SUPPLEMENTAL SECTION

PARTICIPATION OF THE HALIDES IN PHOTOCHEMICAL REACTIONS IN NATURAL WATERS AND TREATED WATERS

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Table S1. Rate constants for relevant reactions of halides and reactive halogen species.

No.	Reaction	Rate Constant	Reference
Chloride reaction			
1*	$Cl^{-}+{}^{\bullet}OH \rightarrow ClOH^{\bullet -}$	4.3×10^{9} M^{-1}s^{-1}	[1]
2	$Cl^{-}+SO_4^{\bullet -} \rightarrow Cl^{\bullet}+SO_4^{2-}$	3.0×10^{8} M^{-1} s^{-1}	[2]
3	$Cl^{\bullet}+SO_4^{2-} \rightarrow Cl^{-}+SO_4^{\bullet -}$	2.5×10^{8} M^{-1} s^{-1}	[2]
4	$Cl^{-}+NO_3^{\bullet} \rightarrow Cl^{\bullet}+NO_3^{-}$	3.5×10^{8} M^{-1} s^{-1}	[3]
5	$Cl^{\bullet}+NO_3^{-} \rightarrow Cl^{-}+NO_3^{\bullet}$	1.0×10^{8} M^{-1} s^{-1}	[3]
6*	$ClOH^{\bullet -} \rightarrow {}^{\bullet}OH+Cl^{-}$	6.1×10^{9} M^{-1}s^{-1}	[1]
7*	$ClOH^{\bullet -}+H^{+} \rightarrow Cl^{\bullet}+H_2O$	2.1×10^{10} M^{-1}s^{-1}	[1]
8*	$ClOH^{\bullet -}+Cl^{-} \rightarrow Cl_2^{\bullet -}+OH^{-}$	1.0×10^{4} M^{-1}s^{-1}	[4]
9*	$Cl^{\bullet}+H_2O \rightarrow ClOH^{\bullet -}+H^{+}$	2.5×10^{5} M^{-1}s^{-1}	[1]
10*	$Cl^{\bullet}+OH^{-} \rightarrow ClOH^{\bullet -}$	1.8×10^{10} M^{-1}s^{-1}	[5]
11*	$Cl^{\bullet}+H_2O_2 \rightarrow HO_2^{\bullet}+Cl^{-}+H^{+}$	2.0×10^{9} M^{-1}s^{-1}	[6]
12*	$Cl^{\bullet}+Cl^{-} \rightarrow Cl_2^{\bullet -}$	8.5×10^{9} M^{-1}s^{-1}	[6]
13*	$Cl^{\bullet}+Cl^{\bullet} \rightarrow Cl_2$	8.8×10^{7} M^{-1}s^{-1}	[7]

14*	$Cl^{\bullet}+HOCl\rightarrow ClO^{\bullet}+H^{+}+Cl^{-}$	3.0×10^{9} $M^{-1}s^{-1}$	[5]
15*	$Cl^{\bullet}+OCl^{-}\rightarrow ClO^{\bullet}+Cl^{-}$	8.3×10^{9} $M^{-1}s^{-1}$	[5]
16*	$Cl_2^{\bullet-}\rightarrow Cl^{\bullet}+Cl^{-}$	6.0×10^{4} $M^{-1}s^{-1}$	[6]
17*	$Cl_2^{\bullet-}+{}^{\bullet}OH\rightarrow HOCl+Cl^{-}$	1.0×10^{9} $M^{-1}s^{-1}$	[8]
18*	$Cl_2^{\bullet-}+Cl_2^{\bullet-}\rightarrow Cl_2+2Cl^{-}$	9.0×10^{8} $M^{-1}s^{-1}$	[6]
19*	$Cl_2^{\bullet-}+Cl^{\bullet}\rightarrow Cl_2+Cl^{-}$	2.1×10^{9} $M^{-1}s^{-1}$	[6]
20*	$Cl_2^{\bullet-}+H_2O_2\rightarrow HO_2^{\bullet}+2Cl^{-}+H^{+}$	1.4×10^{5} $M^{-1}s^{-1}$	[9]
21*	$Cl_2^{\bullet-}+HO_2^{\bullet}\rightarrow O_2+2Cl^{-}+H^{+}$	3.0×10^{9} $M^{-1}s^{-1}$	[9]
22*	$Cl_2^{\bullet-}+O_2^{\bullet-}\rightarrow O_2+2Cl^{-}$	2.0×10^{9} $M^{-1}s^{-1}$	[9]
23*	$Cl_2^{\bullet-}+H_2O\rightarrow Cl^{-}+HClOH^{\bullet}$	1.3×10^{3} $M^{-1}s^{-1}$	[10]
24*	$Cl_2^{\bullet-}+OH^{-}\rightarrow Cl^{-}+ClOH^{\bullet-}$	4.5×10^{7} $M^{-1}s^{-1}$	[4]
25	$Cl_2^{\bullet-}+NO_3^{\bullet}\rightarrow Cl_2+NO_3^{-}$	1.0×10^{9} M^{-1} s^{-1}	[3]
26	$Cl_2^{\bullet-}+NO_2^{\bullet}\rightarrow Cl_2+NO_2^{-}\,or\,2Cl^{-}+NO_2^{+}$	$\leqq1.0\times10^{9}$ M^{-1} s^{-1}	[3]
27*	$HClOH^{\bullet}\rightarrow ClOH^{\bullet-}+H^{+}$	1.0×10^{8} $M^{-1}s^{-1}$	[10]
28*	$HClOH^{\bullet}\rightarrow Cl^{\bullet}+H_2O$	1.0×10^{2} $M^{-1}s^{-1}$	[10]
29*	$HClOH^{\bullet}+Cl^{-}\rightarrow Cl_2^{\bullet-}+H_2O$	5.0×10^{9} $M^{-1}s^{-1}$	[10]
30*	$Cl_2+Cl^{-}\rightarrow Cl_3^{-}$	2.0×10^{4} $M^{-1}s^{-1}$	[11]
31*	$Cl_3^{-}\rightarrow Cl_2+Cl^{-}$	1.1×10^{5} $M^{-1}s^{-1}$	[11]
32*	$Cl_3^{-}+HO_2^{\bullet}\rightarrow Cl_2^{\bullet-}+HCl+O_2$	1.0×10^{9} $M^{-1}s^{-1}$	[12]
33*	$Cl_3^{-}+O_2^{\bullet-}\rightarrow Cl_2^{\bullet-}+Cl^{-}+O_2$	3.8×10^{9} $M^{-1}s^{-1}$	[13]

