## Supporting Information

# Experimental Determination of the Photooxidation of Aqueous I<sup>-</sup> as a Source of Atmospheric I<sub>2</sub>

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#### Method of Hatchard–Parker actinometer

Potassium tris(oxalato) ferrate(III) trihydrate ( $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ ) and sulfuric acid ( $H_2SO_4$ ) were dissolved in deionized water to prepare the solution including  $4.0 \times 10^{-4}$ - $3.0 \times 10^{-2}$  M of potassium tris(oxalato) ferrate(III) (K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]) and 5.0  $\times$  10<sup>-2</sup> M of H<sub>2</sub>SO<sub>4</sub>. Measuring the consumed powers of LED by the digital multi-meter, the all light from LED was irradiated into the 50-cm optical cell filled with the solution including  $K_3$ [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] and H<sub>2</sub>SO<sub>4</sub>. Here the area of irradiation light from LED was typically about 2.3 cm<sup>2</sup>. An aliquot of 10 mL of the solution after the irradiation was diluted by 65.0 mL of deionized water to which 9.91 mg of 1,10phenanthroline  $(C_{12}N_2H_8)$  and 25.0 mL of sulfur acid-sodium acetate buffer solution was added. The buffer solution was prepared with 0.180 M of  $H_2SO_4$  and 0.6 M of sodium acetate (CH<sub>3</sub>CO<sub>2</sub>Na). The mixed solution was sufficiently stirred and was then left to stand in a dark place. After standing for more than a half hour, the solution was poured into a 1-cm square cell and then the absorption spectrum of the solution was measured in the range of 400-700 nm by the absorption spectrophotometer (K-MAC: Lab-Junior). The concentration of tris(1,10-phenantholine) iron(II) ( $[Fe(C_{12}N_2H_8)_3]^{2+}$ ), which is generated by the complex formation of  $Fe(II)^{2+}$  ion and  $C_{12}N_2H_8$  was determined using the value of absorbance at 510 nm where  $[Fe(C_{12}N_2H_8)_3]^{2+}$  has the absorption peak and the reported molar absorption coefficient of  $[Fe(C_{12}N_2H_8)_3]^{2+,S1}$  Here, the values of the quantum yield for the formation of  $Fe(II)^{2+}$  at 365, 405, 436, 468, 480 and 509 nm are reported by Hatchard and Parker<sup>S2</sup>. In present work, the values of the quantum yield for the formation of Fe(II)<sup>2+</sup> at 375, 405, 430, 450 and 470 nm that were necessary to measure photon flux of LEDs by Hatchard–Parker actinometer were not reported. Thus, these values were estimated to be 1.17 at 375 nm, 1.10 at 405 nm, 1.04 at 430 nm, 0.99 at 450 nm and 0.94 at 470 nm by using an interpolation method with the reported values of the quantum yield. Using the concentration of  $[Fe(C_{12}N_2H_8)_3]^{2+}$  which is the same concentration as the concentration of  $Fe(II)^{2+}$  ion photogenerated from K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] by LED irradiation and the reported quantum yield of the photolysis of  $K_3[Fe(C_2O_4)_3]$ , <sup>S2</sup> the photon flux from LED could be determined.

### References

- (S1) Edwards, J. O.; Edwards, K.; Palma, J. The reactions of ferroin complexes. A color-to-colorless freshman kinetic experiment. *J. Chem. Educ.* **1975**, 52(6), 408-409.
- (S2) Hatchard, C. G.; Parker, C. A. A New Sensitive Chemical Actinometer. II. Potassium Ferrioxalate as a Standard Chemical Actinometer. *Proc. R. Soc. Lond. A* **1956**, 235 (1203), 518-536.

#### **Preparation of pH buffer solution**

pH 7.0: 2.9995 g of sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>) was dissolved in about 430 mL of deionized water. After that, 0.20 M of sodium hydroxide (NaOH) aqueous solution was added to the NaH<sub>2</sub>PO<sub>4</sub> solution little by little measuring the pH using a pH meter (HORIBA: D-75). The addition of NaOH aqueous solution into NaH<sub>2</sub>PO<sub>4</sub> solution was halted when the pH reached to 7.0.

pH 8.0: 2.9995 g of NaH<sub>2</sub>PO<sub>4</sub> was dissolved in about 380 mL of deionized water. After that, 0.20 M of NaOH aqueous solution was added to the NaH<sub>2</sub>PO<sub>4</sub> solution up to pH 8.0 in the same way as the case of pH 7.0.

