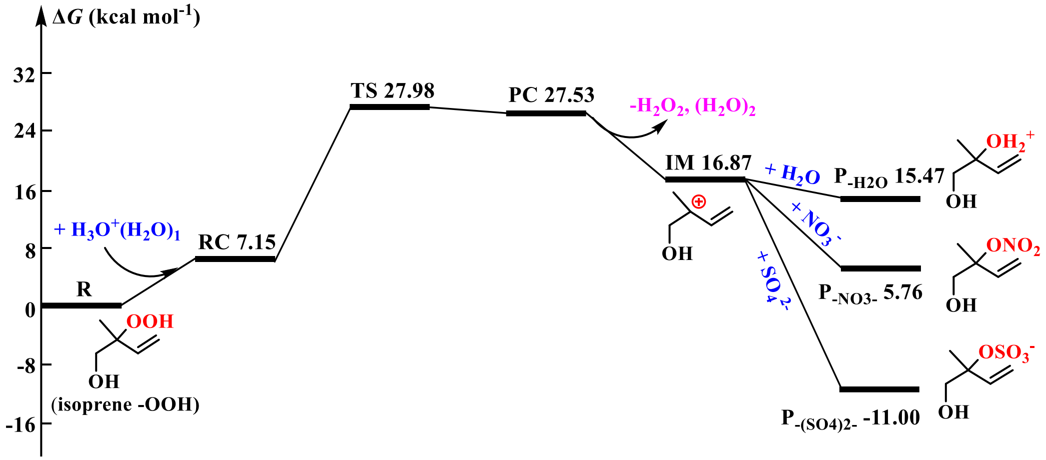


Figure S13. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of isoprene-OOH at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state). RC, TS, PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

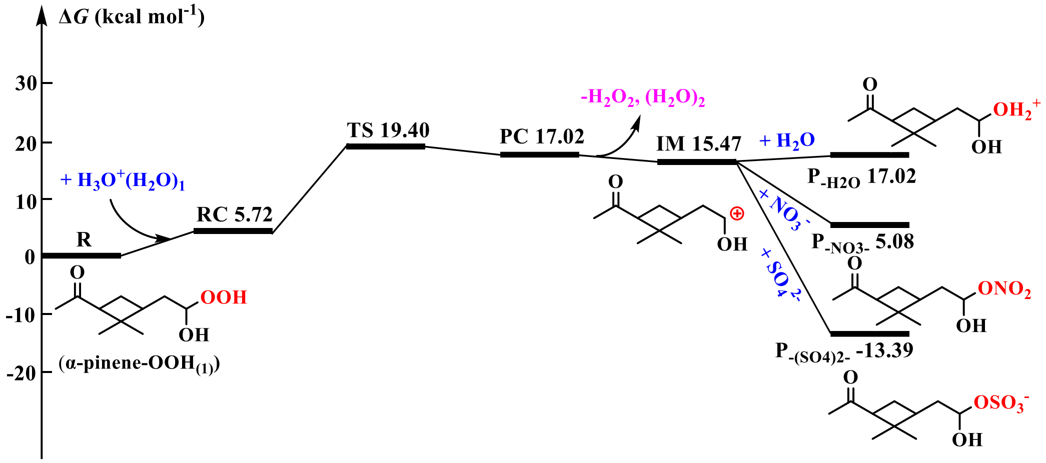


Figure S14. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of α-pinene-OOH$_{(1)}$ at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state). RC, TS, PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

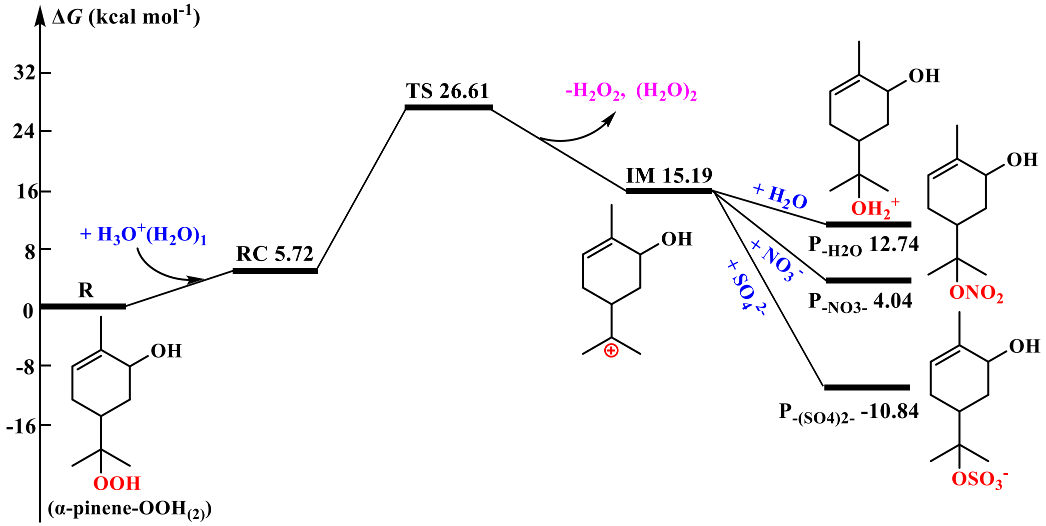


Figure S15. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of α-pinene-OOH$_{(2)}$ at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state). RC, TS, IM and P represent pre-reactive complexes, transition states, intermediates and products, respectively.

