Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for

Reactions of Hydroxyl Radicals with Benzoic Acid and Benzoate

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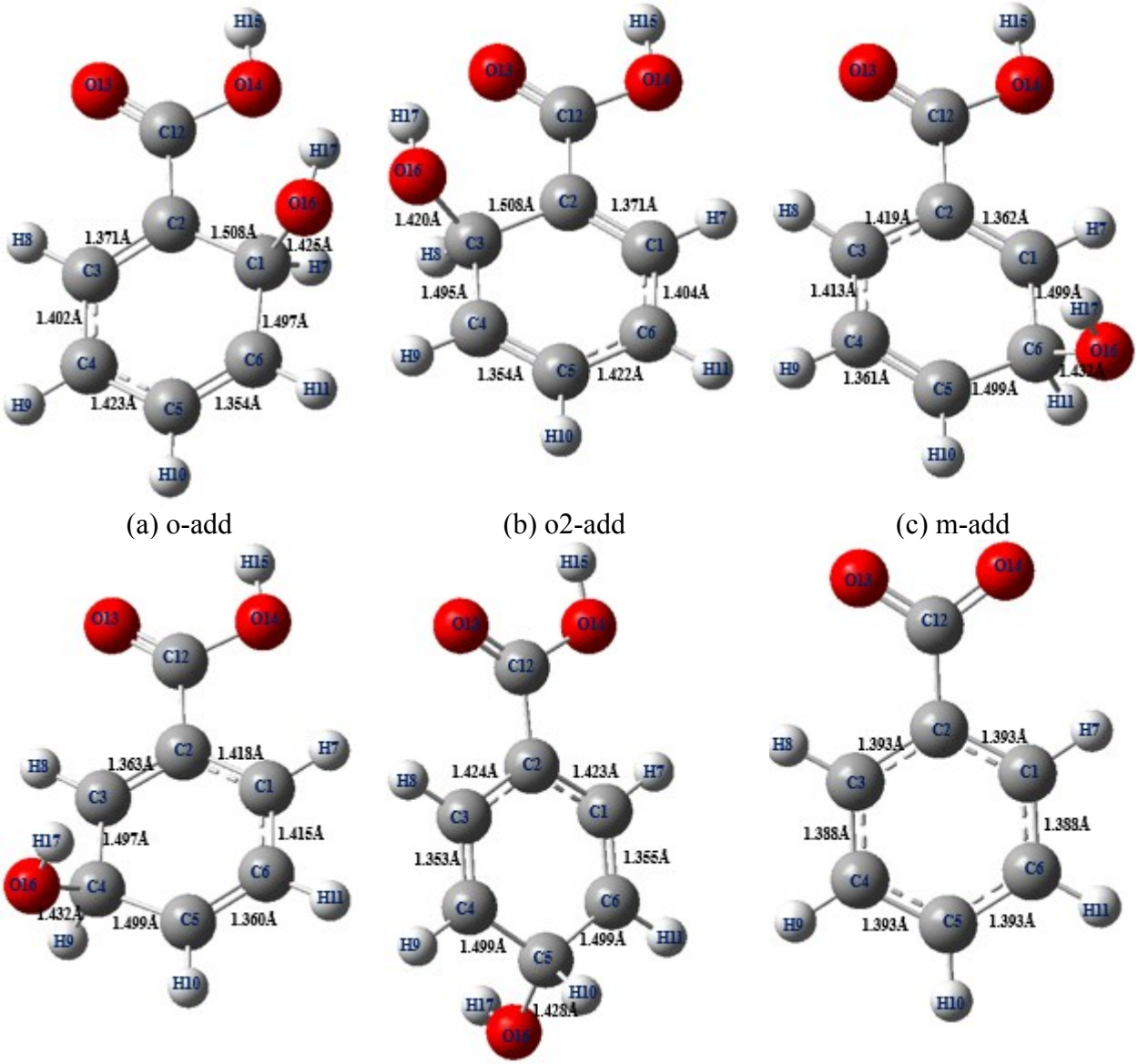


(a) o-add (b) o2-add (c) m-add

(d) m2-add (e) p-add (f) H-abs

Fig. S1 Product complexes (Benzoic acid gas phase)

