Supporting Information

Overlooked Role of Peroxides as Free Radical Precursors in Advanced Oxidation Processes

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This file contains 1 scheme, 6 figures, 5 tables and 25 references.

Scheme Figure and Table Captions

Scheme S1. The reactions of bromine with ·OH and equilibrium speciation of bromine species. Arrow thickness represents the relative significance of each reaction, based on the kinetic modeling results.

Figure S1. Effect of H_2O_2 on photo-reduction of bromate.

Figure S2. UV spectra of BrO_3^- and H_2O_2 and the spectral irradiance of the light source.

Figure S3. Effect of PMS on the photo-reduction of bromate (0.2 mM).

Figure S4. The evolution of dissolved oxygen (DO) under UV and UV/H_2O_2 in the presence or absence of BrO_3^-.

Figure S5. Production of HTPA during UV irradiation.

Figure S6. Mass balance of iodine during exposure to UV (open symbol) and UV/H_2O_2 (solid symbol) processes.

Table S1. Photochemical reactions and equilibrium speciation of H_2O_2.

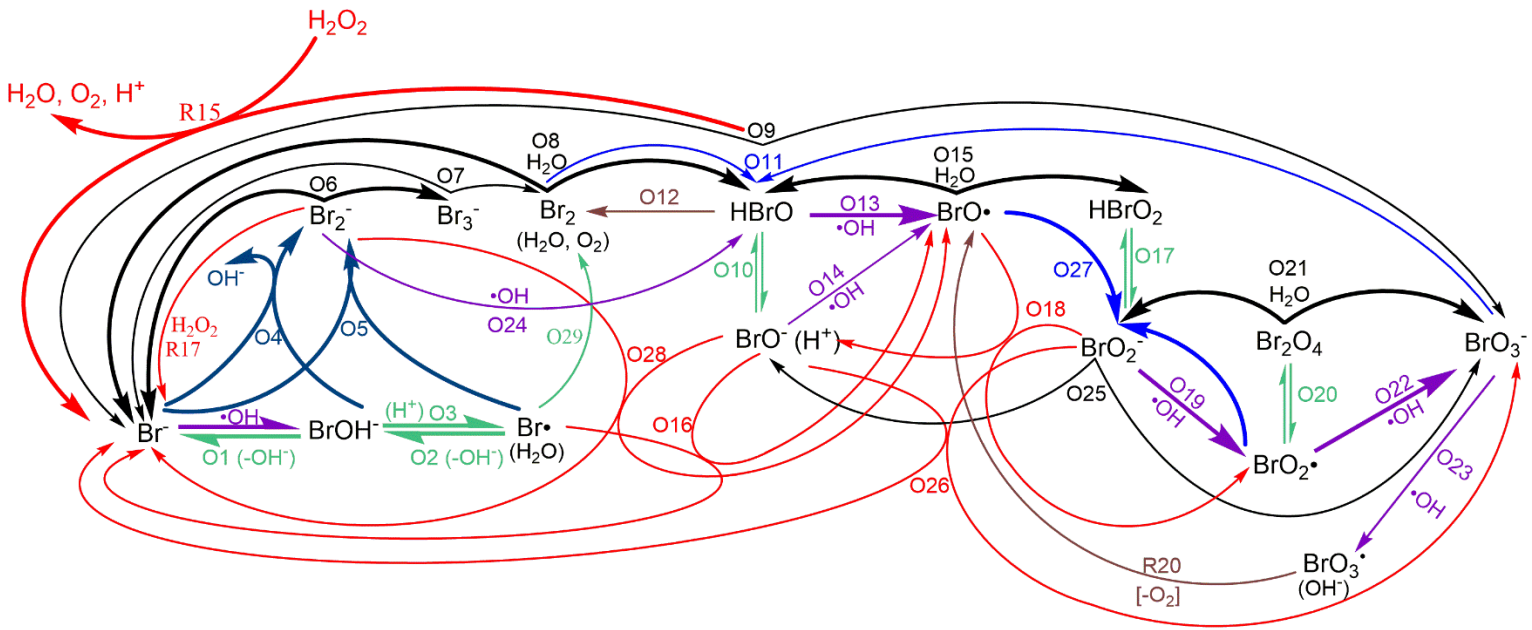
Table S2. Possible reactions of bromine with ·OH and equilibrium speciation reactions involving bromine that are relevant to the oxidation of bromide.

