Supplementary Materials: Theoretical Calculation on the Reaction Mechanisms, Kinetics and Toxicity of Acetaminophen Degradation Initiated by Hydroxyl and Sulfate Radicals in the Aqueous Phase

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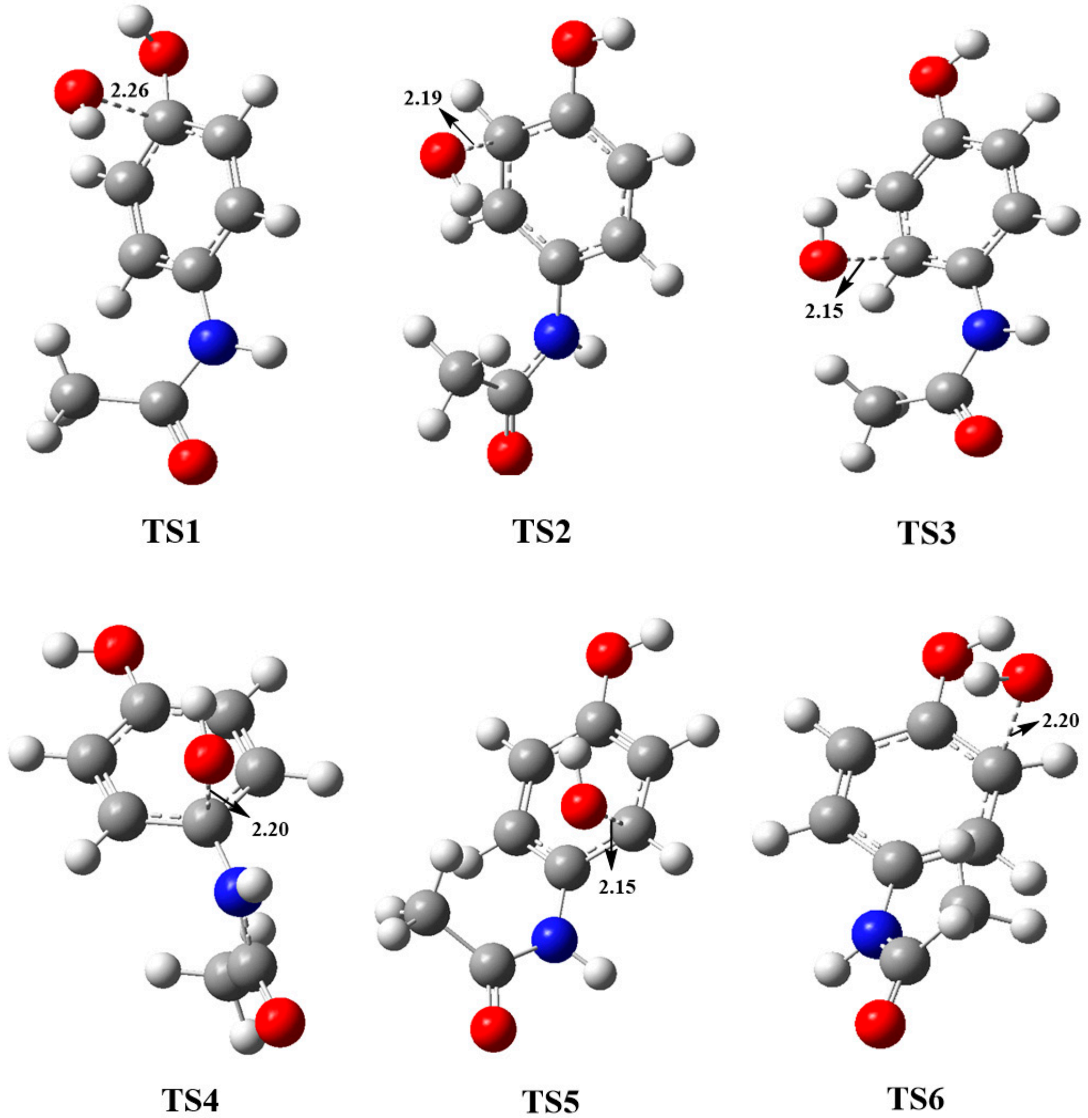

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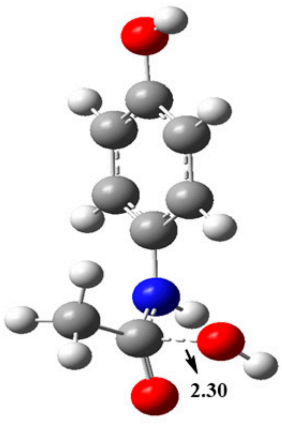