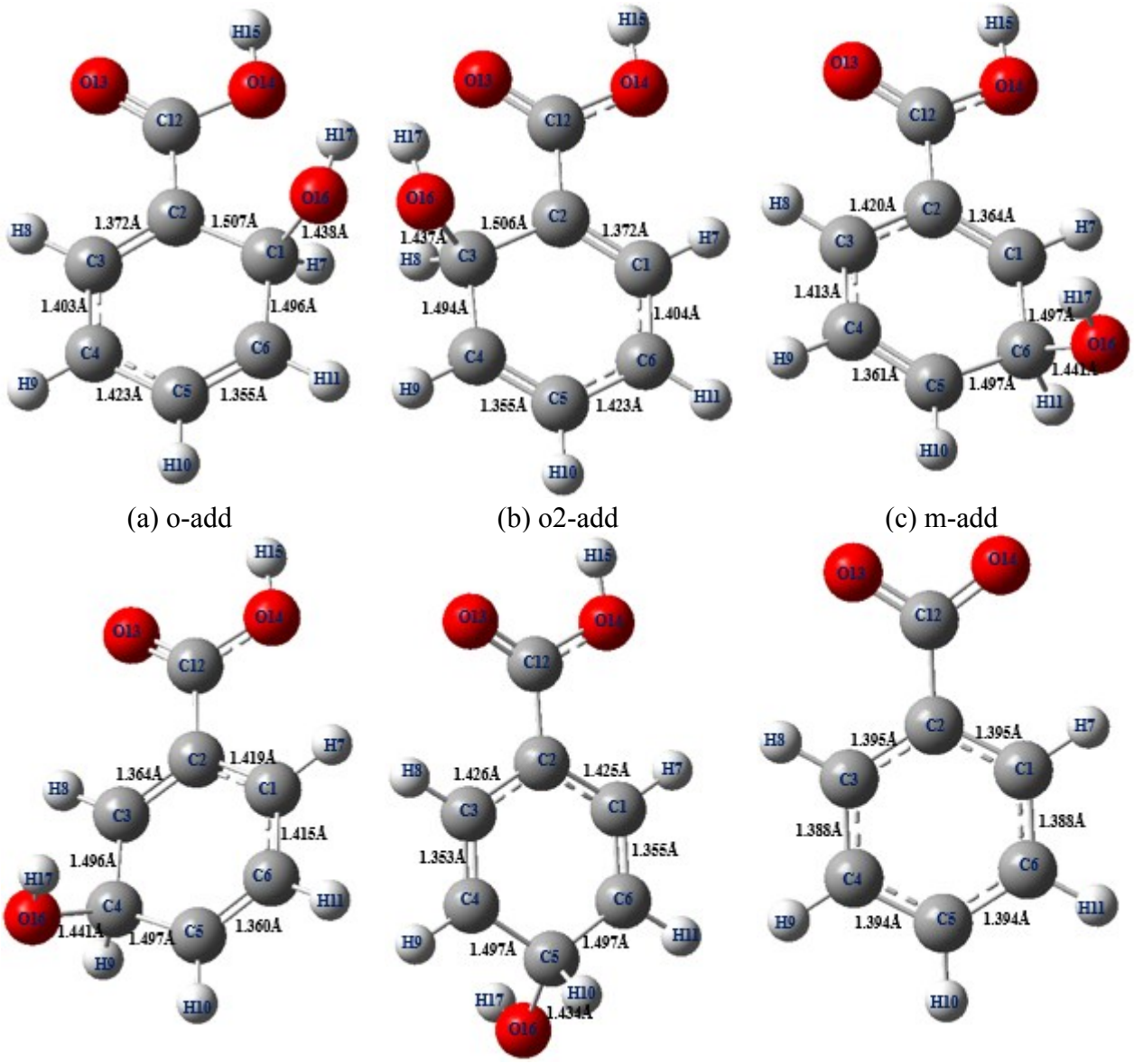
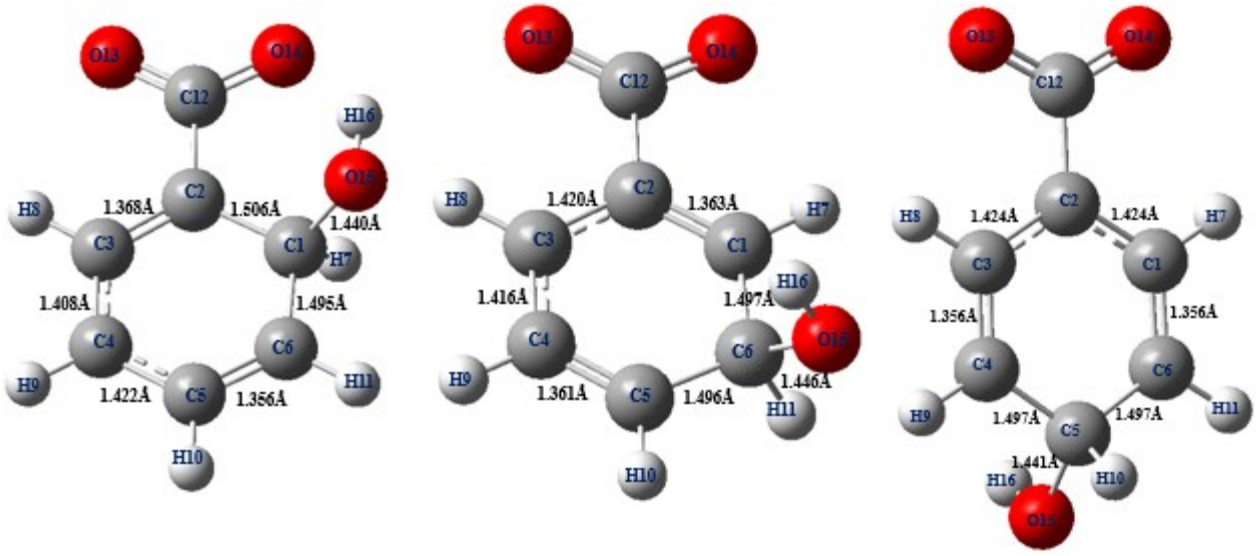


