Hydroxyl radical generation in peroxymonocarbonate/Co^{2+} systems: kinetic and mechanistic insights

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SI.1. Quantum yield (QY) determination of hTA

Quinine sulfate, which exhibits absorbance and emission spectrum similar to those of hTA, was used as the reference for QY determination of hTA. The QY of hTA was calculated according to the following equation:

$$\Phi_{hTA} = \Phi_{Quinine\_sulfate} \times \frac{Grad_{hTA}}{Grad_{Quinine\_sulfate}} \times \frac{\eta^2_{hTA}}{\eta^2_{Quinine\_sulfate}}$$

where Φ is QY, Grad is the gradient of the linear regression (R^2>0.99) of the concentration and fluorescence intensity (FI), η is the refractive index of the solution solvent. QY of quinine sulfate is 54% (reported in the literature). The Grad values were obtained experimentally by plotting FI *vs.* absorbance for five solutions of quinine sulfate and hTA.

The QY of hTA is 63% as the (Grad, R^2) for hTA and quinine sulfate are (3.9 x 10^8, 0.9939) and (3.4 x 10^8, 0.9942), respectively (Figure S1).

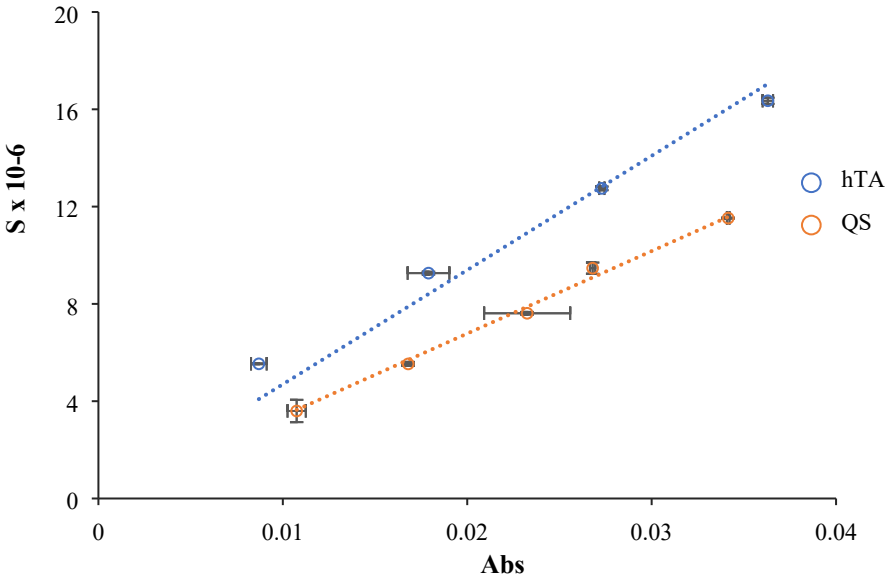

Figure S1. Dependence of fluorescence peak area on the absorbance of hTA and QS solutions.

SI.2. Calibration curve for hTA quantification

SI.2.1. Establishment of a calibration curve

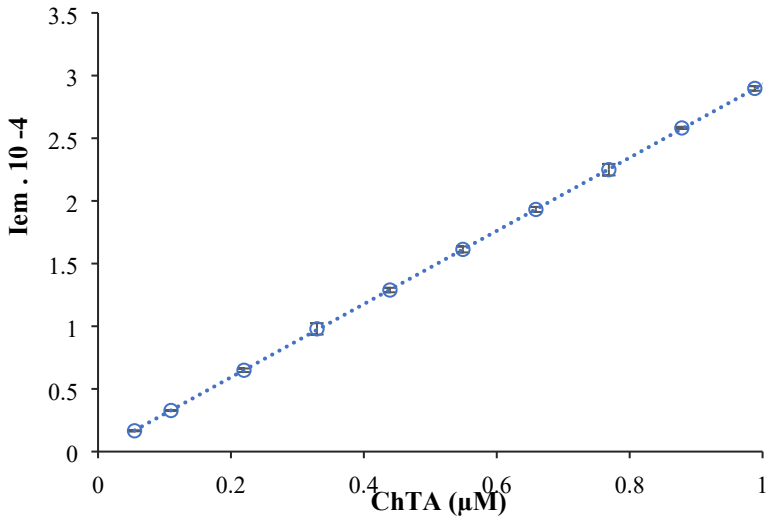

Figure S2. hTA calibration curve.

Linear regression results abtained for a standard equation $I_{em} = a \cdot C_{hTA}$ (µM) + b

a	s_a	b	s_b	s_I	R^2	Freedom degree
29212	42.5	83.526	27.588	47.821	0.99998	9

$$t_{o.5\text{ - calc.}} = \frac{b}{s_b} = 10.04 > 2.26 = t_{0.5\text{ - theory}}(n = 9)$$

Therefore b ≠ 0 is meanningful.

Standrad equation: $\mathbf{I_{em}} = (29212 \pm 96).\ \mathbf{C_{hTA}}$ (µM) + (83.5 ± 62.4).

SI.2.2. Validation of the calibration curve

SI.2.2.1. Experimental determination of LOD, LOQ values

The fluorescence spectra of ten 0.088 µM hTA solutions were recorded, LOD and LOQ values were then calculated by:

$$LOD = 3.SD = 3,\sqrt{\frac{\sum(C_i - \bar{C})^2}{n-1}}\ ;\ LOQ = 10.SD = 10,\sqrt{\frac{\sum(C_i - \bar{C})^2}{n-1}}$$

where $\bar{C}$: average concentration of ten solutions; C_i: concentration of solution i; SD: standard deviation; n: number of measurements.