pH 10.0: 1.0501 g of sodium hydrogen carbonate (NaHCO<sub>3</sub>) was dissolved in about 470 mL of deionized water. After that, 0.20 M of NaOH aqueous solution was added to the NaHCO<sub>3</sub> up to pH 10.0 in the same way as the case of pH 7.0.

pH 11.0: 2.1773 g of dipotassium hydrogen phosphate ( $K_2$ HPO<sub>4</sub>) was dissolved in about 490 mL of deionized water. After that, 0.20 M of NaOH aqueous solution was added to the  $K_2$ HPO<sub>4</sub> solution up to pH 11.0 in the same way as the case of pH 7.0.

pH 13.0: 1.8638 g of sodium chloride (NaCl) was dissolved in about 170 mL of deionized water. After that, 0.20 M of NaOH aqueous solution was added to the NaCl solution up to pH 13.0 in the same way as the case of pH 7.0.

### Chemicals for Hatchard–Parker actinometer and pH buffer solution

All reagents were obtained from commercial sources.  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  (Alfa Aesar: 90%),  $H_2SO_4$  (Kanto Chemical Co., Inc.: >96%),  $C_{12}N_2H_8 \cdot H_2O$  (Wako Pure Chemical Industries, Ltd: >99%),  $CH_3CO_2Na$  (Kanto Chemical Co., Inc.: >98.5%),  $NaH_2PO_4$  (Wako Pure Chemical Industries, Ltd: >98.0%), NaOH (Kanto Chemical Co., Inc.: >97.0%),  $NaHCO_3$  (Kanto Chemical Co., Inc.: >99.5%),  $K_2HPO_4$  (Kanto Chemical Co., Inc.: >99.0%) and NaCl (Kanto Chemical Co., Inc.: >99.5%) were used as received without further purification.

No.	Reactions	Lifetimes $(\tau_n)$ determined from pseudo-first-order rate constants of each reaction	Derivation methods and values used for lifetimes		
1	$I_{(aq)} + h\nu(UV \text{ or } Vis) \rightarrow I^{*}_{(aq)}$	$\tau_1 = 5.6 \times 10^7 \text{ s}$	$\tau_1 = 1/k_{\text{photooxidation}} = 1/(v_1/[I_{(aq)}])^a, v_1 = d[I_{2(g)}]/dt = 1.8 \times 10^{-15} \text{ mol } \text{L}^{-1} \text{ s}^{-1} ^b,$ $[I_{(aq)}] = 1.0 \times 10^{-7} \text{ mol } \text{L}^{-1} ^c$		
2	$I^{*}_{(aq)} \rightarrow [I + e^{-}]_{(aq)}$	$\tau_2$ < a few ns	$\tau_2$ is very fast step because this reaction is an internal electron migration.		
3	$[I + e^{-}]_{(aq)} + H^{+}_{(aq)} \longrightarrow I_{(aq)} + H_{(aq)}$	$\tau_3 = 1.0 \times 10^{-2}  \mathrm{s}$	$\tau_3 = 1/(k_3[\mathrm{H}^+_{(\mathrm{aq})}]), k_3 \approx 1.0 \times 10^{10} \mathrm{L} \mathrm{mol}^{-1} \mathrm{s}^{-1} \mathrm{d}, [\mathrm{H}^+_{(\mathrm{aq})}] = 1.0 \times 10^{-8} \mathrm{mol} \mathrm{L}^{-1} (\mathrm{at} \mathrm{pH} 8.0)$		
4	$[I + e^{-}]_{(aq)} + O_{2(aq)} \rightarrow I_{(aq)} + O_{2^{-}(aq)}$	$ au_4 = 4.5  imes 10^{-7}  { m s}$	$\tau_4 = 1/(k_4[O_{2(aq)}]), k_4 \approx 1.0 \times 10^{10} \text{ Lmol}^{-1} \text{ s}^{-1 d}, [O_{2(aq)}] = 2.2 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ (at DO 7.0 mg } \text{L}^{-1})$		
5	$I_{(aq)} + I_{(aq)} \xrightarrow{\longrightarrow} I_{2}(aq)$	$ au_{5} = 1.1  imes 10^{-3}  m s$	$\tau_5 = 1/(k_5[I_{(aq)}]), k_5 = 8.9 \times 10^9 \mathrm{Lmol^{-1}} \mathrm{s^{-1}}^{e},  [I_{(aq)}] = 1.0 \times 10^{-7} \mathrm{mol} \mathrm{L^{-1}}^{c}$		
6	$2I_2(aq) \rightarrow I_3(aq) + I(aq)$	$\tau_6 = 2.4 \times 10^5 \text{ s}$	$\tau_6 = 1/(k_6[I_2]_{(aq)}), k_6 = 2.3 \times 10^9 \text{ Lmol}^{-1} \text{ s}^{-1}{}^e, [I_2]_{(aq)} = 1.8 \times 10^{-15} \text{ mol } \text{ L}^{-1}{}^f$		
7	$2I_{(aq)} \rightarrow I_{2(aq)}$	$\tau_7~=3.7\times10^4~{\rm s}$	$\tau_7 = 1/(k_7[I_{(aq)}]), k_7 = 1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1 g}, [I_{(aq)}] = 1.8 \times 10^{-15} \text{ mol } \text{L}^{-1 f}$		
8	$I_{(aq)} + I_2(aq) \rightarrow I_3(aq)$	$\tau_8~=1.2\times10^5~{\rm s}$	$\tau_8 = 1/(k_8[I_{(aq)}]), k_8 = 4.6 \times 10^9 \mathrm{Lmol^{-1}} \mathrm{s^{-1}}^g, [I_{(aq)}] = 1.8 \times 10^{-15} \mathrm{mol}\mathrm{L^{-1}}^f$		
9	$I_3^{-}(aq) \longrightarrow I_2(aq) + I^{-}(aq)$	$ au_9 = 1.3  imes 10^{-7}  m s$	$\tau_9 = 1/k_9^{\text{forward}}, k_9^{\text{forward}} = K_9 k_9^{\text{reverse}} = 7.5 \times 10^6 \text{ s}^{-1}, k_9^{\text{reverse}} = 5.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1 g}, K_9 = 1.34 \times 10^{-3} \text{ mol } \text{L}^{-1 g}$		