Fig. S2 Product complexes (Benzoic acid aqueous phase)



(a) o-add (b) m-add (c) p-add

Fig. S3 Product complexes (Benzoate aqueous phase)

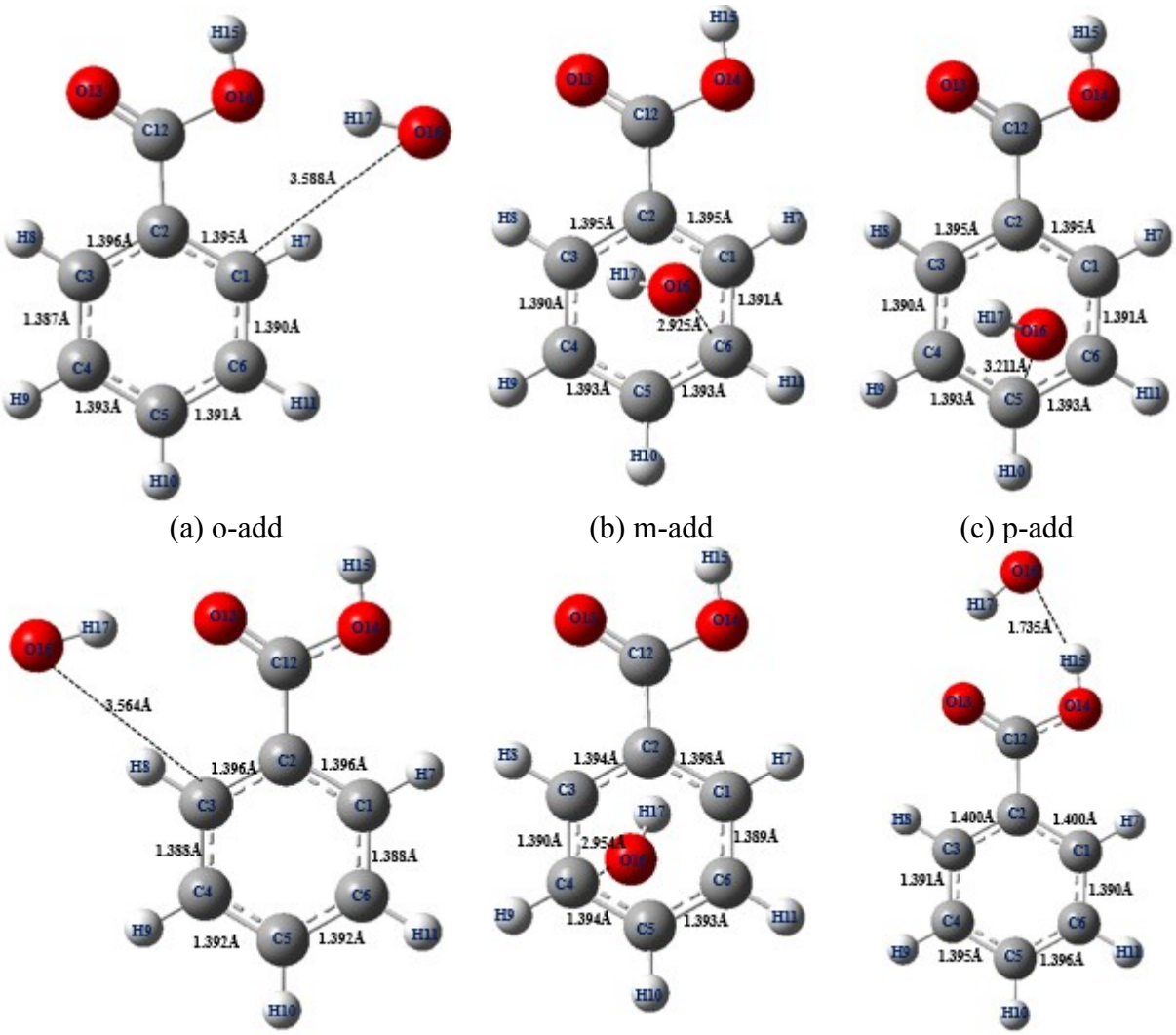


Fig. S4 Pre-reactive complexes (Benzoic acid gas phase)