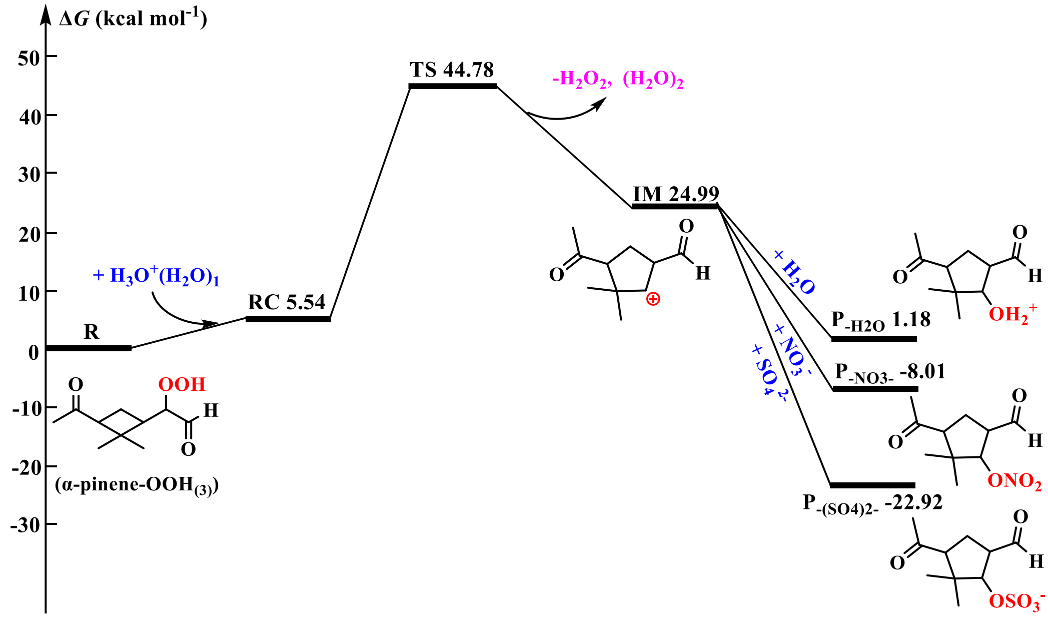


Figure S16. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of α-pinene-$OOH_{(3)}$ at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state). RC, TS, IM and P represent pre-reactive complexes, transition states, intermediates and products, respectively.

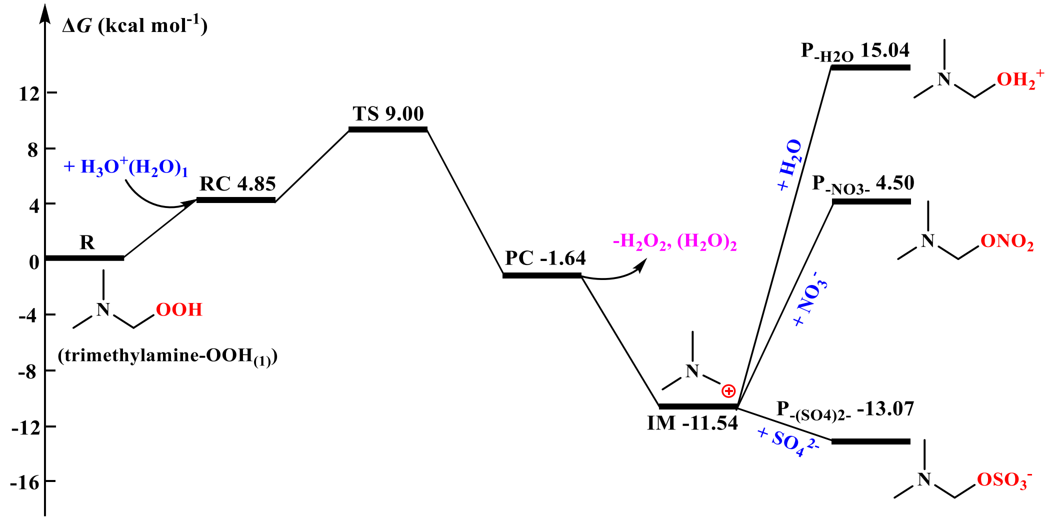


Figure S17. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of trimethylamine-$OOH_{(1)}$ at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state). RC, TS, PC, IM and P represent pre-reactive complexes, transition states, post-reactive complexes, intermediates and products, respectively.