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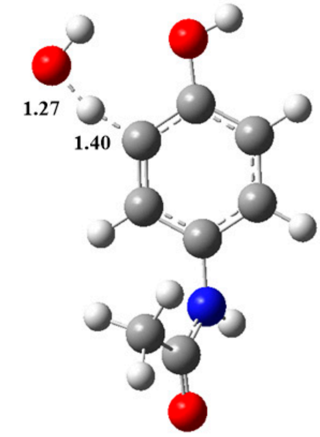

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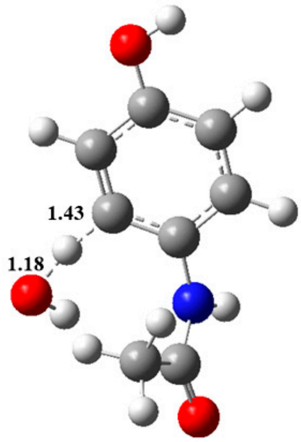

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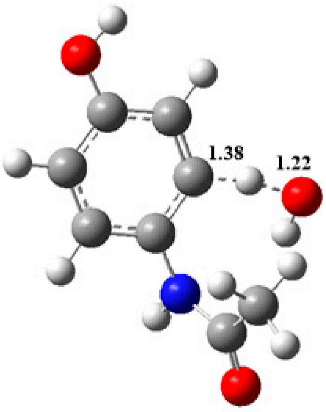

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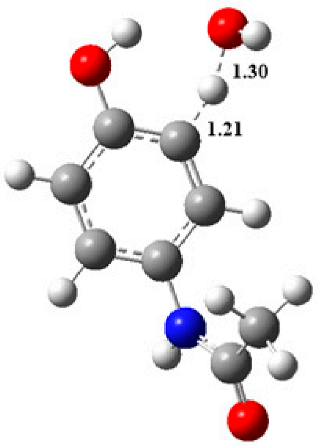

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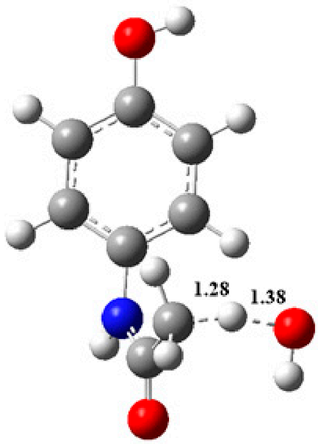

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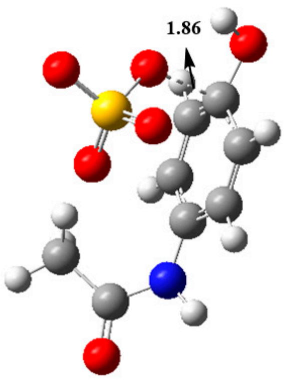

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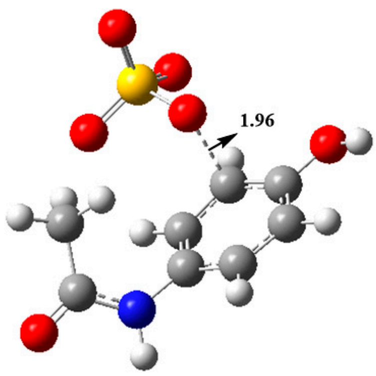

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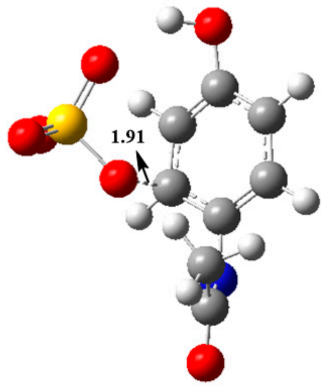