Table S1. Comparison of the pseudo-first rates of each reaction step in the process of the formation of  $I_{2(g)}$  from the photooxidation of  $I_{(aq)}$ .

*a*:  $k_{\text{photoxidation}}$  and  $v_1$  are the photooxidation rate constant of  $\Gamma_{(aq)}$  and the reaction rate of the reaction step 1, respectively. *b*: The value of  $v_1$  is considered to be  $d[I_{2(g)}]/dt$ , which is determined in the present work. *c*:  $[\Gamma_{(aq)}]$  is the maximum value of the typical concentration of  $\Gamma_{(aq)}$  in the sea. *d*: These values have not been reported and are analogized using the rate constants of reactions of  $e_{(aq)} + H^+_{(aq)} \rightarrow H_{(aq)}$  ( $k = 2.3 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ ) and  $e_{(aq)} + O_{2(aq)} \rightarrow O_{2^-(aq)}$  ( $k = 1.9 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ ) reported in ref. S3. *e*: This value is reported in ref. S4. *f*: Here, the value of either  $[I_{2^-(aq)}]$  or  $[I_{(aq)}]$  is set as the concentration determined by the amount of either  $I_{2^-(aq)}$  or  $I_{(aq)}$  formed from the photooxidation of  $\Gamma_{(aq)}$  per one second. Their values are calculated using  $d[I_{2(g)}]/dt$  from the photooxidation of  $\Gamma_{(aq)}$  determined in the present work. *g*: This value is reported in ref. S5.

#### Table S1 references

(S5) Elliot, A. J. A pulse radiolysis study of the reaction of OH with  $I_2$  and the decay of  $I_2^-$ . Can. J. Chem. 1992, 70(6), 1658-1661.

<sup>(</sup>S3) 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<sup>-</sup>) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, 17(2), 513-886.

<sup>(</sup>S4) Liu, Y.; Sheaffer, R. L.; Barker, J. R. Effects of Temperature and ionic strength on the rate and equilibrium constants for the reaction  $I_{aq}^{\bullet} + I_{aq}^{\bullet} \leftrightarrow I_2^{\bullet} A_{aq}$ . J. Phys. Chem. A 2003, 107(48), 10296-10302.

