Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

A new theoretical investigation on ·OH initiated oxidation of Acephate in the environment: mechanism, kinetic, and toxicity

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Table S1. The relative energy (*ΔE*), reaction enthalpy (*ΔH*), Gibbs free energy (*ΔG*), and Gibbs free energy corrections (G_{corre}) for all species in the reaction of acephate with OH radicals in the gas phase at the level of wB97-XD/6-311++G(3df,2pd)//wB97-XD/6-311++G(d,p) (unit is kJ/mol).

Species	wB97XD /6-311++G(d,p)				wB97XD /6-311++G(3df,2pd)	
	Δ*E*	Δ*H*	Δ*G*	G_{corre}	Δ*E*	Δ(*E*+ G_{corre})
R2(Acephate + OH)	0.0	0.0	0.0	270.5	0.0	0.0
A-TSA-1	26.3	20.0	69.1	323.9	19.8	73.2
A-TSB-1	-5.3	-9.3	30.1	301.3	-0.1	30.7
A-TSB-2	-20.7	-26.0	18.1	306.7	-16.9	19.3
A-TSB-3	-20.2	-25.2	17.5	305.5	-17.3	17.6
A-TSB-4	4.5	0.6	43.1	303.6	11.5	44.6
A-TSC-1	62.2	60.0	94.1	303.8	41.1	74.4
A-TSC-2	239.4	236.0	277.1	306.4	243.1	279.0
A-TSC-3	61.8	55.4	104.6	322.6	53.3	105.4
A-TSC-4	118.5	113.2	155.9	316.5	102.6	148.6
A-TSC-5	106.4	100.3	148.4	322.0	97.5	149.0
A-TSC-6	24.7	18.6	66.8	323.8	14.4	67.7
A-PA-1	-29.0	-35.7	14.1	331.3	-43.0	17.8
A-PB-1(A-im1+H_2O)	-78.2	-77.7	-79.3	267.9	-82.0	-84.6
A-PB-2(A-im2+H_2O)	-73.3	-71.9	-77.1	262.7	-74.6	-82.4
A-PB-3(A-im3+H_2O)	-83.2	-81.5	-87.1	262.8	-88.6	-96.4
A-PB-4(A-im4+H_2O)	-37.9	-36.4	-42.5	263.7	-43.5	-50.4
A-PC-1(A-im5+CH_3)	51.3	52.3	47.8	259.7	36.8	26.0
A-PC-2(A-im6+CH_3)	190.2	189.2	190.7	264.2	190.7	184.4
A-PC-3(A-im7+HAc)	-46.3	-49.7	-59.8	261.6	-60.2	-69.1
A-PC-4(A-im8+ A-im9)	-48.9	-52.2	-61.8	259.4	-67.8	-79.0
A-PC-5(A-im6+CH_3O·)	-72.7	-76.4	-81.2	262.4	-76.3	-84.4
A-PC-6(A-im6+CH_3S·)	-162.9	-166.9	-171.3	268.8	-185.5	-187.3

Table S2. The Gibbs free energy (G_{aq}) and solubility energy (ΔG_{solv}) for the reaction of acephate with OH radicals in the aqueous phase. (unit in kJ/mol)