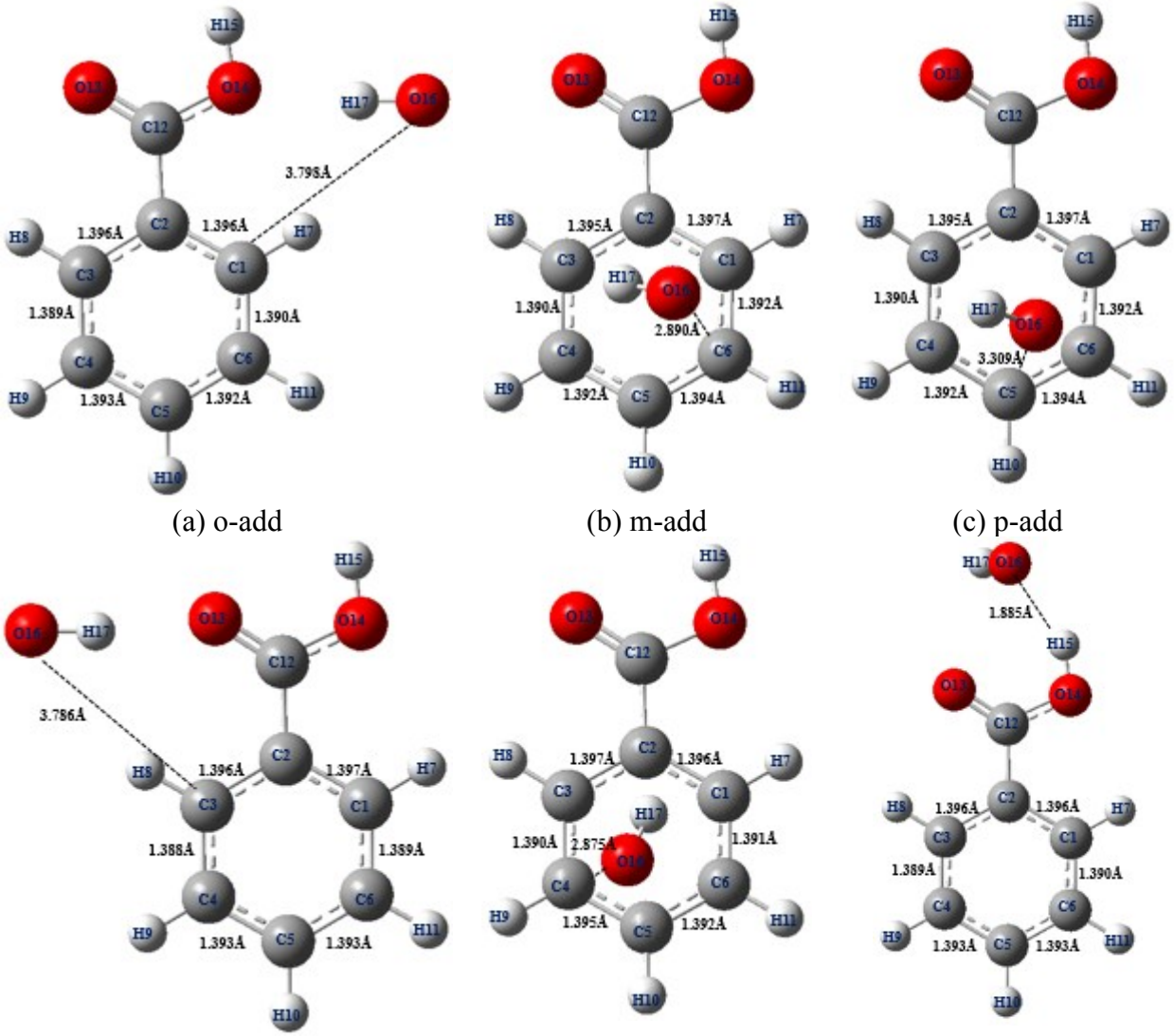
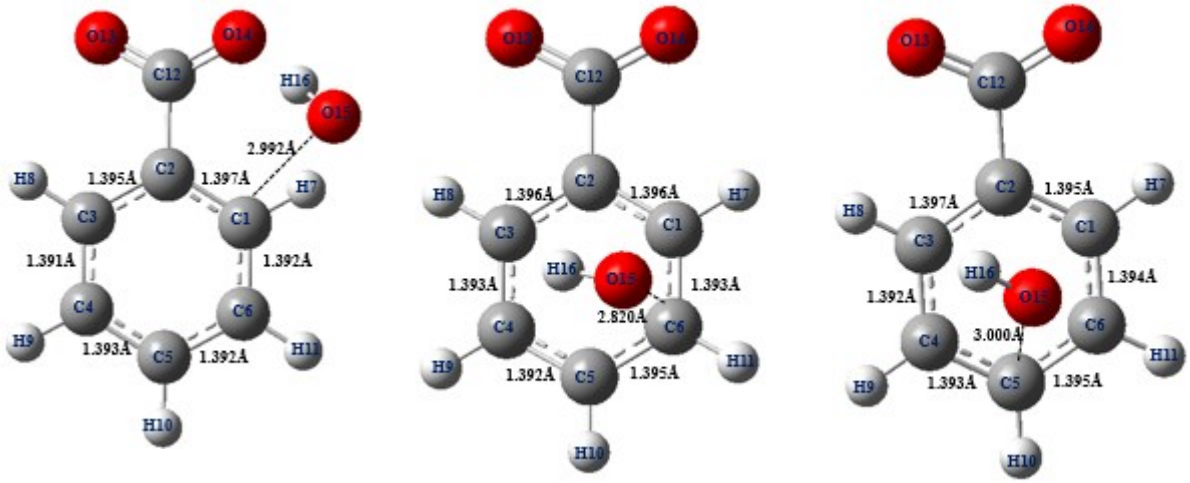