Table S3. Possible reactions involved in the photolytic reduction process of bromate in the absence and presence of H_2O_2.

Table S4. Rate constants (k_1) for H_2O_2 (0.5 mM) and BrO_3^- (0.2 mM) decomposition under different aeration conditions.

Table S5. Some physicochemical properties of bromate and iodate.

Scheme S1. The reactions of bromine with ·OH and equilibrium speciation of bromine species. Arrow thickness represents the relative significance of each reaction, based on the kinetic modeling results. Labels (letter/number) refer to individual reactions identified in Table S2 and S3.



Black: disproportionation (O6-O9, O15, O21, O25)

Red: cross reactions (R15, R17, O16, O18, O26, O28)

Green: dissociation equilibrium (O1-O3, O10, O17, O20, O29)

Blue: comproportionation (O11, O27)

Purple: •OH involved reactions (O1, O13, O14, O19, O22-O24)

Navy: cross-coupling reactions (O4, O5)

Brown: decomposition reactions (O12, R20)

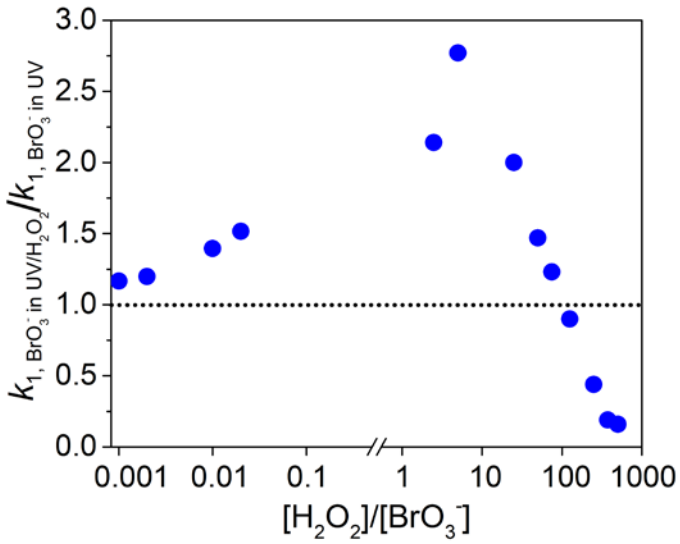


Figure S1. Effect of H_2O_2 on photo-reduction of bromate. Before breakage: $[BrO_3^-]_0$ = 1 μM, light intensity: 5.46 mW/cm^2, after breakage: $[BrO_3^-]_0$ = 0.2 mM, pH = 6.6, light intensity: 5.12 mW/cm^2.

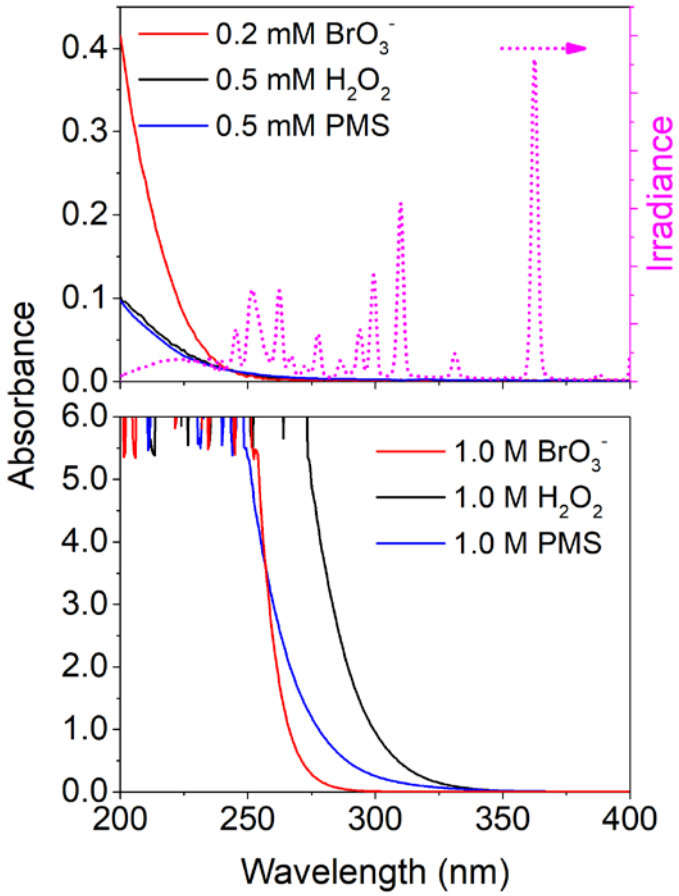


Figure S2. UV spectra of BrO_3^-, PMS and H_2O_2 and the spectral irradiance of the light source.