Species	M05-2X/6-31g(d)			
	$E_{sp(gas)}$	$E_{sp(solv)}$	ΔG_{solv}	G_{aq}[1] (298K)
R2(Acephate + OH)	0.0	0.0	0.0	0.0
A-TSA-1	5.8	24.0	18.2	83.4
A-TSB-1	13.0	25.2	12.2	34.9
A-TSB-2	-9.9	9.9	19.9	31.2
A-TSB-3	-8.3	12.3	20.6	30.3
A-TSB-4	16.8	48.5	31.8	68.4
A-TSC-1	47.8	51.5	3.7	70.1
A-TSC-2	238.6	263.2	24.6	295.7
A-TSC-3	37.5	56.8	19.2	116.8
A-TSC-4	95.7	99.4	3.7	144.3
A-TSC-5	82.5	80.3	-2.2	138.7
A-TSC-6	4.0	33.5	29.5	89.3
A-PA-1	-73.4	-50.9	22.5	32.4
A-PB-1(A-im1+H_2O)	-54.3	-68.1	-13.7	-106.2
A-PB-2(A-im2+H_2O)	-43.4	-47.5	-4.1	-94.4
A-PB-3(A-im3+H_2O)	-52.6	-56.5	-3.9	-108.2
A-PB-4(A-im4+H_2O)	-15.8	-9.7	6.1	-52.2
A-PC-1(A-im5+CH_3)	57.8	69.7	12.0	30.1
A-PC-2(A-im6+CH_3)	191.9	224.5	32.6	209.1
A-PC-3(A-im7+HAc)	-54.2	-40.0	14.1	-62.8
A-PC-4(A-im8+ A-im9)	-61.6	-51.3	10.2	-76.7
A-PC-5(A-im6+$CH_3O\cdot$)	-71.0	-56.5	14.6	-77.8
A-PC-6(A-im6+$CH_3S\cdot$)	-187.1	-178.6	8.5	-186.7

[1]G_{aq}: Gibbs free energy of a solute in an aqueous solution can be calculated as follows: G_{aq} (298K) = G_{corre} + E_{SP} + ΔG_{solv} + 7.921(ΔG_{1M}(298K)), and Gcorre is the Gibbs free energy corrected value of the structure optimized in the gas phase. E_{SP} is the single-point energy of a well optimized structure in the gas phase. $E_{sp(gas)}$ and $E_{sp(solv)}$ is calculated at M05-2X/6-31g(d) theory level. $\Delta G_{solv} = E_{sp(gas)} - E_{sp(solv)}$; $V_m = \frac{RT}{P}$; $\Delta G_{1M}(298K) = RT\ln V_m = 7.921$

Table S3. The relative energy (*ΔE*), reaction enthalpy (*ΔH*), Gibbs free energy (*ΔG*), and Gibbs free energy corrections (G_{corre}) for the subsequent reactions of A-im2 and A-im3 at wB97-XD/6-311++G(3df,2pd)//wB97-XD/6-311++G(d,p) levels of theory (unit in kJ/mol).

Species	wB97XD /6-311++G(d,p)				wB97XD /6-311++G(3df,2pd)	
	ΔE	ΔH	ΔG	G_{corre}	ΔE	$\Delta(E+ G_{corre})$
(A-im2 + O_2+NO)	0.0	0.0	0.0	169.6	0.0	0.0
A-im2-1	-132.6	-137.1	-90.6	230.9	-154.2	-92.8
A-im2-2	-205.2	-213.2	-116.6	287.9	-242.4	-124.1
A-im2-3+ NO_2	-221.8	-227.8	-181.8	224.3	-241.1	-186.3
A-im2-4+ HCHO	-174.7	-178.0	-177.5	171.9	-189.3	-187.0
A-im2-TS	-83.1	-88.1	-42.8	218.8	-48.2	0.9
(A-im3 + O_2+NO)	0.0	0.0	0.0	169.7	0.0	0.0
A-im3-1	-5.7	-10.5	39.6	233.0	-106.9	-43.5
A-im3-2	-183.6	-192.1	-92.0	248.3	-217.0	-95.4
A-im3-3+ NO_2	-175.9	-181.9	-136.1	224.6	-190.0	-135.1
A-im3-4+ HCHO	-182.8	-185.8	-187.8	172.6	-189.8	-186.9
A-im3-TS	-146.7	-152.5	-106.8	223.6	-160.2	-106.3

Table S4. The acute and chronic toxicity class (mg L^{-1}).

Classification	Acute toxicity[2]	Chronic toxicity[3]
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

[2]Criteria set by the European Union (described in Annex VI of Directive 67/548/EEC);

[3]Criteria set by the Chinese hazard evaluation guidelines for new chemical substances (HJ/T 154–2004).