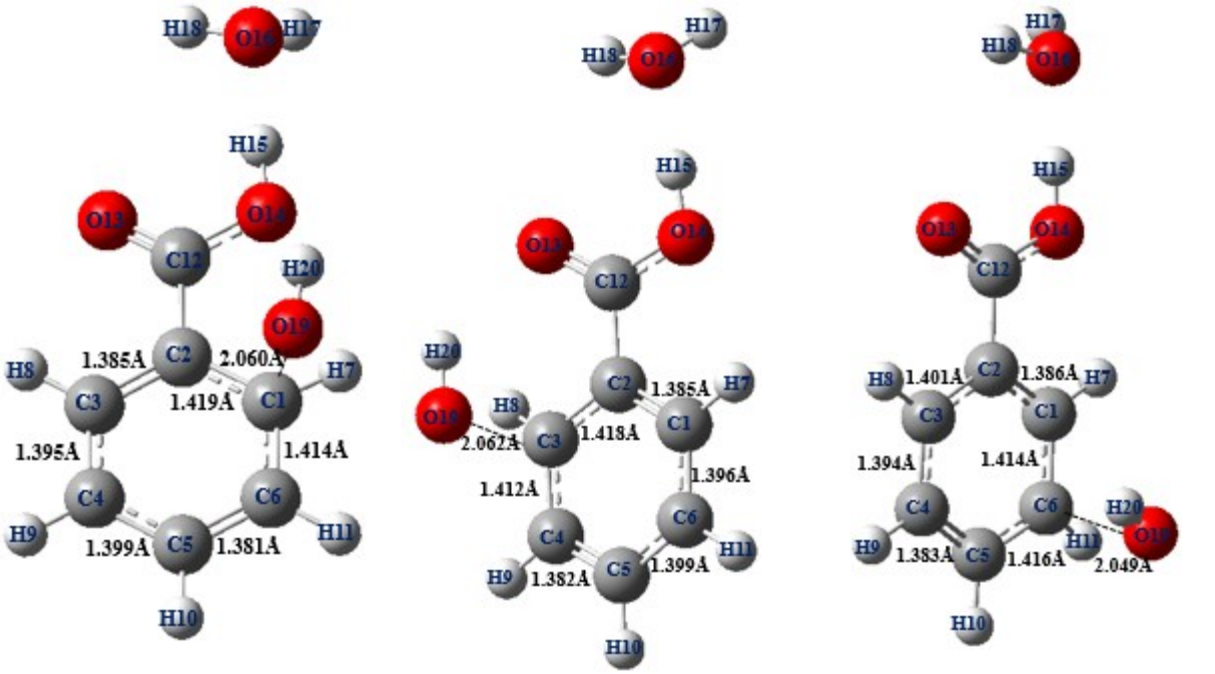