34*	$Cl_2 + \mathrm{H_2O} \rightarrow Cl^- + HOCl + H^+$	15 $M^{-1}s^{-1}$	[14]
35*	$Cl_2 + \mathrm{H_2O_2} \rightarrow O_2 + 2HCl$	1.3×10^4 $M^{-1}s^{-1}$	[13]
36*	$Cl_2 + O_2^{\bullet-} \rightarrow O_2 + Cl_2^{\bullet-}$	1.0×10^9 $M^{-1}s^{-1}$	[13]
37*	$Cl_2 + HO_2^{\bullet} \rightarrow H^+ + O_2 + Cl_2^{\bullet-}$	1.0×10^9 $M^{-1}s^{-1}$	[12]
38*	$ClO_2^{\bullet} + {}^{\bullet}OH \rightarrow ClO_3^- + H^+$	4×10^9 $M^{-1}s^{-1}$	[15]
39	$ClO_2^{\bullet} + O_3 \rightarrow ClO_3^- + O_2$	6×10^8 $M^{-1}s^{-1}$	[15]
40*	$HOCl \rightleftarrows ClO^- + H^+$	$K_{eq} = 2.82\times10^{-8}$	[16]
41*	$HOCl + H_2O_2 \rightarrow HCl + H_2O + O_2$	1.1×10^4 $M^{-1}s^{-1}$	[17]
42*	$OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$	1.7×10^5 $M^{-1}s^{-1}$	[17]
43*	$HOCl + {}^{\bullet}OH \rightarrow ClO^{\bullet} + H_2O$	2.0×10^9 $M^{-1}s^{-1}$	[13]
44*	$HOCl + O_2^{\bullet-} \rightarrow Cl^{\bullet} + OH^- + O_2$	7.5×10^6 $M^{-1}s^{-1}$	[13]
45*	$HOCl + HO_2^{\bullet} \rightarrow Cl^{\bullet} + OH^- + O_2$	7.5×10^6 $M^{-1}s^{-1}$	[13]
46	$HOCl + NO_2^- \rightleftarrows ClNO_2 + OH^-$	$K_{eq} = 1.1\times10^{-4}$	[18]
47	$ClNO_2 + NO_2^- \rightarrow N_2O_4 + Cl^-$	1.3×10^4 $M^{-1}s^{-1}$	[18]
48*	$OCl^- + {}^{\bullet}OH \rightarrow ClO^{\bullet} + OH^-$	8.8×10^9 $M^{-1}s^{-}$	[13]
49*	$OCl^- + O_2^{\bullet-} + H_2O \rightarrow Cl^{\bullet} + 2OH^- + O_2$	7.5×10^6 $M^{-1}s^{-}$	[13]
50*	$OCl^- + {}^{\bullet}OH \rightarrow ClO_2^- + H^+$	$>1\times10^9$ $M^{-1}s^{-1}$	[15]
51	$Cl^- + O_3 \rightarrow ClO^- + O_2$	$<3\times10^3$ $M^{-1}s^{-1}$	[19]
52	$OCl^- + O_3 \rightarrow ClO_2^- + O_2$	30 $M^{-1}s^{-1}$	[15]
53	$OCl^- + O_3 \rightarrow Cl_2 + 2O_2$	110 $M^{-1}s^{-1}$	[15]

54	$ClO_2^- + O_3 \rightarrow ClO_3^- + O_2$	4×10^{6} M^{-1}s^{-1}	[15]
55*	$ClO_2^- + {}^{\bullet}OH \rightarrow ClO_2^{\bullet} + OH^-$	6×10^{9} M^{-1}s^{-1}	[15]
56	$HSO_5^- + Cl^- \rightarrow HOCl + SO_4^{2-}$	2.1×10^{-3} M^{-1}s^{-1}	[20]
Bromide reactions			
57*	$Br^- + {}^{\bullet}OH \rightarrow BrOH^{\bullet -}$	1.1×10^{10} M^{-1}s^{-1}	[13]
58	$Br^- + O_3 \rightarrow BrO^- + O_2$	160 M^{-1}s^{-1}	[21]
59	$Br^- + SO_4^{\bullet -} \rightarrow Br^{\bullet} + SO_4^{2-}$	3.5×10^{9} M^{-1} s^{-1}	[22]
60	$Br^- + NO_3^{\bullet} \rightarrow Br^{\bullet} + NO_3^-$	4×10^{9} M^{-1} s^{-1}	[23]
61*	$Br^{\bullet} + H_2O \rightarrow BrOH^{\bullet -} + H^+$	1.4 M^{-1}s^{-1}	[5]
62*	$Br^{\bullet} + OH^- \rightarrow BrOH^{\bullet -}$	1.6×10^{10}M^{-1}s^{-1}	[24]
63*	$BrOH^{\bullet -} \rightarrow {}^{\bullet}OH + Br^-$	3.3×10^{7} M^{-1}s^{-1}	[24]
64*	$BrOH^{\bullet -} \rightarrow Br^{\bullet} + OH^-$	4.2×10^{6}M^{-1}s^{-1}	[24]
65*	$BrOH^{\bullet -} + H^+ \rightarrow Br^{\bullet} + H_2O$	4.4×10^{10}M^{-1}s^{-1}	[24]
66*	$BrOH^{\bullet -} + Br^- \rightarrow Br_2^{\bullet -} + OH^-$	1.9×10^{8} M^{-1}s^{-1}	[24]
67*	$Br^{\bullet} + Br^- \rightarrow Br_2^{\bullet -}$	1.2×10^{10} M^{-1}s^{-1}	[13]
68*	$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$	1.0×10^{9} M^{-1}s^{-1}	[13]
69*	$Br^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Br^-$	4.0×10^{9} M^{-1}s^{-1}	[13]
70*	$Br^{\bullet} + HO_2^{\bullet} \rightarrow H^+ + O_2 + Br^-$	1.0×10^{9} M^{-1}s^{-1}	[13]
71	$Br^{\bullet} + O_3 \rightarrow BrO^{\bullet} + O_2$	1.5×10^{8} M^{-1}s^{-1}	[21]
72*	$Br_2^{\bullet -} \rightarrow Br^{\bullet} + Br^-$	1.9×10^{4} M^{-1}s^{-1}	[13]