Table S5a. The k^{TST} and Wigner tunneling correction of factor (X) of the dominant channels in the reaction of acephate with OH radicals at 1 atm and 298-1500 K in the gas phase.

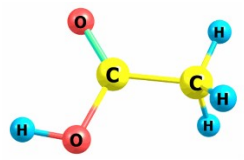
pathway	k^{TST} (cm^3 $molecule^{-1}$ $\cdot s^{-1}$)	X	T (K)
acephate +OH→A-PB-1 (k^{TST}_{B}-1)	1.34×10^{-12}	1.65	298
	9.46×10^{-13}	1.29	400
	8.64×10^{-13}	1.23	500
	1.08×10^{-12}	1.09	800
	1.42×10^{-12}	1.06	1000
	2.81×10^{-12}	1.03	1500
acephate +OH→A-PB-2 (k^{TST}_{B}-2)	1.73×10^{-10}	2.00	298
	2.15×10^{-11}	1.56	400
	7.05×10^{-12}	1.36	500
	1.89×10^{-12}	1.14	800
	1.48×10^{-12}	1.09	1000
	1.47×10^{-12}	1.04	1500
acephate +OH→A-PB-3 (k^{TST}_{B}-3)	2.23×10^{-10}	1.97	298
	3.03×10^{-11}	1.54	400
	1.05×10^{-11}	134	500
	3.01×10^{-12}	1.13	800
	2.41×10^{-12}	1.09	1000
	2.45×10^{-12}	1.04	1500
acephate +OH→A-PB-4 (k^{TST}_{B}-4)	7.08×10^{-15}	4.00	298
	1.39×10^{-14}	2.66	400
	2.29×10^{-14}	2.07	500
	6.92×10^{-14}	1.42	800
	1.21×10^{-13}	1.27	1000
	3.50×10^{-13}	1.12	1500

Table S5b. The k'^{TST} and Wigner tunneling correction factor (X') of the dominant channels in the reaction of acephate with OH radicals at 1 atm and 278-348 K in the aqueous phase.

pathway	k'^{TST} (cm^3 $molecule^{-1}$ $\cdot s^{-1}$)	X'	T (K)
acephate +OH→A-PB-1 ($k'^{TST}_{B\text{-}1}$)	3.11×10^{-14}	1.97	298
	2.72×10^{-14}	2.11	278
	2.91×10^{-14}	2.04	288
	3.31×10^{-14}	1.91	308
	3.52×10^{-14}	1.85	318
	3.73×10^{-14}	1.80	328
	3.95×10^{-14}	1.75	338
	4.17×10^{-14}	1.71	348
acephate +OH→A-PB-2 ($k'^{TST}_{B\text{-}2}$)	3.18×10^{-13}	1.73	298
	3.56×10^{-13}	1.84	278
	3.36×10^{-13}	1.78	288
	3.03×10^{-13}	1.68	308
	2.90×10^{-13}	1.64	318
	2.79×10^{-13}	1.60	328
	2.68×10^{-13}	1.57	338
	1.53×10^{-13}	1.53	348
acephate +OH→A-PB-3 ($k'^{TST}_{B\text{-}3}$)	6.60×10^{-13}	1.84	298
	8.01×10^{-13}	1.97	278
	7.24×10^{-13}	1.90	288
	6.06×10^{-13}	1.79	308
	5.60×10^{-13}	1.74	318
	5.21×10^{-13}	1.70	328
	4.88×10^{-13}	1.66	338
	4.59×10^{-13}	1.60	348

Table S6. Hodge and Sterner Toxicity Scale

Toxicity rating	**Commonly used term**	**LD_{50} (mg/Kg)**
1	Extremely Toxic	Less than 1 mg/Kg
2	Highly Toxic	1-50
3	Moderately Toxic	50-500
4	Slightly Toxic	500-5000
5	Practically non-Toxic	5000-15000