Fig. S5 Pre-reactive complexes (Benzoic acid aqueous phase)



(a) o-add (b) m-add (e) p-add

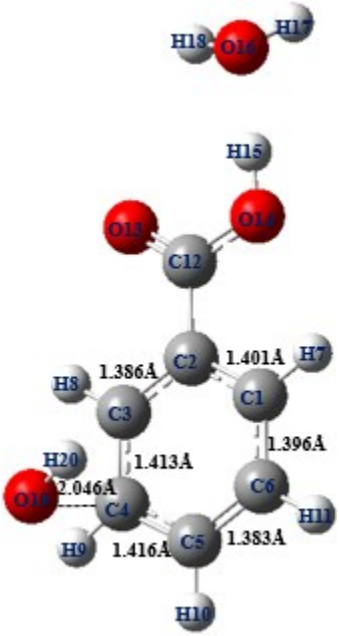
Fig. S6 Pre-reactive complexes (Benzoate aqueous phase)



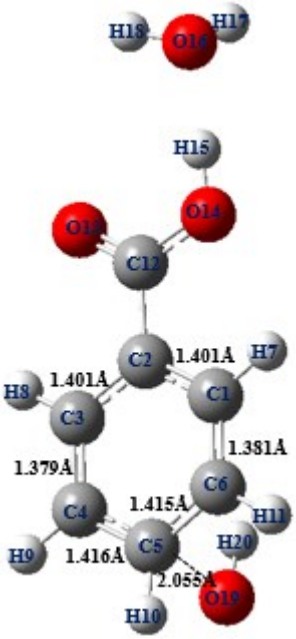
(a) o-add

(b) o2-add

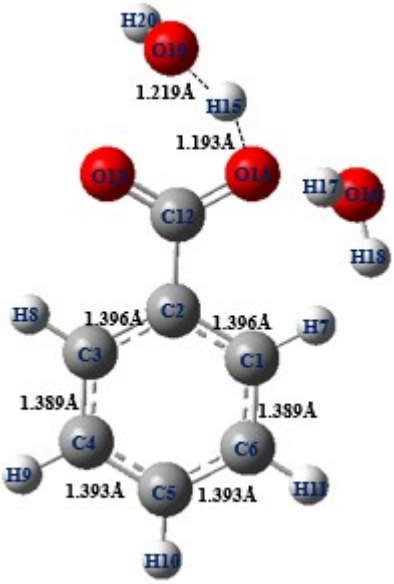
(c) m-add



(d) m2-add



(e) p-add



(f) H-abs

Fig. S7 Transitions states with one explicit water molecule (Benzoic acid aqueous phase)