73*	$Br_2^{\bullet-}+Br_2^{\bullet-} \rightarrow Br_2+2Br^-$	1.9×10^9 $M^{-1}s^{-1}$	[13]
74*	$Br_2^{\bullet-}+Br^{\bullet} \rightarrow Br_2+Br^-$	2.0×10^9 $M^{-1}s^{-1}$	[13]
75*	$Br_2^{\bullet-}+H_2O_2 \rightarrow HO_2^{\bullet}+2Br^- + H^+$	5.0×10^2 $M^{-1}s^{-1}$	[13]
76*	$Br_2^{\bullet-}+HO_2^{\bullet} \rightarrow O_2+2Br^- + H^+$	1.0×10^8 $M^{-1}s^{-1}$	[25]
77*	$Br_2^{\bullet-}+HO_2^{\bullet} \rightarrow HO_2^-+2Br^-$	4.4×10^9 $M^{-1}s^{-1}$	[13]
78*	$Br_2^{\bullet-}+O_2^{\bullet-} \rightarrow O_2+2Br^-$	1.7×10^8 $M^{-1}s^{-1}$	[25]
79*	$Br_2^{\bullet-}+OBr^- \rightarrow BrO^{\bullet}+2Br^-$	6.2×10^7 $M^{-1}s^{-1}$	[13]
80*	$Br_2^{\bullet-}+{}^{\bullet}OH \rightarrow HOBr+Br^-$	1.0×10^9 $M^{-1}s^{-1}$	[25]
81*	$Br_2^{\bullet-}+OH^- \rightarrow BrOH^{\bullet-}+Br^-$	2.7×10^6 $M^{-1}s^{-1}$	[26]
82*	$Br_2+Br^- \rightarrow Br_3^-$	9.6×10^8 $M^{-1}s^{-1}$	[13]
83*	$Br_2+HO_2^{\bullet} \rightarrow Br_2^{\bullet-}+O_2 + H^+$	1.1×10^8 $M^{-1}s^{-1}$	[13]
84*	$Br_2+O_2^{\bullet-} \rightarrow Br_2^{\bullet-} + O_2$	5.6×10^9 $M^{-1}s^{-1}$	[13]
85*	$Br_2+H_2O \rightarrow HOBr + O_2$	97 $M^{-1}s^{-1}$	[13]
86*	$Br_2+H_2O_2 \rightarrow 2HBr + O_2$	1.3×10^3 $M^{-1}s^{-1}$	[25]
87*	$Br_3^- \rightarrow Br_2+Br^-$	5.5×10^7 $M^{-1}s^{-1}$	[13]
88*	$Br_3^-+HO_2^{\bullet} \rightarrow Br_2^{\bullet-}+HBr + O_2$	1.0×10^7 $M^{-1}s^{-1}$	[13]
89*	$Br_3^-+O_2^{\bullet-} \rightarrow Br_2^{\bullet-}+Br^- + O_2$	3.8×10^9 $M^{-1}s^{-1}$	[13]
90*	$BrO^{\bullet} + BrO^{\bullet} \rightarrow BrO_2^- + OBr^-$	5×10^9 $M^{-1}s^{-1}$	[27]
91*	$2BrO^{\bullet} + H_2O \rightarrow BrO_2^- + OBr^- + 2H^+$	4.9×10^9 $M^{-1}s^{-1}$	[28]
92*	$BrO^{\bullet} + BrO_2^- \rightarrow OBr^-+BrO_2^{\bullet}$	3.4×10^8 $M^{-1}s^{-1}$	[28]