	$\mathcal{E}_{iodide}(\lambda)$		$\mathcal{E}_{iodide}(\lambda)$		Evolution $\lambda$		$\mathcal{E}_{\text{rodide}}(\lambda)$
λ / nm	$/ 10^{-2} \text{ M}^{-1}$	λ / nm	$/ 10^{-2} \text{ M}^{-1}$	λ / nm	/ 10 <sup>-2</sup> M <sup>-1</sup>	λ / nm	$/ 10^{-2} \text{ M}^{-1}$
/ 1111	cm <sup>-1</sup>	/ IIII	cm <sup>-1</sup>	· · · · · · · · · · · · · · · · · · ·	cm <sup>-1</sup>		cm <sup>-1</sup>
290	2.04	324	0.76	358	0.46	392	0.21
291	1.97	325	0.75	359	0.45	393	0.21
292	1.89	326	0.73	360	0.45	394	0.20
293	1.83	327	0.71	361	0.44	395	0.20
294	1.77	328	0.70	362	0.43	396	0.19
295	1.72	329	0.69	363	0.42	397	0.19
296	1.67	330	0.68	364	0.42	398	0.18
297	1.63	331	0.67	365	0.41	399	0.18
298	1.59	332	0.66	366	0.40	400	0.17
299	1.54	333	0.65	367	0.39	401	0.17
300	1.51	334	0.64	368	0.38	402	0.17
301	1.46	335	0.63	369	0.37	403	0.16
302	1.41	336	0.63	370	0.36	404	0.16
303	1.36	337	0.62	371	0.36	405	0.15
304	1.33	338	0.61	372	0.35	406	0.15
305	1.28	339	0.60	373	0.34	407	0.15
306	1.24	340	0.60	374	0.33	408	0.14
307	1.19	341	0.59	375	0.33	409	0.14
308	1.16	342	0.58	376	0.32	410	0.14
309	1.12	343	0.57	377	0.31	411	0.13
310	1.09	344	0.57	378	0.30	412	0.13
311	1.05	345	0.56	379	0.29	413	0.13
312	1.02	346	0.55	380	0.29	414	0.13
313	0.98	347	0.54	381	0.28	415	0.12
314	0.94	348	0.54	382	0.28	416	0.12
315	0.90	349	0.53	383	0.27	417	0.11
316	0.87	350	0.52	384	0.26	418	0.11
317	0.86	351	0.51	385	0.25	419	0.11
318	0.84	352	0.51	386	0.25	420	0.11
319	0.83	353	0.50	387	0.25	421	0.10
320	0.82	354	0.20	388	0.23	422	0.10
321	0.80	355	0.49	389	0.24	422 423	0.10
321	0.00	355	0.48	300	0.23	-123 1121	0.10
323	0.77	357	0.47	391	0.22	425	0.09

Table S2. Values of molar absorption coefficient of iodide ion in aqueous phase in the region of 290-425 nm.

λ / nm	$\mathcal{E}_{\text{iodide}}(\lambda)$ / 10 <sup>-2</sup> M <sup>-1</sup> cm <sup>-1</sup>	λ / nm	$\mathcal{E}_{\text{iodide}}(\lambda)$ / 10 <sup>-2</sup> M <sup>-1</sup> cm <sup>-1</sup>	λ / nm	$\mathcal{E}_{\text{iodide}}(\lambda)$ / 10 <sup>-2</sup> M <sup>-1</sup> cm <sup>-1</sup>	λ / nm	$\mathcal{E}_{\text{iodide}}(\lambda)$ / 10 <sup>-2</sup> M <sup>-1</sup> cm <sup>-1</sup>
426	0.09	445	0.06	464	0.03	483	0.01
427	0.09	446	0.06	465	0.03	484	0.01
428	0.09	447	0.05	466	0.01	485	0.01
429	0.08	448	0.05	467	0.00	486	0.01
430	0.08	449	0.04	468	0.02	487	0.01
431	0.08	450	0.05	469	0.02	488	0.01
432	0.08	451	0.04	470	0.02	489	0.01
433	0.08	452	0.04	471	0.01	490	0.00
434	0.08	453	0.05	472	0.00	491	0.00
435	0.07	454	0.04	473	0.01	492	0.00
436	0.07	455	0.04	474	0.02	493	0.00
437	0.07	456	0.03	475	0.02	494	0.00
438	0.06	457	0.03	476	0.02	495	0.00
439	0.06	458	0.04	477	0.02	496	0.00
440	0.06	459	0.04	478	0.02	497	0.00
441	0.06	460	0.03	479	0.01	498	0.00
442	0.06	461	0.03	480	0.00	499	0.00
443	0.06	462	0.03	481	0.01	500	0.00
444	0.06	463	0.03	482	0.00		

Table S3. Values of molar absorption coefficient of iodide ion in aqueous phase in the region of 426-500 nm.