The results are presented in Table S1.

Table S1. Determination of LOD, LOQ

No.	Nominal concentration of hTA (µM)	I_{em} (AU)	C_{hTA} (µM) calculated from the calibration equation
1	0.088	2589	0.0858
2		2600	0.0861
3		2701	0.0896
4		2606	0.0864
5		2585	0.0857
6		2561	0.0848
7		2505	0.0829
8		2390	0.0893

9		2683	0.0890
10		2629	0.0872
Average ($\overline{C}$)			0.0867
SD			2.13×10^{-3}
LOD			6.4 nM
LOQ			21.3 nM

SI.2.2.2. Precision and accuracy of the calibration equation

The results are presented in Table S2.

Table S2. Measurement of the concentration of various hTA solutions

No.	Low conc. ($C_{nominal}$ = 0.0878 µM)		Medium conc. ($C_{nominal}$ = 0.4392 µM)		High conc. ($C_{nominal}$ = 1.0432 µM)	
	I_{em} (AU)	$C_{calc.}$ (µM)	I_{em} (AU)	$C_{calc.}$ (µM)	I_{em} (AU)	$C_{calc.}$ (µM)
1	2589	0.0858	13204	0.4492	30875	1.0541
2	2600	0.0861	13113	0.4460	31059	1.0604
3	2701	0.0896	12856	0.4373	31061	1.0605
4	2606	0.0864	12755	0.4338	30793	1.0513
5	2585	0.0857	13041	0.4436	30137	1.0288
6	2561	0.0848	12601	0.4285	30132	1.0286
7	2505	0.0829	12824	0.4362	30333	1.0355
8	2690	0.0893	12712	0.4323	30005	1.0243
9	2683	0.0890	12983	0.4416	30449	1.0395
10	2629	0.0872	13095	0.4454	30282	1.0338
Average ($\overline{C}$)		0.0867		0.4394		1.0417

Table S3. Precision and accuracy of the calibration curve

hTA solution	Low conc.	Medium conc.	High conc.
C_{hTA} (µM)	0.0878	0.4392	1.0432
$C_{average}$ (µM)	0.0867	0.4394	1.0417
SD	$2.13.\ 10^{-3}$	$6.78.10^{-3}$	$13.7.10^{-3}$
RSD %	2.45	1.54	1.31
RSD % (AOAC)	21	15	11
Δ%	1.34	0.03	0.15
Δmax% (AOAC)	15		

SI.2.3. •OH formation in different systems

Table S4. hTA formation rate (r) and $[^{\bullet}OH]_{ss}$ at varying TA concentraions (4 mM HCO_3^-, 8 mM H_2O_2, 0.678 µM Co^{2+})

C_{TA} (mM)	C_{TA} (µM)	r (mMs^{-1})	ln(C_{TA})	ln(r)	$[^{\bullet}OH]_{ss}.10^{16}$ (M)
0.006	6	1.38	1.795	0.319	8.66
0.012	12	1.22	2.488	0.201	3.85

0.048	48	4.32	3.874	1.462	3.40
0.072	72	10.07	4.280	2.309	5.28
0.090	90	16.57	4.503	2.808	6.95
0.120	120	20.86	4.791	3.038	6.56
0.150	150	24.75	5.014	3.209	6.23

Table S5. $[^{\bullet}OH]_{ss}$ at varying concentraions of HCO_3^-: H_2O_2 mixture (0.048 mM TA, 0.678 µM Co^{2+})

HCO_3^-: H_2O_2 molar ratio	**Kinetic equation**	**R^2**	$k_2''.10^3$	**$[^{\bullet}OH]_{ss}.10^{16}$, M**
0.4 : 1 (mM)	$C_{hTA} = (0.892t + 8.83).10^{-3}$	0.9934	0.892	0.70
1 : 2.5 (mM)	$C_{hTA} = (1.708t + 6.23).10^{-3}$	0.9948	1.708	1.34
2 : 5 (mM)	$C_{hTA} = (3.108t - 0.12).10^{-3}$	0.9950	3.108	2.44
4 : 10 (mM)	$C_{hTA} = (4.317t + 25.5).10^{-3}$	0.9997	4.317	3.39
6 : 15 (mM)	$C_{hTA} = (5.400t + 7.21).10^{-3}$	0.9991	5.400	4.25
8 : 10 (mM)	$C_{hTA}=(6.547t + 8.83).10^{-3}$	0.9993	6.547	5.15

Table S6. $[^{\bullet}OH]_{ss}$ at varying Co^{2+}concentraions (0.048 mM TA, 4 mM HCO_3^-, 10 mM H_2O_2)

$C_{Co^{2+}}$ (µM)	**Kinetic equation**	**R^2**	$k_2''.10^3$	**$[^{\bullet}OH]_{ss}.10^{16}$ (M)**
0.170	$C_{hTA} = (1.387t + 24.2).10^{-3}$	0.9840	1.387	1.09
0.339	$C_{hTA} = (1.659t + 19.2). 10^{-3}$	0.9852	1.659	1.31
0.679	$C_{hTA} = (4.317t + 25.5). 10\text{-}3$	0.9997	4.317	3.40
1.358	$C_{hTA} = (6.026t + 8.21). 10^{-3}$	0.9993	6.026	4.74
1.697	$C_{hTA} = (9.664t + 4.93). 10^{-3}$	0.9929	9.664	7.60
3.394	$C_{hTA} = (20.89t -7.62). 10^{-3}$	0.9962	20.886	16.43