93*	$2BrO_2^{\bullet} \rightarrow Br_2O_4$	1.4×10^{9} M^{-1}s^{-1}	[28]
94*	$Br_2O_4 \rightarrow 2BrO_2^{\bullet}$	7.4×10^{7} M^{-1}s^{-1}	[28]
95*	$BrO_2^{\bullet} + Br_2^{\bullet -} \rightarrow Br^- + BrO^{\bullet} + OBr^-$	8.0×10^{7} M^{-1}s^{-1}	[28]
96*	$2BrO_2^{\bullet} + H_2O \rightarrow BrO_2^- + BrO_3^- + 2H^+$	4.2×10^{7} M^{-1}s^{-1}	[28]
97*	$HOBr \rightleftarrows BrO^- + H^+$	K$_{eq}$ = 1.58×10^{-9}	[29]
98*	$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	5.0×10^{9} M^{-1}s^{-1}	[30]
99*	$HOBr + HO_2^- \rightarrow Br^- + H_2O + O_2$	7.6×10^{8} M^{-1}s^{-1}	[31]
100*	$HOBr + H_2O_2 \rightarrow HBr + H_2O + O_2$	1.5×10^{4} M^{-1}s^{-1}	[31]
101*	$HOBr + {}^{\bullet}OH \rightarrow BrO^{\bullet} + H_2O$	2.0×10^{9} M^{-1}s^{-1}	[13]
102*	$HOBr + O_2^{\bullet -} \rightarrow BrOH^{\bullet -}$	3.5×10^{9} M^{-1}s^{-1}	[31]
103*	$HOBr + HO_2^{\bullet} \rightarrow BrOH^{\bullet -} + H^+$	3.5×10^{9} M^{-1}s^{-1}	[13]
104*	$HOBr + Br^{\bullet} \rightarrow BrO^{\bullet} + H^+ + Br^-$	5×10^{7} M^{-1}s^{-1}	[28]
105	$HOBr + NO_2^- \rightleftarrows BrNO_2 + OH^-$	K$_{eq}$ = 5.6×10^{-6}	[32]
106	$BrNO_2 + NO_2^- \rightarrow N_2O_4 + H^+$	1.4×10^{4} M^{-1}s^{-1}	[32]
107*	$OBr^- + Br^{\bullet} \rightarrow BrO^{\bullet} + Br^-$	4.1×10^{9} M^{-1}s^{-1}	[28]
108*	$OBr^- + H_2O_2 \rightarrow Br^- + H_2O + O_2$	1.2×10^{6} M^{-1}s^{-1}	[31]
109*	$OBr^- + {}^{\bullet}OH \rightarrow BrO^{\bullet} + OH^-$	4.5×10^{9} M^{-1}s^{-1}	[13]
110*	$OBr^- + O_2^{\bullet -} + H_2O \rightarrow Br^{\bullet} + 2OH^- + O_2$	2.0×10^{8} M^{-1}s^{-1}	[13]
111	$OBr^- + O_3 \rightarrow BrO_2^- + O_2$	100 M^{-1}s^{-1}	[21]
112	$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$	8.9×10^{4} M^{-1}s^{-1}	[21]

113*	$BrO_2^- + Br_2^{\bullet -} \rightarrow Br^- + BrO^\bullet + OBr^-$	8.0×10^7 M^{-1}s^{-1}	[28]
114	$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$	> 1×10^5 M^{-1} s^{-1}	[21]
115	$Br^- + HSO_5^- \rightarrow HOBr + SO_4^{2-}$	0.7 M^{-1} s^{-1}	[20]
Iodide reactions			
116	$I^- + {}^\bullet OH \rightarrow HOI^{\bullet -}$	1.1×10^{10} M^{-1}s^{-1}	[33]
117	$HOI + HOI \rightarrow IO_2^- + I^- + 2H^+$	0.3 M^{-1}s^{-1}	[34]
118	$HOI + OI^- \rightarrow IO_2^- + I^- + H^+$	15 M^{-1}s^{-1}	[34]
119	$HOI + HOI + HCO_3^- \rightarrow IO_2^- + I^- + 2H^+ + HCO_3^-$	50 M^{-2}s^{-1}	[34]
120	$HOI + HOI + CO_3^{2-} \rightarrow IO_2^- + I^- + 2H^+ + CO_3^{2-}$	5000 M^{-2}s^{-1}	[34]
121	$HOI + HOI + B(OH)_4^- \rightarrow IO_2^- + I^- + 2H^+ + B(OH)_4^-$	1700 M^{-2}s^{-1}	[34]
122	$I^- + HOI + H^+ \rightleftarrows I_2 + H_2O$	K=1.84×10^{12}	[34]
123	$I^- + I_2 \rightleftarrows I_3^-$	K=724	[34]
124	$I^- + O_3 \rightarrow OI^- + O_2$	2×10^9 M^{-1}s^{-1}	[21]
125	$OI^- + 2O_3 \rightarrow IO_3^- + 2O_2$	1.6×10^6 M^{-1}s^{-1}	[21]
126	$HOI + 2O_3 \rightarrow IO_3^- + 2O_2 + H^+$	3.6×10^4 M^{-1}s^{-1}	[21]
127	$I^- + HSO_5^- \rightarrow HOI + SO_4^{2-}$	1.1×10^3 M^{-1} s^{-1}	[20]
128	$I^- + SO_5^{2-} \rightarrow OI^- + SO_4^{2-}$	218 M^{-1} s^{-1}	[35]
129	$HOI + HSO_5^- \rightarrow IO_2^- + SO_4^{2-} + 2H^+$	112 M^{-1} s^{-1}	[35]
130	$OI^- + HSO_5^- \rightarrow IO_2^- + SO_4^{2-} + H^+$	1.7×10^6 M^{-1} s^{-1}	[35]
131	$OI^- + SO_5^{2-} \rightarrow IO_2^- + SO_4^{2-}$	1.5×10^5 M^{-1} s^{-1}	[35]
Mixed halide reactions: Chloride and bromide			
132*	$HOBr + Cl^- \rightarrow BrCl + OH^-$	44 M^{-1}s^{-1}	[36]