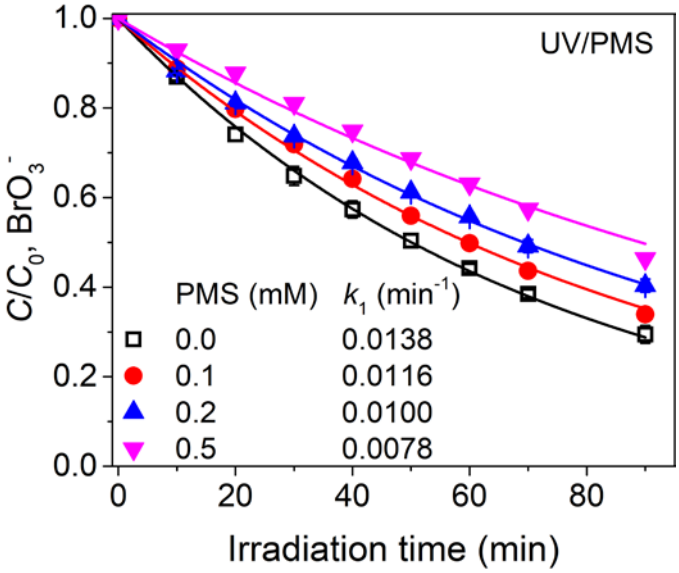


Figure S3. Effect of PMS on the photo-reduction of bromate (0.2 mM). pH = 6.8, light intensity: 5.62 mW/cm^2.

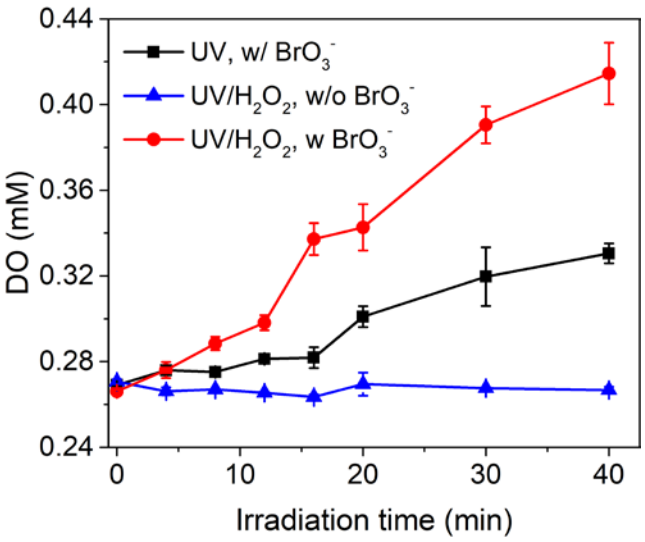


Figure S4. The evolution of dissolved oxygen (DO) in the UV and UV/H_2O_2 processes. $[BrO_3^-]_0$ = 0.2 mM, $[H_2O_2]_0$ = 0.5 mM, pH = 6.6, light intensity: 5.12 mW/cm^2.