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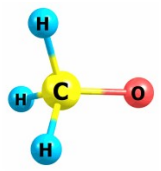
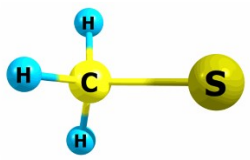
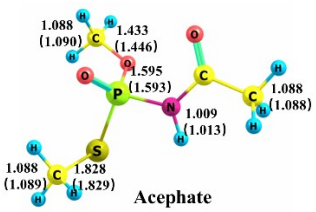


OCH_3



SCH_3



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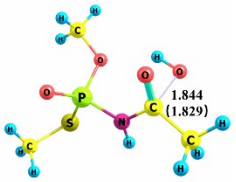

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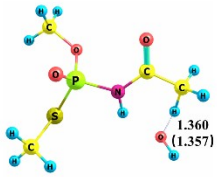

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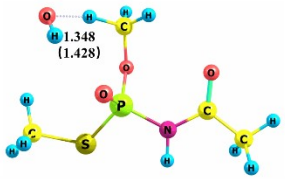

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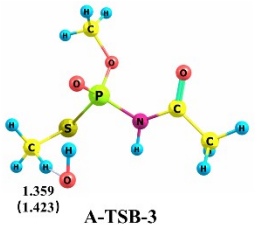

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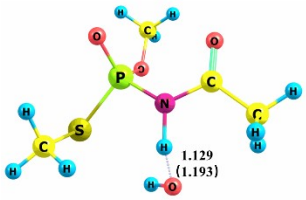

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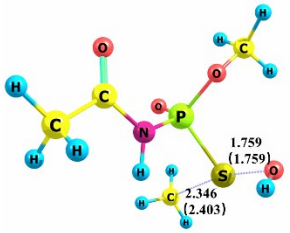

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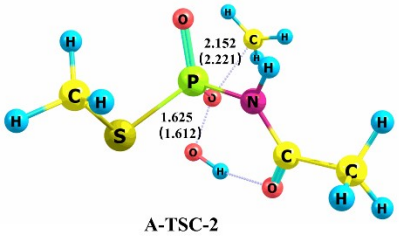

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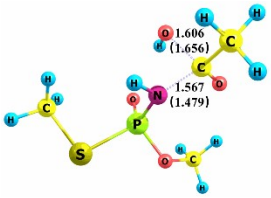

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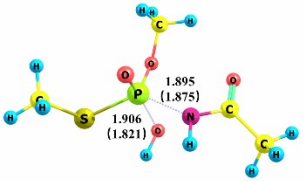

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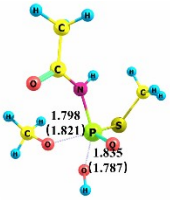

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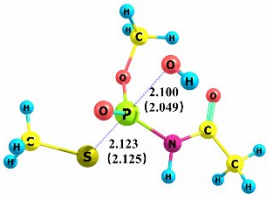

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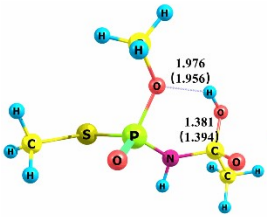

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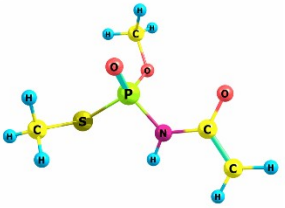

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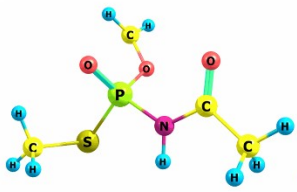

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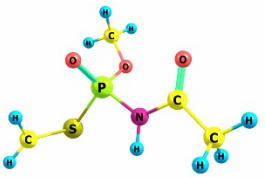