133*	$HOCl + Br^- \rightarrow BrCl + OH^-$	$1.0\times10^{-2}M^{-1}s^{-1}$	[36]
134*	$BrCl + H_2O \rightarrow HOBr + Cl^- + H^+$	$1.0\times10^{5}M^{-1}s^{-1}$	[13]
135*	$BrCl + H_2O_2 \rightarrow HBr + HCl + H_2O$	$1.3\times10^{4}M^{-1}s^{-1}$	[13]
136*	$BrCl + O_2^{\bullet-} \rightarrow BrCl^{\bullet-} + O_2$	$4.0\times10^{9}M^{-1}s^{-1}$	[13]
137*	$BrCl + HO_2^{\bullet} \rightarrow BrCl^{\bullet-} + O_2 + H^+$	$5.0\times10^{8}M^{-1}s^{-1}$	[13]
138*	$BrCl + Cl^- \rightarrow BrCl_2^-$	$1.0\times10^{6}M^{-1}s^{-1}$	[11]
139*	$BrCl_2^- \rightarrow BrCl + Cl^-$	$1.7\times10^{5}s^{-1}$	[11]
140*	$BrCl + Br^- \rightarrow Br_2Cl^-$	$3.0\times10^{8}M^{-1}s^{-1}$	[13]
141*	$Br_2Cl^- \rightarrow BrCl + Br^-$	$1.7\times10^{4}s^{-1}$	[13]
142*	$Br_2 + Cl^- \rightarrow Br_2Cl^-$	$5.0\times10^{4}M^{-1}s^{-1}$	[13]
143*	$Br_2Cl^- \rightarrow Br_2 + Cl^-$	$3.8\times10^{4}s^{-1}$	[13]
144*	$Cl_2 + Br^- \rightarrow BrCl_2^-$	$6.0\times10^{9}M^{-1}s^{-1}$	[11]
145*	$BrCl_2^- \rightarrow Cl_2 + Br^-$	$9.0\times10^{3}s^{-1}$	[11]
146*	$Br_2Cl^- + Cl^- \rightarrow BrCl_2^- + Br^-$	$1.0\times10^{5}M^{-1}s^{-1}$	[13]
147*	$BrCl_2^- + Br^- \rightarrow Br_2Cl^- + Cl^-$	$3.0\times10^{8}\ M^{-1}s^{-1}$	[11]
148*	$ClOH^{\bullet-} + Br^- \rightarrow BrCl^{\bullet-} + OH^-$	$1.0\times10^{9}\ M^{-1}s^{-1}$	[13]
149*	$Cl^{\bullet} + Br^- \rightarrow BrCl^{\bullet-}$	$1.2\times10^{10}\ M^{-1}s^{-1}$	[13]
150*	$Cl_2^{\bullet-} + Br^- \rightarrow BrCl^{\bullet-} + Cl^-$	$4.0\times10^{9}\ M^{-1}s^{-1}$	[11]
151*	$BrOH^{\bullet-} + Cl^- \rightarrow BrCl^{\bullet-} + OH^-$	$1.9\times10^{8}\ M^{-1}s^{-1}$	[13]
152*	$Br^{\bullet} + Cl^- \rightarrow BrCl^{\bullet-}$	$1.0\times10^{8}\ M^{-1}s^{-1}$	[13]

153*	$Br_2^{\bullet-} + Cl^- \rightarrow BrCl^{\bullet-} + Br^-$	4.3×10^6 M^{-1}s^{-1}	[11]
154*	$Br_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Br_2 + 2Cl^-$	4.0×10^9 M^{-1}s^{-1}	[13]
155*	$BrCl^{\bullet-} + OH^{\bullet} \rightarrow BrCl + OH^-$	1.0×10^9 M^{-1}s^{-1}	[13]
156*	$BrCl^{\bullet-} + HO_2^{\bullet} \rightarrow Br^- + Cl^- + O_2 + H^+$	1.0×10^9 M^{-1}s^{-1}	[13]
157*	$BrCl^{\bullet-} + O_2^{\bullet-} \rightarrow Br^- + Cl^- + O_2$	6.0×10^8 M^{-1}s^{-1}	[13]
158*	$BrCl^{\bullet-} + H_2O_2 \rightarrow Br^- + HCl + HO_2^{\bullet}$	5.0×10^3 M^{-1}s^{-1}	[13]
159*	$BrCl^{\bullet-} + OH^- \rightarrow ClOH^{\bullet-} + Br^-$	3.0×10^6 M^{-1}s^{-1}	[13]
160*	$BrCl^{\bullet-} + OH^- \rightarrow BrOH^{\bullet-} + Cl^-$	2.0×10^7 M^{-1}s^{-1}	[13]
161*	$BrCl^{\bullet-} + BrCl^{\bullet-} \rightarrow Br^- + Cl^- + BrCl$	4.7×10^9 M^{-1}s^{-1}	[13]
162*	$BrCl^{\bullet-} + Cl_2^{\bullet-} \rightarrow 2Cl^- + BrCl$	2.0×10^9 M^{-1}s^{-1}	[13]
163*	$BrCl^{\bullet-} + Br_2^{\bullet-} \rightarrow Br_2 + Cl^- + Br^-$	4.0×10^9 M^{-1}s^{-1}	[13]
164*	$BrCl^{\bullet-} \rightarrow Cl^{\bullet} + Br^-$	1.9×10^3 M^{-1}s^{-1}	[37]
165*	$BrCl^{\bullet-} \rightarrow Cl^- + Br^{\bullet}$	6.1×10^4 M^{-1}s^{-1}	[37]
166*	$BrCl^{\bullet-} + Br^- \rightarrow Br_2^{\bullet-} + Cl^-$	8.0×10^9 M^{-1}s^{-1}	[11]
167*	$BrCl^{\bullet-} + Cl^- \rightarrow Cl_2^{\bullet-} + Br^-$	1.1×10^2 M^{-1}s^{-1}	[11]
168*	$Cl_2Br^- + H_2O \rightleftarrows HOBr + H^+ + 2Cl^-$	K$_{eq}$ = 3×10^{-6} M^{-3}	[14]
Mixed halide reactions: Chloride and iodide			
169	$HOCl + I^- \rightarrow HOI + Cl^-$	4.3×10^8 M^{-1}s^{-1}	[21]
170	$OCl^- + I^- \rightarrow OI^- + Cl^-$	< 30 M^{-1}s^{-1}	[21]
171	$2HOCl + HOI \rightarrow IO_3^- + 2Cl^- + 3H^+$	8.2 M^{-1}s^{-1}	[21]
172	$2OCl^- + HOI \rightarrow IO_3^- + 2Cl^- + H^+$	52 M^{-1}s^{-1}	[21]