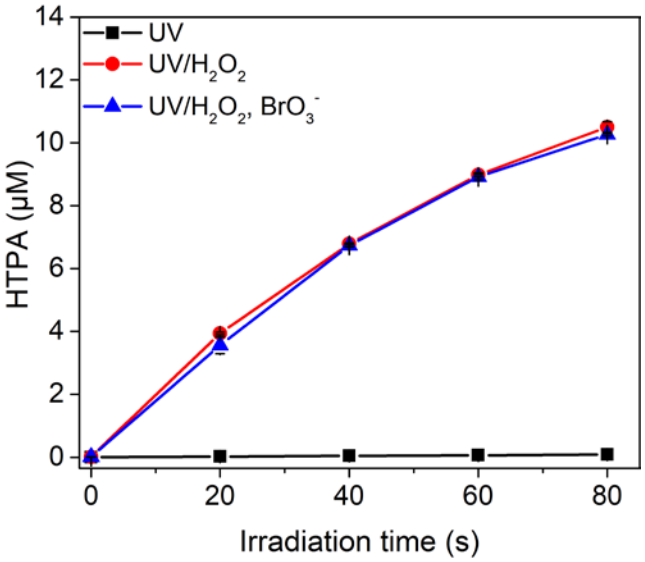


Figure S5. Production of HTPA in the UV and UV/H_2O_2 processes. $[BrO_3^-]_0$ = 0.2 mM, $[H_2O_2]_0$ = 0.5 mM, $[TPA]_0$ = 0.1 mM, pH = 6.5, light intensity: 7.41 mW/cm^2.

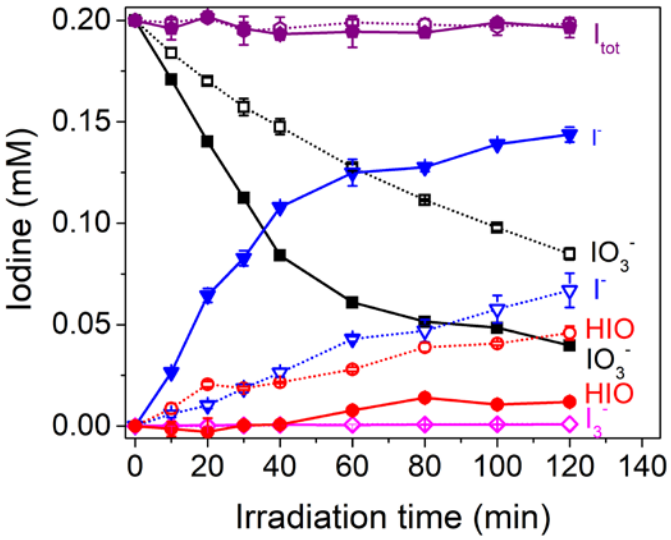


Figure S6. Mass balance of iodine in the UV (open symbol) and UV/H_2O_2 (solid symbol) processes. $[IO_3^-]_0$ = 0.2 mM, $[H_2O_2]_0$ = 0.5 mM, pH = 6.7, light intensity: 6.71 mW/cm^2.

Table S1. Photochemical reactions and equilibrium speciation of H_2O_2.

Code	Reaction	k (M^{-1} s^{-1})	pK_a	Ref.
H1	$H_2O_2 + h\nu \rightarrow 2{\cdot}OH$ ($\Phi = 1.0$)	--	--	1
H2	$2{\cdot}OH \rightarrow H_2O_2$	5.5×10^9	--	2
H3	${\cdot}OH \rightarrow O^{\cdot-} + H^+$	--	11.9	2
H4	$H_2O_2 + {\cdot}OH \rightarrow HO_2{\cdot} + H_2O$	2.7×10^7	--	1,2
H5	$HO_2{\cdot} + {\cdot}OH \rightarrow O_2 + H_2O$	6×10^9	--	2
H6	$HO_2^- + {\cdot}OH \rightarrow O_2^{\cdot-} + H_2O$	7.5×10^9	--	2
H7	$H_2O_2 \leftrightarrows HO_2^- + H^+$	--	11.6	3
H8	$HO_2{\cdot} \leftrightarrows O_2^{\cdot-} + H^+$	--	4.8	3

--: Data is unavailable.

Table S2. Possible reactions of bromine with ·OH and equilibrium speciation reactions involving bromine that are relevant to the oxidation of bromide. References refer to Supporting Information.