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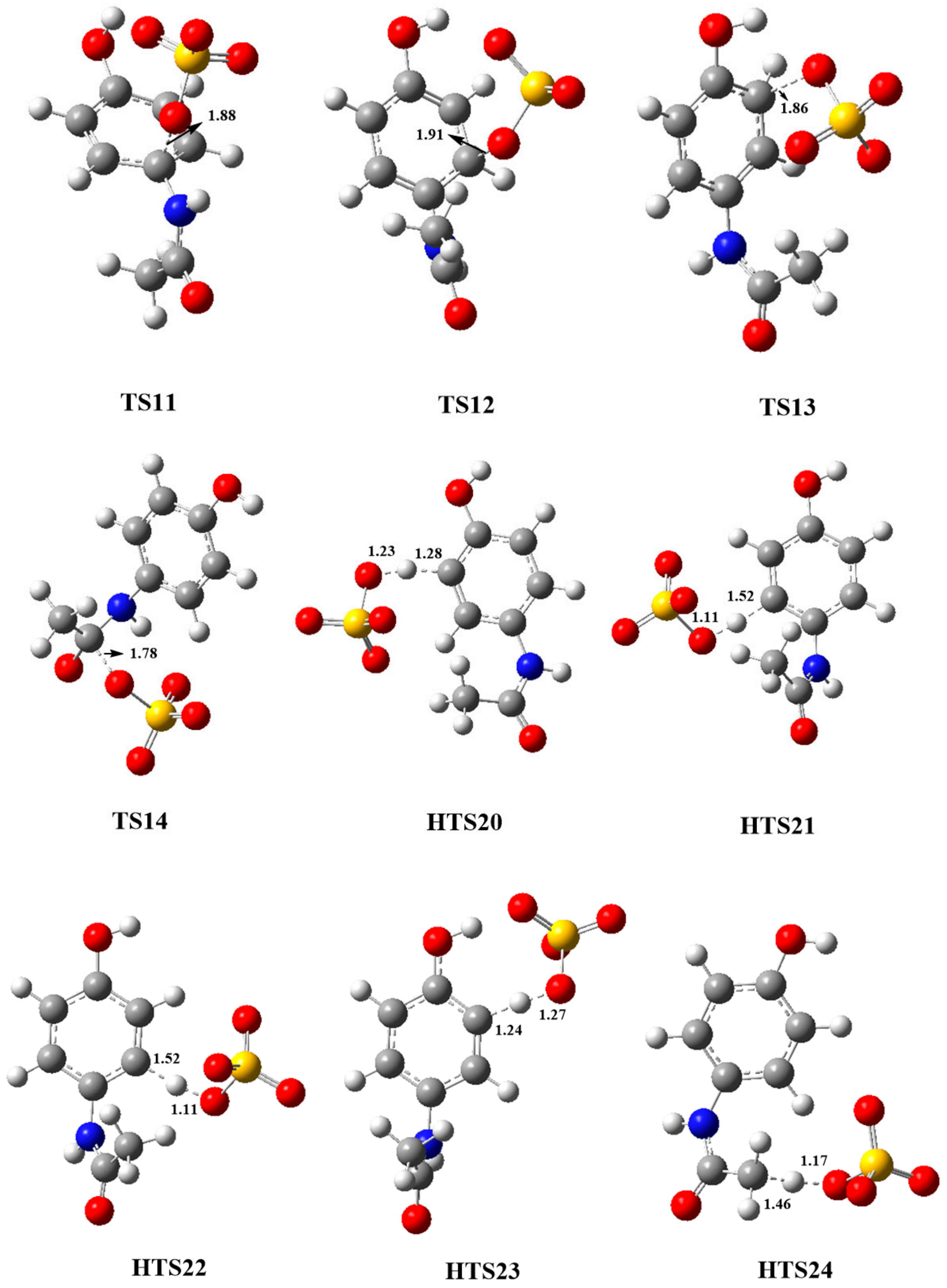

Figure S1. Optimized geometries involving the transition states of AAP with •OH and $SO_4^{\bullet-}$ at the M06-2X/6-31+G(d,p) level. Here, =H =C =O =S =N.

Table S1. Calculated rate constants of AAP with •OH from 198 to 338 K and 1 atm.

Paths	**198**	**218**	**238**	**258**	**278**	**298**	**318**	**338**
Path1	8.04E+07	9.44E+07	8.82E+07	8.42E+07	8.17E+07	8.04E+07	7.99E+07	8.00E+07
Path2	1.87E+08	2.49E+08	2.24E+08	2.07E+08	1.95E+08	1.87E+08	1.82E+08	1.79E+08
Path3	1.51E+07	1.25E+07	1.30E+07	1.36E+07	1.43E+07	1.51E+07	1.59E+07	1.68E+07
Path4	3.22E+08	5.08E+08	4.32E+08	3.81E+08	3.46E+08	3.22E+08	3.04E+08	2.92E+08
Path5	3.33E+07	3.51E+07	3.40E+07	3.34E+07	3.32E+07	3.33E+07	3.36E+07	3.41E+07
Path6	9.02E+09	7.84E+09	6.01E+09	4.86E+09	4.10E+09	3.56E+09	3.18E+09	2.90E+09
Path7	6.75E+02	2.04E+01	6.00E+01	1.51E+02	3.36E+02	6.75E+02	1.25E+03	2.17E+03
Path15	7.36E-04	7.95E-03	5.80E-02	3.14E-01	1.34E+00	4.75E+00	1.44E+01	3.88E+01
Path16	4.40E-03	3.55E-02	2.03E-01	8.95E-01	3.21E+00	9.75E+00	2.60E+01	6.20E+01
Path17	4.51E-04	4.36E-03	2.89E-02	1.44E-01	5.74E-01	1.91E+00	5.51E+00	1.41E+01
Path18	1.28E+02	4.16E+02	1.11E+03	2.57E+03	5.30E+03	1.15E+04	1.75E+04	2.89E+04
Path19	9.61E+01	3.51E+02	1.03E+03	2.59E+03	5.73E+03	1.13E+04	2.11E+04	3.65E+04
$k_{total\text{-}aq}$	9.65E+09	8.74E+09	6.80E+09	5.58E+09	4.77E+09	4.20E+09	3.80E+09	3.51E+09