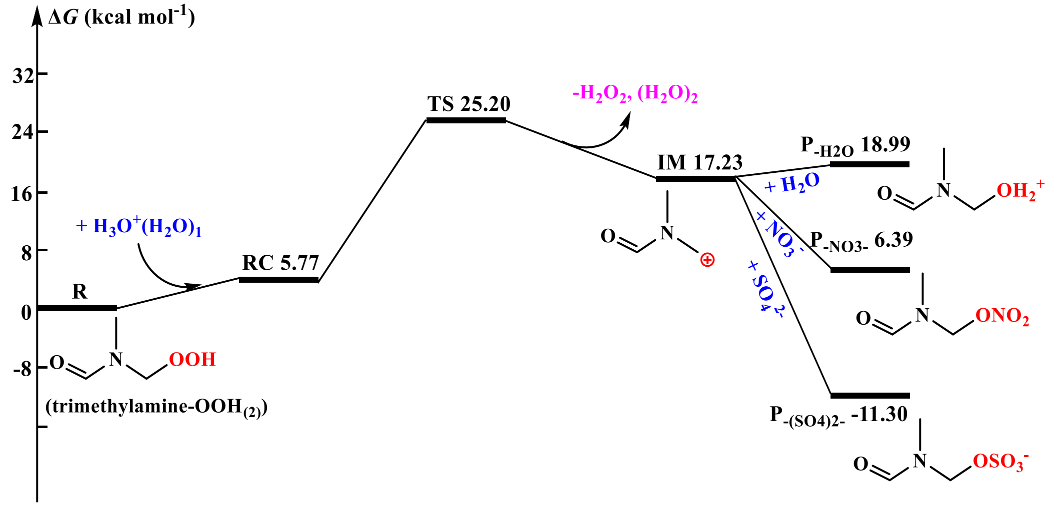


Figure S18. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of trimethylamine-$OOH_{(2)}$ at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state). RC, TS, IM and P represent pre-reactive complexes, transition states, intermediates and products, respectively.

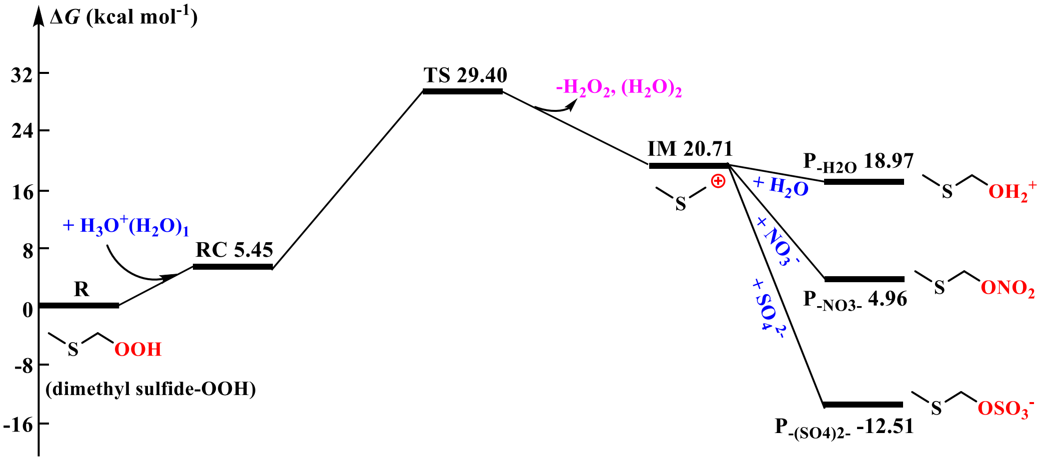


Figure S19. Calculated schematic free-energy surfaces for acid-catalyzed hydrolysis of dimethyl sulfide-OOH at the SMD/M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) level. The free energies of ROOH and $H_3O^+(H_2O)_1$ are set to zero (reference state). RC, TS, IM and P represent pre-reactive complexes, transition states, intermediates and products, respectively.

Table S1. Calculated acid-catalyzed hydrolysis second-order reaction rate constants (k_A) and the corresponding lifetimes ($\tau_{1/e}$) of selected 45 ROOHs model compounds under two selected scenarios (Inland regions, China (pH 3.8) and Southeastern United States (pH 0.9)).