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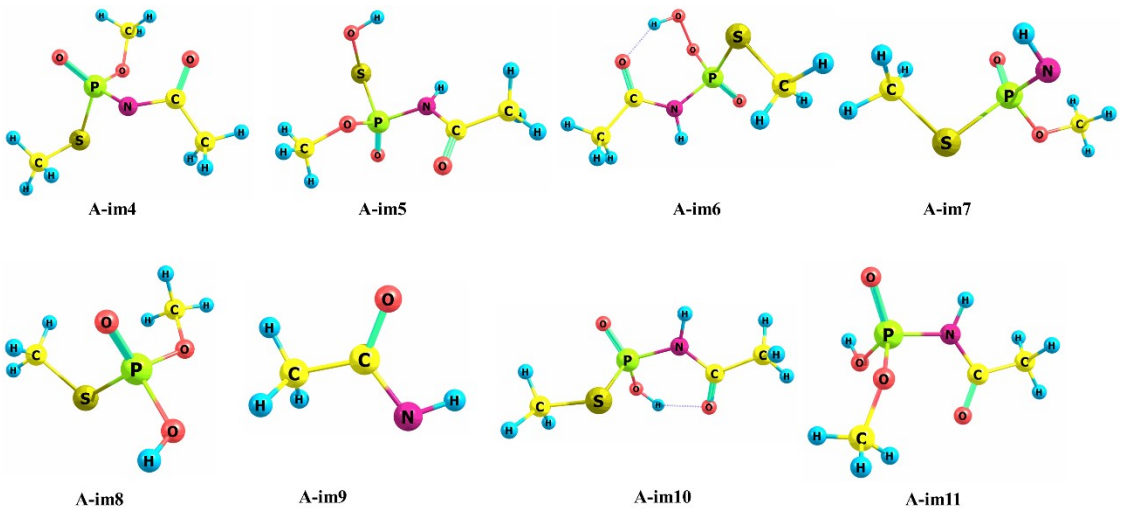

Figure S1. Geometrical parameters of each species in the title reaction in gas and aqueous phase obtained at the wB97-XD/6-311++G(d,p) levels of theory. The upper values are in the gas phase and the lower ones are in the aqueous phase. (bond lengths in ° and bond angles in Å)