Mixed halide reactions: Bromide and iodide			
173	$OBr^{-}+I^{-}+H^{+}\rightarrow IBr+OH^{-}$	6.8×10^{5} $M^{-1}s^{-1}$	[38]
174	$HOBr+I^{-}\rightarrow IBr+OH^{-}$	5.0×10^{9} $M^{-1}s^{-1}$	[38]
175	$IBr+OH^{-}\rightarrow HOI+Br^{-}$	6×10^{9} $M^{-1}s^{-1}$	[38]
176	$IBr+H_2O\rightarrow HOI+Br^{-}+H^{+}$	8×10^{5} $M^{-1}s^{-1}$	[38]
177	$IBr+I^{-}\rightarrow I_2+Br^{-}$	2.1×10^{9} $M^{-1}s^{-1}$	[38]
178	$HOBr+OI^{-}\rightarrow IO_2^{-}+Br^{-}+H^{+}$	1.9×10^{6} $M^{-1}s^{-1}$	[39]
179	$OBr^{-}+OI^{-}\rightarrow IO_2^{-}+Br^{-}$	1.8×10^{3} $M^{-1}s^{-1}$	[39]
180	$HOBr\,/\,OBr^{-}+IO_2^{-}\rightarrow IO_3^{-}+Br^{-}$	Very fast	[39]
Bicarbonate reactions			
181*	$^{\bullet}OH+CO_3^{2-}\rightarrow CO_3^{\bullet-}+OH^{-}$	3.9×10^{8} M^{-1} s^{-1}	[33]
182*	$^{\bullet}OH+HCO_3^{-}\rightarrow CO_3^{\bullet-}+H_2O$	8.6×10^{6} M^{-1} s^{-1}	[33]
183*	$^{\bullet}OH+CO_3^{\bullet-}\rightarrow product$	3.0×10^{9} M^{-1} s^{-1}	[40]
184*	$O_2^{\bullet-}+CO_3^{\bullet-}\rightarrow CO_3^{2-}+O_2$	6.0×10^{8} M^{-1} s^{-1}	[40]
185*	$CO_3^{\bullet-}+CO_3^{\bullet-}\rightarrow product$	3.0×10^{7} M^{-1} s^{-1}	[40]
186	$S_2O_8^{2-}+CO_3^{\bullet-}\rightarrow CO_3^{2-}+S_2O_8^{\bullet-}$	3.0×10^{7} M^{-1} s^{-1}	[41]
187	$SO_4^{\bullet-}+HCO_3^{-}\rightarrow CO_3^{\bullet-}+HSO_4^{-}$	2.8×10^{6} M^{-1} s^{-1}	[42]
188	$SO_4^{\bullet-}+CO_3^{2-}\rightarrow CO_3^{\bullet-}+SO_4^{2-}$	6.1×10^{6} M^{-1} s^{-1}	[43]
189*	$OCl^{-}+CO_3^{\bullet-}\rightarrow OCl^{\bullet}+CO_3^{2-}$	5.7×10^{5} $M^{-1}s^{-1}$	[44]
190*	$Cl^{\bullet}+CO_3^{2-}\rightarrow Cl^{-}+CO_3^{\bullet-}$	5.0×10^{8} $M^{-1}s^{-1}$	[13]
191*	$Cl^{\bullet}+HCO_3^{-}\rightarrow Cl^{-}+CO_3^{\bullet-}+H^{+}$	2.2×10^{8} $M^{-1}s^{-1}$	[13]

192*	$Cl_2^{\bullet-} + CO_3^{2-} \rightarrow 2Cl^- + CO_3^{\bullet-}$	1.6×10^8 M^{-1} s^{-1}	[13]
193*	$Cl_2^{\bullet-} + HCO_3^- \rightarrow 2Cl^- + CO_3^{\bullet-} + H^+$	8.0×10^7 M^{-1} s^{-1}	[13]
194*	$Br_2^{\bullet-} + CO_3^{2-} \rightarrow 2Br^- + CO_3^{\bullet-}$	1.1×10^5 M^{-1} s^{-1}	[13]
195*	$Br_2^{\bullet-} + HCO_3^- \rightarrow 2Br^- + CO_3^{\bullet-} + H^+$	8.0×10^4 M^{-1} s^{-1}	[13]
196*	$Br^\bullet + CO_3^{2-} \rightarrow Br^- + CO_3^{\bullet-}$	3.4×10^4 M^{-1} s^{-1}	[44]
197*	$Br^\bullet + CO_3^{2-} \rightarrow Br^- + CO_3^{\bullet-}$	2.0×10^6 M^{-1} s^{-1}	[13]
198*	$Br^\bullet + HCO_3^- \rightarrow Br^- + CO_3^{\bullet-} + H^+$	1.0×10^6 M^{-1} s^{-1}	[13]
199*	$BrCl^{\bullet-} + HCO_3^- \rightarrow Br^- + HCl + CO_3^{\bullet-}$	3.0×10^6 M^{-1} s^{-1}	[13]
200*	$BrCl^{\bullet-} + CO_3^{2-} \rightarrow Br^- + Cl^- + CO_3^{\bullet-}$	6.0×10^6 M^{-1} s^{-1}	[13]
Other reactions in modeling			
201*	$H_2O \rightleftarrows H^+ + OH^-$	$K_{eq} = 1.0\times10^{-14}$	
202*	$H_2O_2 \rightleftarrows H^+ + HO_2^-$	$K_{eq} = 2.5\times10^{-12}$	[29]
203*	$HO_2^\bullet \rightarrow H^+ + O_2^{\bullet-}$	$K_{eq} = 1.6\times10^{-5}$	[45]
204*	$HCO_3^- + H^+ \rightarrow H_2CO_3$	1.0×10^{10} M^{-1}s^{-1}	
205*	$H_2CO_3 \rightarrow HCO_3^- + H^+$	$K_{eq} = 4.5\times10^{-7}$ s^{-1}	[46]
206*	$HCO_3^- \rightarrow CO_3^{2-} + H^+$	$K_{eq} = 4.4\times10^{-11}$ s^{-1}	[46]
207*	$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$	5.5×10^{10}M^{-1}s^{-1}	[33]
208*	$^\bullet OH + OH^- \rightarrow O^{\bullet-} + H_2O$	1.2×10^{10}M^{-1}s^{-1}	[33]
209*	$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + HO_2$	2.7×10^9M^{-1}s^{-1}	[33]
210*	$^\bullet OH + HO_2^- \rightarrow HO_2^\bullet + OH^-$	7.5×10^9 M^{-1}s^{-1}	[33]