Code	Reaction	k (M^{-1} s^{-1})	Ref.
O1	$Br^- + \cdot OH \leftrightarrows BrOH^-$	1.0×10^{10}	3
O2	$BrOH^- \leftrightarrows Br\cdot + OH^-$	1.3×10^{10}	3
O3	$BrOH^- + H^+ \rightarrow Br\cdot + H_2O$	4.4×10^{10}	3
O4	$BrOH^- + Br^- \rightarrow Br_2^- + OH^-$	2.0×10^{8}	3
O5	$Br\cdot + Br^- \leftrightarrows Br_2^-$	1.0×10^{10}	3
O6	$Br_2^- + Br_2^- \rightarrow Br_3^- + Br^-$	2.0×10^{9}	3
O7	$Br_3^- \leftrightarrows Br_2 + Br^-$	1.0×10^{10}	3
O8	$Br_2 + H_2O \leftrightarrows HBrO + H^+ + Br^-$	97	4,5
O9	$3HBrO \rightarrow BrO_3^- + 2Br^- + 3H^+$	--	6
O10	$HBrO \leftrightarrows BrO^- + H^+$ ($pK_a = 8.8$)	--	7
O11	$2Br_2 + H^+ + BrO_3^- + 2H_2O \rightarrow 5HBrO$	--	8
O12	$4HBrO \rightarrow 2Br_2 + 2H_2O + O_2$	--	8
O13	$HBrO + \cdot OH \rightarrow BrO\cdot + H_2O$	2.0×10^{9}	2,9
O14	$BrO^- + \cdot OH \rightarrow BrO\cdot + OH^-$	4.5×10^{9}	3
O15	$2BrO\cdot + H_2O \rightarrow BrO^- + BrO_2^- + 2H^+$	5.0×10^{9}	3
O16	$HBrO + Br\cdot \rightarrow BrO\cdot + Br^- + H^+$	4.0×10^{9}	3
O17	$HBrO_2 \leftrightarrows BrO_2^- + H^+$ ($pK_a = 3.43$)	--	3
O18	$BrO\cdot + BrO_2^- \rightarrow BrO^- + BrO_2\cdot$	3.4×10^{8}	3
O19	$BrO_2^- + \cdot OH \rightarrow BrO_2\cdot + OH^-$	1.9×10^{9}	2,10
O20	$BrO_2\cdot + BrO_2\cdot \leftrightarrows Br_2O_4$	1.4×10^{9}	3
O21	$Br_2O_4 + H_2O \leftrightarrows BrO_2^- + BrO_3^- + 2H^+$	4.2×10^{7}	8
O22	$BrO_2\cdot + \cdot OH \rightarrow BrO_3^- + H^+$	2.0×10^{9}	3
O23	$BrO_3^- + \cdot OH \rightarrow BrO_3\cdot + OH^-$	5.0×10^{6}	2
O24	$Br_2^- + \cdot OH \rightarrow HBrO + Br^-$	1.0×10^{9}	2,11
O25	$2BrO_2^- \leftrightarrows BrO_3^- + BrO^-$	--	12
O26	$BrO^- + BrO_2^- \rightarrow BrO_3^- + Br^-$	--	6
O27	$BrO\cdot + BrO_2\cdot + H_2O \rightarrow 2BrO_2^- + 2H^+$	5.0×10^{9}	3
O28	$Br_2^- + HBrO \rightarrow BrO\cdot + 2Br^- + H^+$	8.0×10^{7}	11
O29	$Br\cdot + Br\cdot \rightarrow Br_2$	1.0×10^{9}	3

--: Data is unavailable.

Table S3. Possible reactions involved in the photolytic reduction process of bromate in the absence and presence of H_2O_2. References refer to Supporting Information.