Table S2. Calculated rate constants of AAP with $SO_4^{\bullet-}$ from 198 to 338 K and 1 atm.

Paths	**198**	**218**	**238**	**258**	**278**	**298**	**318**	**338**
Path8	9.43E+16	6.50E+15	7.13E+14	1.12E+14	2.32E+13	6.00E+12	1.86E+12	6.67E+11
Path9	2.08E+14	2.85E+13	5.53E+12	1.40E+12	4.37E+11	1.61E+11	6.78E+10	3.19E+10
Path10	1.76E+14	2.87E+13	6.44E+12	1.85E+12	6.43E+11	2.60E+11	1.19E+11	6.04E+10
Path11	2.14E+13	3.50E+12	7.92E+11	2.29E+11	8.03E+10	3.28E+10	1.51E+10	7.74E+09
Path12	1.70E+14	2.78E+13	6.24E+12	1.79E+12	6.23E+11	2.52E+11	1.16E+11	5.85E+10
Path13	5.65E+18	2.66E+17	2.12E+16	2.53E+15	4.13E+14	8.65E+13	2.22E+13	6.76E+12
Path14	1.46E-11	3.47E-10	4.91E-09	4.67E-08	3.26E-07	1.77E-06	7.86E-06	2.95E-05
Path20	3.98E-02	1.93E-01	7.25E-01	2.25E+00	6.02E+00	1.43E+01	3.07E+01	6.10E+01
Path21	1.18E+00	4.02E+00	1.12E+01	2.69E+01	5.75E+01	1.11E+02	2.00E+02	3.37E+02
Path22	2.81E+00	8.72E+00	2.25E+01	5.06E+01	1.02E+02	1.88E+02	3.23E+02	5.24E+02
Path23	1.70E-02	8.03E-02	2.96E-01	9.03E-01	2.38E+00	5.55E+00	1.18E+01	2.31E+01
Path24	4.59E+09	1.71E+09	7.59E+08	3.84E+08	2.16E+08	1.33E+08	8.70E+07	6.05E+07
$k_{total\text{-}aq}$	5.74E+18	2.73E+17	2.19E+16	2.65E+15	4.38E+14	9.32E+13	2.44E+13	7.59E+12

Table S3. The acute and chronic toxicity class (mg L^{-1}).

Classification	**Acute toxicity**[1]	**Chronic toxicity**[2]
Not harmful	LC_{50}>100 or EC_{50}>100	ChV>10
Harmful	10< LC_{50} <100 or 10< EC_{50} <100	1< ChV <10
Toxic	1< LC_{50} <10 or 1< EC_{50} <10	0.1< ChV <1
Very toxic	LC_{50}<1 or EC_{50}<1	ChV<0.1

[1]Criteria set by the European Union (described in Annex VI of Directive 67/548/EEC);.
[2]Criteria set by the Chinese hazard evaluation guidelines for new chemical substances (HJ/T 154–2004).

Table S4. Eco-toxicity values of AAP and its transformation intermediates to aquatic organisms (mg L^{-1}).

		AAP	**IM1**	**IM13**	**IM8**	**IM6**
Acute Toxicity	Fish (LC_{50})	323	7.08	186	120	21.4
	Daphnia (LC_{50})	63.1	21.4	933	562	77.6
	Green algae (EC_{50})	26.3	3.47	0.73	34.7	64.6
Chronic Toxicity (ChV)	Fish	26.3	5.50	6.2×10^3	2.0×10^3	64.6
	Daphnia	5.13	1.95	602	269	14.8
	Green algae	37.2	5.50	692	347	29.5