211*	$^{\bullet}OH + HO_2^{\bullet} \rightarrow O_2 + H_2O$	$6.6\times10^{9} M^{-1}s^{-1}$	[40]
212*	$^{\bullet}OH + O_2^{\bullet-} \rightarrow O_2 + OH^-$	$7.0\times10^{9} M^{-1}s^{-1}$	[40]
213*	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	$8.3\times10^{9} M^{-1}s^{-1}$	[33]
214*	$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^- + O_2$	$7.5\times10^{9} M^{-1}s^{-1}$	[33]
215*	$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + ^{\bullet}OH + H_2O$	$3 M^{-1}s^{-1}$	[33]
216*	$O_2^{\bullet-} + H_2O_2 \rightarrow O_2 + ^{\bullet}OH + OH^-$	$7.5\times10^{9} M^{-1}s^{-1}$	[33]
217*	$H_2O_2 + CO_3^{\bullet-} \rightarrow HCO_3^- + HO_2^{\bullet}$	$4.5\times10^{5} M^{-1}s^{-1}$	[47]
218*	$HO_2^- + CO_3^{\bullet-} \rightarrow CO_3^{2-} + HO_2^{\bullet}$	$3.0\times10^{7} M^{-1}s^{-1}$	[47]

* Reactions in modeling (163 in total).

REFERENCES

1. Jayson, G. G.; Parsons, B. J.; Swallow, A. J., Some Simple, Highly Reactive, Inorganic Chlorine Derivatives in Aqueous-Solution - Their Formation Using Pulses of Radiation and Their Role in Mechanism of Fricke Dosimeter. *J Chem Soc Farad T 1* **1973**, (9), 1597-1607.
2. Das, T. N., Reactivity and role of SO5•- radical in aqueous medium chain oxidation of sulfite to sulfate and atmospheric sulfuric acid generation. *J. Phys. Chem. A* **2001,** 105, (40), 9142-9155.
3. Poskrebyshev, G. A.; Huie, R. E.; Neta, P., The Rate and Equilibrium Constants for the Reaction NO3• + Cl- ⇄ NO3- + Cl• in Aqueous Solutions. *J. Phys. Chem. A* **2003,** 107, (12), 1964-1970.
4. Grigorev, A. E.; Makarov, I. E.; Pikaev, A. K., Formation of Cl2- in the Bulk Solution during the Radiolysis of Concentrated Aqueous-Solutions of Chlorides. *High Energ. Chem.* **1987,** 21, (2), 99-102.
5. Klaning, U. K.; Wolff, T., Laser Flash-Photolysis of Hclo, Clo-, Hbro, and Bro- in Aqueous-Solution - Reactions of Cl-Atoms and Br-Atoms. *PCCP* **1985,** 89, (3), 243-245.
6. Yu, X. Y.; Barker, J. R., Hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions. II. Quantum yield of HO center dot(Aq) radicals. *J. Phys. Chem. A* **2003,** 107, (9), 1325-1332.
7. Wu, D.; Wong, D.; Dibartolo, B., Evolution of Cl2- in Aqueous Nacl Solutions. *J. Photochem.* **1980,** 14, (4), 303-310.
8. Technology, N. I. o. S. a., NDRL/NIST Solution Kinetics Database on the Web. http://kinetics.nist.gov/solution/ **2002**.
9. Neta, P.; Huie, R. E.; Ross, A. B., Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1988,** 17, (3), 1027-1284.
10. Mcelroy, W. J., A Laser Photolysis Study of the Reaction of So4- with Cl- and the Subsequent Decay of Cl2- in Aqueous-Solution. *J. Phys. Chem.* **1990,** 94, (6), 2435-2441.
11. Ershov, B. G., Kinetics, mechanism and intermediates of some radiation-induced reactions in aqueous solutions. *Usp. Khim.* **2004,** 73, (1), 107-120.

12. Bjergbakke, E.; Navaratnam, S.; Parsons, B. J.; Swallow, A. J., Reaction between Ho2 and Chlorine in Aqueous-Solution. *J. Am. Chem. Soc.* **1981,** 103, (19), 5926-5928.
13. Matthew, B. M.; Anastasio, C., A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 1 - bromide solutions. *Atmos. Chem. Phys.* **2006,** 6, 2423-2437.
14. Wang, T. X.; Margerum, D. W., Kinetics of Reversible Chlorine Hydrolysis - Temperature-Dependence and General Acid Base-Assisted Mechanisms. *Inorg. Chem.* **1994,** 33, (6), 1050-1055.
15. Siddiqui, M. S., Chlorine-ozone interactions: Formation of chlorate. *Water Res.* **1996,** 30, (9), 2160-2170.
16. Maetzke, A.; Knak Jensen, S. J., Reaction paths for production of singlet oxygen from hydrogen peroxide and hypochlorite. *Chem. Phys. Lett.* **2006,** 425, (1–3), 40-43.
17. Connick, R. E., The Interaction of Hydrogen Peroxide and Hypochlorous Acid in Acidic Solutions Containing Chloride Ion. *J. Am. Chem. Soc.* **1947,** 69, (6), 1509-1514.
18. Lahoutifard, N.; Lagrange, P.; Lagrange, J., Kinetics and mechanism of nitrite oxidation by hypochlorous acid in the aqueous phase. *Chemosphere* **2003,** 50, (10), 1349-1357.
19. Hoigné, J.; Bader, H.; Haag, W. R.; Staehelin, J., Rate constants of reactions of ozone with organic and inorganic compounds in water—III. Inorganic compounds and radicals. *Water Res.* **1985,** 19, (8), 993-1004.
20. Lente, G.; Kalmár, J.; Baranyai, Z.; Kun, A.; Kék, I.; Bajusz, D.; Takács, M.; Veres, L.; Fábián, I., One- Versus Two-Electron Oxidation with Peroxomonosulfate Ion: Reactions with Iron(II), Vanadium(IV), Halide Ions, and Photoreaction with Cerium(III). *Inorg. Chem.* **2009,** 48, (4), 1763-1773.
21. von Gunten, U., Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res.* **2003,** 37, (7), 1469-1487.
22. Peyton, G. R., The free-radical chemistry of persulfate-based total organic-carbon analyzers. *Mar. Chem.* **1993,** 41, (1-3), 91-103.
23. Neta, P.; Huie, R. E., Rate constants for reactions of nitrogen oxide (NO3) radicals in aqueous solutions. *J. Phys. Chem.* **1986,** 90, (19), 4644-4648.
24. Zehavi, D.; Rabani, J., Oxidation of Aqueous Bromide Ions by Hydroxyl Radicals - Pulse Radiolytic Investigation. *J. Phys. Chem.* **1972,** 76, (3), 312-319.
25. Wagner, I.; Strehlow, H., On the Flash-Photolysis of Bromide Ions in Aqueous-Solutions. *PCCP* **1987,** 91, (12), 1317-1321.
26. Mamou, A.; Rabani, J.; Behar, D., Oxidation of Aqueous Br- by Oh Radicals, Studied by Pulse-Radiolysis. *J. Phys. Chem.* **1977,** 81, (15), 1447-1448.
27. Pinkernell, U.; von Gunten, U., Bromate minimization during ozonation: Mechanistic considerations. *Environ. Sci. Technol.* **2001,** 35, (12), 2525-2531.
28. Lutze, H. V.; Bakkour, R.; Kerlin, N.; von Sonntag, C.; Schmidt, T. C., Formation of bromate in sulfate radical based oxidation: Mechanistic aspects and suppression by dissolved organic matter. *Water Res.* **2014,** 53, (0), 370-377.
29. 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.
30. Eigen, M.; Kustin, K., Kinetics of Halogen Hydrolysis. *J. Am. Chem. Soc.* **1962,** 84, (8), 1355-1361.
31. VonGunten, 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.