Code	Reaction	k (M^{-1} s^{-1})	Ref.
R1	$BrO_3^- + hv \rightarrow (BrO_3^-)^* \rightarrow BrO_3\cdot + e_{aq}^-$ ($\Phi = 0.08$)	--	6,13
R2	$BrO_3^- + hv \rightarrow (BrO_3^-)^* \rightarrow BrO_2\cdot + O^{\cdot-}$	--	13,14
R3	$BrO_3^- + hv \rightarrow (BrO_3^-)^* \rightarrow BrO_2^- + O(^3P)$ ($\Phi = (7.4 \pm 0.6) \times 10^{-3}$)	--	13,15
R4	$BrO_3^- + hv + H^+ \rightarrow (BrO_3^-)^* \rightarrow HBrO + O_2$ ($\Phi = 0.19$)	--	6,13
R5	$BrO_2\cdot + O^{\cdot-} + H^+ \rightarrow HBrO + O_2$	--	13
R6	$BrO_2^- + H^+ + O(^3P) \rightarrow O_2 + HBrO$	--	10,13
R7	$BrO_3^- + e_{aq}^- + H_2O \rightarrow BrO_2\cdot + 2OH^-$	3.0×10^9	10
R8	$HBrO_2 + e_{aq}^- \rightarrow BrO\cdot + OH^-$	1.1×10^{10}	2
R9	$HBrO + e_{aq}^- \rightarrow Br\cdot + OH^-$	1.5×10^{10}	2
R10	$HBrO + hv \rightarrow Br\cdot + \cdot OH$	--	6
R11	$BrO^- + hv + H^+ \rightarrow (BrO^-)^* \rightarrow BrO\cdot + \cdot H$	--	6,13
R12	$BrO^- + hv \rightarrow (BrO^-)^* \rightarrow Br\cdot + O^{\cdot-}$	--	6
R13	$BrO\cdot + hv \rightarrow Br\cdot + O\cdot$	--	16
R14	$HBrO + hv \rightarrow Br^- + 1/2O_2 + H^+$	--	6
R15	$HBrO + H_2O_2 \rightarrow Br^- + H^+ + H_2O + O_2$	1.5×10^4	17
R15-1	$HBrO + HO_2^- \rightarrow Br^- + H_2O + O_2$	$(7.6 \pm 1.3) \times 10^8$	17
R15-2	$BrO^- + H_2O_2 \rightarrow Br^- + H_2O + O_2$	$(1.2 \pm 0.2) \times 10^6$	17
R16	$Br\cdot + H_2O_2 \rightarrow O_2^{\cdot-} + Br^- + 2H^+$	4.0×10^9	11
R17	$Br_2^- + H_2O_2 \rightarrow O_2^{\cdot-} + 2Br^- + 2H^+$	5.0×10^2	11
R18	$HBrO + O_2^{\cdot-} + Br^- \rightarrow O_2 + Br_2^- + OH^-$	3.5×10^9	17
R19	$BrO_3^- + O^{\cdot-} + H^+ \rightarrow BrO_3\cdot + OH^-$	1.7×10^6	2
R20	$BrO_3\cdot \rightarrow BrO\cdot + O_2$	--	13
R21	$O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-}$	--	5,14
R22	$e_{aq}^- + O_2 \rightarrow O_2^{\cdot-}$	1.9×10^{10}	2
R23	$e_{aq}^- + \cdot OH \rightarrow OH^-$	3.0×10^{10}	2

--: Data is unavailable.

Table S4. Rate constants (k_1) for H_2O_2 (0.5 mM) and BrO_3^- (0.2 mM) decomposition under different aeration conditions.

Chemical	**Solution**	**Light intensity (mW/cm^2)**	**k_1 (min^{-1})**			
			Ambient	N_2	N_2O	O_2
H_2O_2	H_2O_2	4.70	0.008	0.008	0.007	0.007
	H_2O_2 + BrO_3^-	4.70	0.012	0.014	0.013	0.012
BrO_3^-	H_2O_2 + BrO_3^-	5.12	0.011	0.010	0.011	0.011

Table S5. Some physicochemical properties of bromate and iodate.

X^n	Formula	pK_a		Redox pair	E^0 (V)	
	X = Br or I	Br	I		Br	I
+5	HXO_3/XO_3^-	-8.0[18]	0.8[22]	XO_3^-/X^-	1.4[25]	1.0[25]
+4	X_2O_4					
+3	HXO_2/XO_2^-	3.43[19]	6.0[23]			
+1	HXO/XO^-	8.8[20]	10.4[24]	HXO/X^-	1.3[25]	1.0[25]
0	X_2					
-1	HX/X^-	-8.8[21]	-9.5[21]			