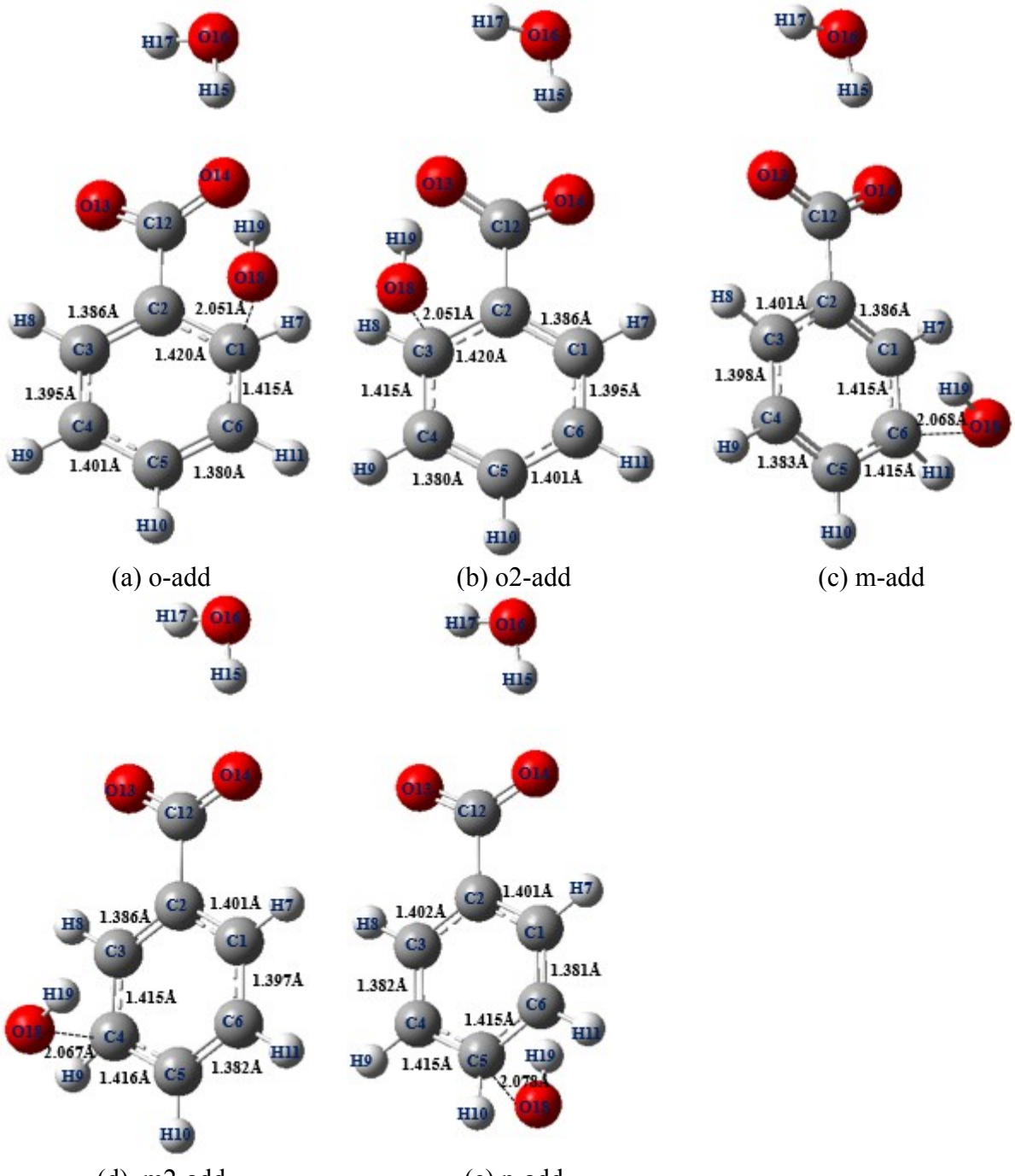


Fig. S8 Transitions states with one explicit water molecule (Benzoate aqueous phase)

Table S1. Relative energy (Re: Kcal/mol) to isolated reactants for benzoic acid reacting with OH radicals in the gas phase.

Species	Re	Species	Re
o-add pre-reactant complexes	-2.85	m2-add pre-reactant complexes	-3.04
o-add transition states	3.30	m2-add transition states	2.56
o-add adducts	-18.92	m2-add adducts	-15.88
o2-add pre-reactant complexes	-5.46	p-add pre-reactant complexes	-3.15
o2-add transition states	2.75	p-add transition states	2.38
o2-add adducts	-20.34	p-add adducts	-16.91
m-add pre-reactant complexes	-3.17	H-abs pre-reactant complexes	-2.87
m-add transition states	2.40	H-abs transition states	3.90
m-add adducts	-16.15	H-abs adducts	-11.67

Table S2. Relative energy (Re: Kcal/mol) to isolated reactants for benzoic acid reacting with OH radicals in the aqueous phase.