32. Lahoutifard, N.; Lagrange, P.; Lagrange, J.; Scott, S. L., Kinetics and Mechanism of Nitrite Oxidation by HOBr/BrO- in Atmospheric Water and Comparison with Oxidation by HOCl/ClO. *J. Phys. Chem. A* **2002,** 106, (49), 11891-11896.
33. 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. *J. Phys. Chem. Ref. Data* **1988,** 17, (2), 513-886.
34. Bichsel, Y.; von Gunten, U., Hypoiodous acid: kinetics of the buffer-catalyzed disproportionation. *Water Res.* **2000,** 34, (12), 3197-3203.
35. Li, J.; Jiang, J.; Zhou, Y.; Pang, S.-Y.; Gao, Y.; Jiang, C.; Ma, J.; Jin, Y.; Yang, Y.; Liu, G.; Wang, L.; Guan, C., Kinetics of Oxidation of Iodide (I–) and Hypoiodous Acid (HOI) by Peroxymonosulfate (PMS) and Formation of Iodinated Products in the PMS/I–/NOM System. *Environmental Science & Technology Letters* **2017,** 4, (2), 76-82.
36. Sander, R.; Vogt, R.; Harris, G. W.; Crutzen, P. J., Modelling the chemistry of ozone, halogen compounds, and hydrocarbons in the arctic troposphere during spring. *Tellus B* **1997,** 49, (5), 522-532.
37. Donati, A. Spectroscopic and Kinetic Investigations of Halogen Containing Radicals in the Tropospheric Aqueous Phase. University of Leipzig, Leipzig, Germany, 2002.
38. Troy, R. C.; Margerum, D. W., Non-metal redox kinetics: Hypobromite and hypobromous acid reactions with iodide and with sulfite and the hydrolysis of bromosulfate. *Inorg. Chem.* **1991,** 30, (18), 3538-3543.
39. Criquet, J.; Allard, S.; Salhi, E.; Joll, C. A.; Heitz, A.; von Gunten, U., Iodate and Iodo-Trihalomethane Formation during Chlorination of Iodide-Containing Waters: Role of Bromide. *Environ. Sci. Technol.* **2012,** 46, (13), 7350-7357.
40. Crittenden, J. C.; Hu, S.; Hand, D. W.; Green, S. A., A kinetic model for H2O2/UV process in a completely mixed batch reactor. *Water Res.* **1999,** 33, (10), 2315-2328.
41. 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.
42. Huie, R. E.; Clifton, C. L., Temperature dependence of the rate constants for reactions of the sulfate radical, SO4-, with anions. *J. Phys. Chem.* **1990,** 94, (23), 8561-8567.
43. Zuo, Z. H.; Cai, Z. L.; Katsumura, Y.; Chitose, N.; Muroya, Y., Reinvestigation of the acid-base equilibrium of the (bi)carbonate radical and pH dependence of its reactivity with inorganic reactants. *Radiat. Phys. Chem.* **1999,** 55, (1), 15-23.
44. Huie, R. E.; Clifton, C. L.; Neta, P., Electron-transfer reaction-rates and equilibria of the carbonate and sulfate radical-anions. *Radiat. Phys. Chem.* **1991,** 38, (5), 477-481.
45. National Insititute of Standards and Technology NDRL/NIST Solution Kinetics Database on the Web. http://kinetics.nist.gov/solution/ (accessed August 27, 2013),
46. Acero, J. L.; von Gunten, U., Influence of carbonate on the ozone/hydrogen peroxide based advanced oxidation process for drinking water treatment. *Ozone-Sci Eng* **2000,** 22, (3), 305-328.
47. Draganic, Z. D.; Negronmendoza, A.; Sehested, K.; Vujosevic, S. I.; Navarrogonzales, R.; Albarransanchez, M. G.; Draganic, I. G., Radiolysis of Aqueous-Solutions of Ammonium Bicarbonate over a Large Dose Range. *Radiat. Phys. Chem.* **1991,** 38, (3), 317-321.