References

1. Gligorovski, S.; Strekowski, R.; Barbati, S.; Vione, D. Environmental implications of hydroxyl radicals (·OH). *Chem. Rev.* **2015,** *115* (24), 13051-92.
2. Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O^-) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988,** *17* (2), 513-886.
3. von Gunten, U.; Oliveras, Y. Advanced oxidation of bromide-containing waters: bromate formation mechanisms. *Environ. Sci. Technol.* **1998,** *32* (1), 63-70.
4. Yang, Y.; Pignatello, J. J.; Ma, J.; Mitch, W. A. Comparison of halide impacts on the efficiency of contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation processes (AOPs). *Environ. Sci. Technol.* **2014,** *48* (4), 2344-2351.
5. Schwarz, H. A.; Bielski, B. H. J. Reactions of hydroperoxo and superoxide with iodine and bromine and the iodide (I_2^-) and iodine atom reduction potentials. *J. Phys. Chem.* **1986,** *90* (7), 1445-1448.
6. Farkas, L.; Klein, F. S. On the Photo-chemistry of some ions in solution. *J. Phys. Chem.* **1948,** *16* (9), 886-893.
7. Matheson, M. S.; Rabani, J. J. R. Pulse radiolysis of aqueous hydrogen solutions. I. rate constants for reaction of e_{aq}^- with itself and other transients. *J. Phys. Chem.* **1965,** *69* (4), 1324-1335.
8. Alves, W. A.; Côrtes, C. E. S.; Faria, R. B. Formation of high concentrations of BrO_2 in acidic bromate solutions. *Inorg. Chem.* **2004,** *43* (14), 4112-4114.
9. Kläning, U. K.; Wolff, T. Laser flash photolysis of HClO, ClO^-, HBrO, and BrO^- in aqueous solution. reactions of Cl^- and Br^- atoms. *Ber. Bunsenges. Phys. Chem.* **1985,** *89* (3), 243-245.
10. Treinin, A., The photochemistry of oxyanions. *Isr. J. Chem.* **1970,** *8* (2), 103-113.

11. Wagner, I.; Strehlow, H. On the flash photolysis of bromide ions in aqueous solutions. *Phys. Chem.* **1987,** *91* (12), 1317-1321.

12. Cronkhite, J. M.; Stickel, R. E.; Nicovich, J. M.; Wine, P. H. Laser flash photolysis studies of radical-radical reaction kinetics: the HO_2 + BrO reaction. *J. Phys. Chem. A* **1998,** *102* (33), 6651-6658.

13. Zuo, Z.; Katsumura. Y, Formation of hydrated electron and BrO_3 radical from laser photolysis of BrO_3^- aqueous solution. *J. Chem. Soc. Faraday Trans.* **1998,** *94* (24), 3577-3580.

14. Amichai, O.; Treinin, A. flash photolysis of the oxybromine anions. *Isr. J. Chem.* **1969,** *7* (3), 351-359.

15. Amichai, O.; Treinin, A. Chemical reactivity of $O(^3P)$ atoms in aqeous solution. *Chem. Phys. Lett.* **1969,** *3* (8), 611-613.

16. Phillip, N. H.; Gürten, E.; Diyamandoğlu, V. Transformation of bromine species during decomposition of bromate under UV light from low pressure mercury vapor lamps. *Ozone: Sci. Eng.* **2006,** *28* (4), 217-228.

17. von Gunten, U.; Oliveras, Y. Kinetics of the reaction between hydrogen peroxide and hypobromous acid: implication on water treatment and natural systems. *Water Res.* **1997,** *31* (4), 900-906.

18. Chen, W. f.; Zhang, Z. Y.; Li, Q.; Wang, H. Y. Adsorption of bromate and competition from oxyanions on cationic surfactant-modified granular activated carbon (GAC). *Chem. Eng. J.* **2012,** *203* (1), 319-325.

19. Faria, R. D. B.; Epstein, I. R.; Kustin, K. Kinetics of disproportionation and pK_a of bromous acid. *J. Phys. Chem.* **1994,** *98* (4), 1363-1367.

20. Von Gunten, U.; Oliveras, Y. Kinetics of the reaction between hydrogen peroxide and hypobromous acid: implication on water treatment and natural Systems. *Water Res.* **1997,** *31* (4), 900-906.

21. Trummal, A.; Lipping, L.; Kaljurand, I.; Koppel, I. A.; Leito, I. Acidity of strong acids in water and dimethyl sulfoxide. *J. Phys. Chem. A.* **2016,** *120* (20), 3663-3669.

22. Burgot, J. L. *Oxidoreductimetry: Direct and Indirect Todometries in Ionic Equilibria in Analytical Chemistry*. Springer: New York, US, 2012; pp 313-345.

23. Schmitz, G. Inorganic reactions of iodine(III) in acidic solutions and free energy of iodous acid formation. *Int. J. Chem. Kinet.* **2008,** *40* (10), 647-652.

24. Yves, B.; von Gunten, U. Hypoiodous acid: kinetics of the buffer-catalyzed disproportionation. *Water Res.* **2000,** *34* (12), 3197-3203.

25. Bard, A. J.; Parsons. R.; Jordan, J. *Standard Potentials in Aqueous Solution*. CRC press: London, UK, 1985.