Species	Re	Species	Re
o-add pre-reactant complexes	-0.56	m2-add pre-reactant complexes	-1.99
o-add transition states	2.59	m2-add transition states	2.11
o-add adducts	-17.83	m2-add adducts	-14.75
o2-add pre-reactant complexes	-2.61	p-add pre-reactant complexes	-2.02
o2-add transition states	2.39	p-add transition states	2.46
o2-add adducts	-18.30	p-add adducts	-18.03
m-add pre-reactant complexes	-2.02	H-abs pre-reactant complexes	-2.87
m-add transition states	1.97	H-abs transition states	4.27
m-add adducts	-14.83	H-abs adducts	-2.99

Table S3. Relative energy (Re: Kcal/mol) to isolated reactants for benzoate reacting with OH radicals in the aqueous phase.

Species	Re	Species	Re
o-add pre-reactant complexes	-5.80	p-add pre-reactant complexes	-2.08
o-add transition states	0.15	p-add transition states	1.04
o-add adducts	-18.43	p-add adducts	-17.27
m-add pre-reactant complexes	-2.20		
m-add transition states	1.02		
m-add adducts	-15.2		

Table S4. The $<S^2>$ values for open-shell systems for benzoic acid reacting with OH radicals in the gas phase.

Species	$<S^2>$	Species	$<S^2>$
o-add pre-reactant complexes	0.7528	m2-add pre-reactant complexes	0.7532
o-add transition states	0.7866	m2-add transition states	0.7840
o-add adducts	0.7850	m2-add adducts	0.7875
o2-add pre-reactant complexes	0.7527	p-add pre-reactant complexes	0.7532
o2-add transition states	0.7871	p-add transition states	0.7861
o2-add adducts	0.7841	p-add adducts	0.7796
m-add pre-reactant complexes	0.7532	H-abs pre-reactant complexes	0.7528
m-add transition states	0.7839	H-abs transition states	0.7596
m-add adducts	0.7866	H-abs adducts	0.7598

Table S5. The $<S^2>$ values for open-shell systems for benzoic acid reacting with OH radicals in the aqueous phase.

Species	$<S^2>$	Species	$<S^2>$
o-add pre-reactant complexes	0.7527	m2-add pre-reactant complexes	0.7535
o-add transition states	0.7817	m2-add transition states	0.7797
o-add adducts	0.7830	m2-add adducts	0.7877
o2-add pre-reactant complexes	0.7527	p-add pre-reactant complexes	0.7535
o2-add transition states	0.7817	p-add transition states	0.7824
o2-add adducts	0.7827	p-add adducts	0.7783
m-add pre-reactant complexes	0.7535	H-abs pre-reactant complexes	0.7533
m-add transition states	0.7796	H-abs transition states	0.7592
m-add adducts	0.7871	H-abs transition states	0.7597

Table S6. The $<S^2>$ values for open-shell systems for benzoate reacting with OH radicals in the aqueous phase.

Species	$<S^2>$	Species	$<S^2>$
o-add pre-reactant complexes	0.7529	p-add pre-reactant complexes	0.7538
o-add transition states	0.7802	p-add transition states	0.7784
o-add adducts	0.7834	p-add adducts	0.7789
m-add pre-reactant complexes	0.7538		
m-add transition states	0.7777		
m-add adducts	0.7844		

Table S7. Reaction rate constants of benzoic acid (BA) and benzoate (BZ) with hydroxyl radical.

Reaction path	BA gas phase (cm^3 $molecule^{-1}$ s^{-1})	BA aqueous phase ($M^{-1}s^{-1}$)	BZ aqueous phase ($M^{-1}s^{-1}$)
o-add	5.21×10^{-17}	1.68×10^{3}	5.98×10^{4}
o2-add	9.25×10^{-17}	1.32×10^{3}	5.98×10^{4}
m-add	2.01×10^{-16}	2.81×10^{3}	1.17×10^{4}
m2-add	1.44×10^{-16}	1.61×10^{3}	1.17×10^{4}
p-add	2.10×10^{-16}	2.11×10^{3}	1.10×10^{4}
H-abs	9.41×10^{-18}	2.14×10^{-1}	