Model compounds	***X/Y***	**k_A (L mol^{-1} s^{-1})**	**$\tau_{1/e,\ pH\ 3.8}$**	**$\tau_{1/e,\ pH\ 0.9}$**
CH_3CH_2OOH	—	1.58×10^{-21}	4.6×10^{19} d	5.8×10^{16} d
$CH(CH_3)_2OOH$	—	1.12×10^{-14}	6.5×10^{12} d	8.2×10^{9} d
$C(CH_3)_3OOH$	—	5.50×10^{-7}	1.3×10^{5} d	1.7×10^{2} d
$CH_2(X)OOH$	NH_2	1.01×10^{3}	6.3 s	< 1 s
	OH	1.94×10^{-5}	3.8×10^{3} d	4.7 d
	OCH_3	4.45×10^{-8}	1.6×10^{6} d	2.1×10^{3} d
	SH	6.77×10^{-16}	1.1×10^{14} d	1.4×10^{11} d
	$CH=CH_2$	8.11×10^{-18}	9.0×10^{15} d	1.1×10^{13} d
	PH_2	2.08×10^{-16}	3.5×10^{14} d	4.4×10^{11} d
	F	1.07×10^{-27}	—	—
	Cl	4.63×10^{-30}	—	—
	CHO	1.43×10^{-25}	—	—
$CH(CH_3)(X)OOH$	NH_2	5.60×10^{4}	< 1 s	< 1 s
	OH	3.20×10^{-1}	5.5 h	24.8 s
	OCH_3	3.24×10^{-3}	22.6 d	40.9 min
	SH	1.40×10^{-9}	5.2×10^{7} d	6.6×10^{4} d
	$CH=CH_2$	1.62×10^{-9}	4.5×10^{7} d	5.7×10^{4} d
	PH_2	2.73×10^{-14}	2.7×10^{12} d	3.4×10^{9} d
	F	1.05×10^{-25}	—	—
	Cl	2.88×10^{-29}	—	—
	CHO	3.73×10^{-25}	—	—
$C(CH_3)_2(X)OOH$	NH_2	3.10×10^{7}	< 1 s	< 1 s
	OH	4.87×10^{2}	13.0 s	< 1 s
	OCH_3	3.93×10^{1}	2.7 min	< 1 s
	SH	1.36×10^{-5}	5.4×10^{3} d	6.8 d
	$CH=CH_2$	7.72×10^{-7}	9.5×10^{4} d	1.2×10^{2} d
	PH_2	2.42×10^{-8}	3.0×10^{6} d	3.8×10^{3} d
	F	1.62×10^{-14}	—	—
	Cl	6.65×10^{-16}	—	—
	CHO	2.54×10^{-19}	—	—

$C(CH_3)_2(CH_2(X))OOH$	NH_2	7.38×10^{-8}	—	—
	OH	1.49×10^{-8}	—	—
	OCH_3	4.66×10^{-10}	—	—
	SH	3.03×10^{-9}	—	—
	$CH{=}CH_2$	2.11×10^{-7}	—	—
	PH_2	2.19×10^{-8}	—	—
	F	2.04×10^{-10}	—	—
	Cl	5.36×10^{-11}	—	—
	CHO	1.17×10^{-10}	—	—
$C(CH_3)_2(O(Y))OOH$	CH_2CH_3	2.17×10^{1}	4.9 min	< 1 s
	$CH_2CH_3CH_3$	1.76×10^{1}	6.0 min	< 1 s
	$CH(CH_3)_2$	4.16×10^{2}	15.2 s	< 1 s
	$C(CH_3)_3$	1.81×10^{3}	3.5 s	< 1 s
	$CH{=}CH_2$	1.62×10^{-3}	45.1 d	1.4 h
	CHO	5.80×10^{-9}	1.3×10^{7} d	1.6×10^{4} d

Table S2. Calculated acid-catalyzed hydrolysis second-order reaction rate constants (k_A) and the corresponding lifetimes ($\tau_{1/e}$) of 7 atmospheric ROOHs under two selected scenarios (Inland regions, China (pH 3.8) and Southeastern United States (pH 0.9)).

Compounds Name	k_A **(L mol^{-1} s^{-1})**	$\tau_{1/e,\ pH\ 3.8}$	$\tau_{1/e,\ pH\ 0.9}$
trimethylamine-OOH$_{(1)}$	1.56×10^{6}	< 1 s	< 1 s
α-pinene-OOH$_{(1)}$	3.68×10^{-2}	2 d	3.6 min
trimethylamine-OOH$_{(2)}$	2.05×10^{-6}	3.6×10^{4} d	45 d
α-pinene-OOH$_{(2)}$	1.90×10^{-7}	3.8×10^{5} d	484 d
isoprene-OOH	1.88×10^{-8}	3.9×10^{6} d	4.9×10^{3} d
dimethyl sulfide-OOH	1.71×10^{-9}	4.3×10^{7} d	5.4×10^{4} d
α-pinene-OOH$_{(3)}$	8.99×10^{-21}	8.1×10^{18} d	1.0×10^{16} d