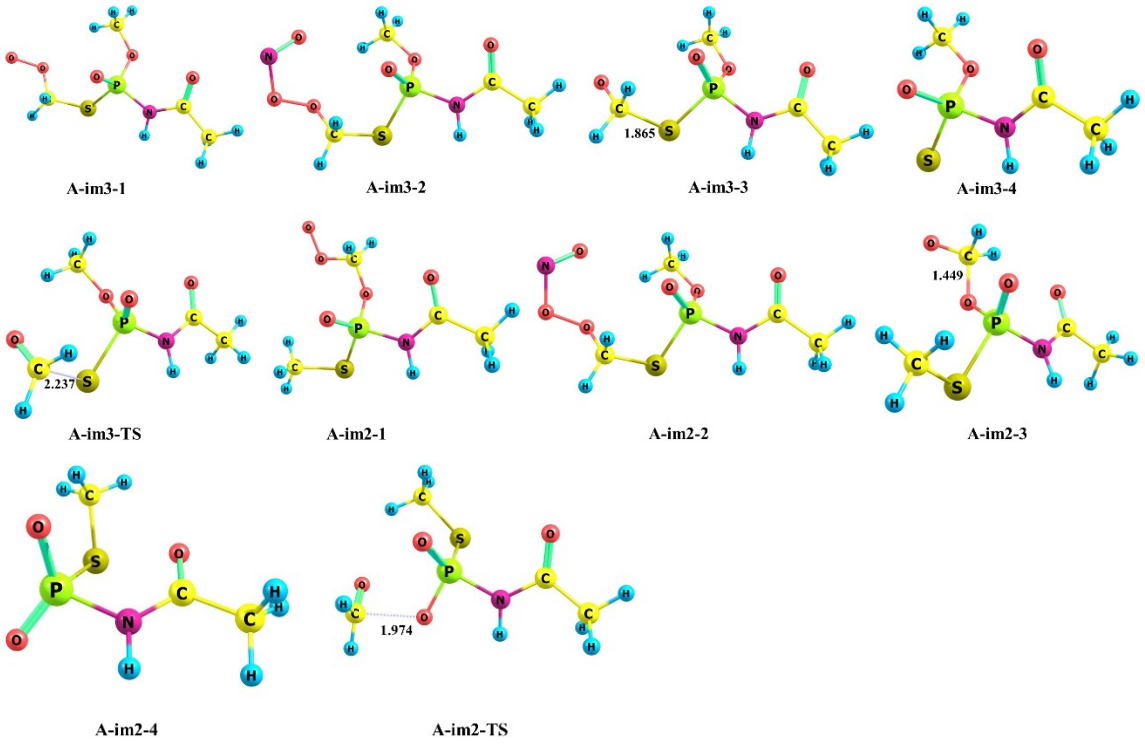

Figure S2. Geometrical parameters of each species in the subsequent reactions of A-im2 and A-im3 obtained at the wB97-XD/6-311++G(d,p) levels of theory (bond lengths in Å and bond angles in °)

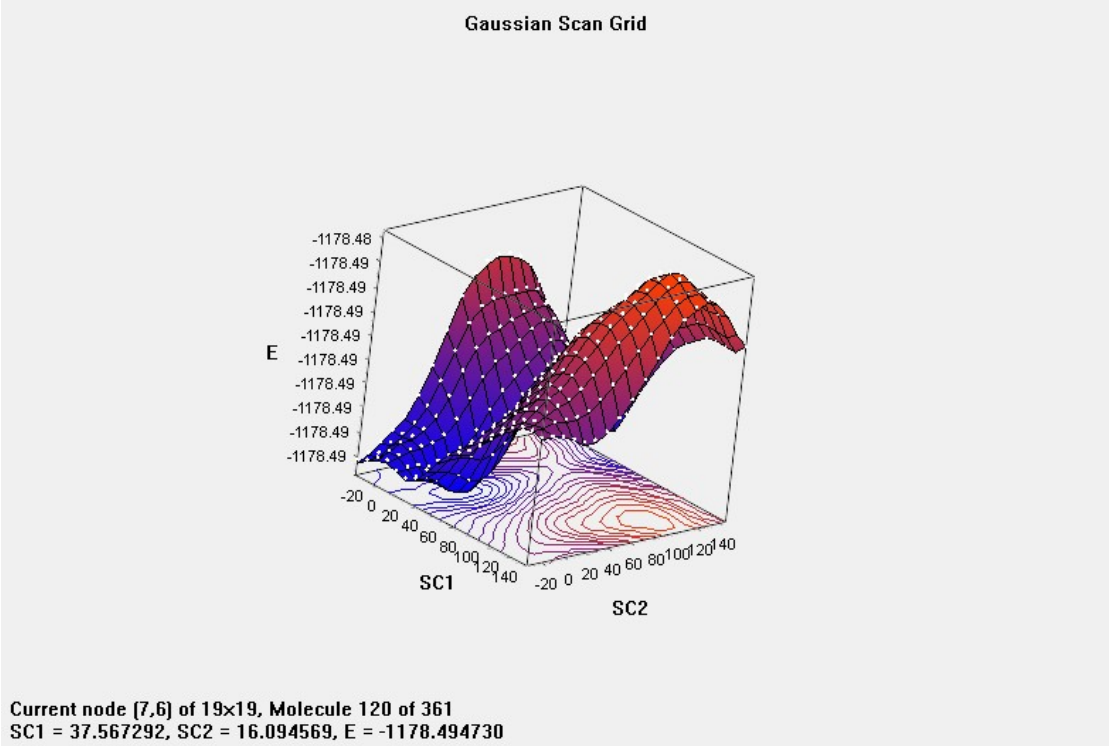

Figure S3. Scan of the two rotatable dihedral angles in acephate (i.e. COPO and CSPO)