	The value				
	)	Generation from the surface reaction of $I_{(aq)}^{-}$ with $O_{3(g)}$			
Reporters	This work	Truesdale <sup>S6</sup> Miyake and Tsunogai <sup>S7</sup>		Carpenter et al. <sup>S8</sup>	
Experimental conditions to note	pH 5.6, DO 7.8 mg L <sup>-1</sup> artificial seawater				
	$2.2 \times 10^{-8} \times [I_{(aq)}]_{sea} = 1.8 \times 10^{-8} \times [I_{(aq)}]_{sea}$				
Monthly average of $I_{2(g)}$ generation rate / mol L <sup>-1</sup> Month <sup>-1</sup>	$1.4 \times 10^{-9}$ a, b	$7.2 \times 10^{-9}$			
Annual global emission of $I_{2(g)} \ / \ Gg \ year^{\text{-}1}$	392 <sup><i>a</i>, <i>c</i></sup>		400	$\sim 3.7  imes 10^{3  d,  e} \ (340^{ d, f})$	
Experimental methods and procedures for the estimation of $I_{2(g)}$ generation rate.	The values are estimated using the determined values of $\varepsilon_{\text{lodide}}(\lambda)$ and $\Phi_{\text{lodide}}(\lambda)$ .	The values are determined from the observation of the formation of $I_{3^-(aq)}$ by the irradiation of sun light into KI aqueous solution.	The values are determined from the observation of the formation of gaseous $I_{2(g)}$ by the irradiation of UV lamp with filters that transmit 250-560 nm into sea water.	The generations of HOI and $I_2$ by the surface reaction of $I_{(aq)}$ with $O_{3(g)}$ are experimentally measured by the spectrometry and the iodine oxide particle detection. The emission of HOI and $I_2$ were estimated by using model calculations.	

Table S4. Values of  $I_2$  generation rate and annual global emission of  $I_2$  estimated from our experimental results and reported by other studies.

*a*: This value is calculated by using  $1 \times 10^{-7}$  mol L<sup>-1</sup> as the maximum value of the typical concentration of  $\Gamma_{(aq)}$  in the sea. *b*: This value is calculated being multiplied the value of  $I_{2(g)}$  generation rate per second with SZA0° by  $2.592 \times 10^6$  s month<sup>-1</sup> and 0.25 which is the correction factor of sunlight intensity meaning that the ratio of monthly average of sunlight intensity to sunlight intensity at noon. *c*: This value is calculated being multiplied the value of monthly average of  $I_{2(g)}$  generation rate by 12.17 months year<sup>-1</sup> and  $3.628 \times 10^{18}$  cm<sup>2</sup> (sea surface area of earth) and 254 (molecular weight) assuming that the sea depth contributing the  $I_{2(g)}$  formation is 30 cm. *d*: This value is calculated being multiplied the reported value ( $7 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup>) by  $3.154 \times 10^7$  s year<sup>-1</sup> and  $3.628 \times 10^{18}$  cm<sup>2</sup> (sea surface area of earth) and 254 (molecular weight) and then being divide by  $N_A$ . *e*: This value is the sum of the emissions of I<sub>2</sub> and HOI. *f*: This value is only emission of I<sub>2</sub>.

## Table S4 references

(S6) Truesdale, V. W. On the feasibility of some photochemical reactions of iodide in seawater. Marine Chem. 2007, 104 (3-4), 266-281.

(S7) Miyake, Y.; Tsunogai, S. Evaporation of Iodine from the Ocean. J. Geophys. Res. 1963, 68 (13), 3989-3993.

(S8) Carpenter, L. J.; MacDonald, S. M.; Show, M. D.; Kumar, R.; Saunders, R. W.; Parthipan, R.; Wilson, J.; Plane, J. M. C. Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine. *Nat. Geosci.* 2013, 6, 108-111.



**Figure S1.** Schematic diagram of the experimental setup of UV-Vis absorption spectrometry. PMT and AD converter stand for photomultiplier tube and analog-to-digital converter, respectively.



Figure S2. Absorption spectra of 0.50 M of KI aqueous solutions at pH 5.6 prepared using deionized water, which were bubbled with either (a)  $O_2$  (DO 7.8 mg L<sup>-1</sup>) or (b)  $N_2$  (DO 0.8 mg L<sup>-1</sup>) for more than one hour under dark conditions. The measurements were conducted at room temperature and atmospheric pressure.



**Figure S3.** The plots of the concentrations of  $I_{3^{-}(aq)}$  formed from the photooxidation of iodide ions by the 375-nm LED (~2.0 × 10<sup>15</sup> photons cm<sup>-2</sup> s<sup>-1</sup>) as a function of the irradiated photon fluence in the case of using (a) NaI and (b) KI aqueous solution. The solid lines are the linear least-squares fits.



Figure S4. The plots of the generation rate of  $I_{3^-(aq)}$  formed from the photooxidation of iodide ions by the 375-nm LED (~2.0 × 10<sup>15</sup> photons cm<sup>-2</sup> s<sup>-1</sup>) as a function of the several concentrations of  $I^-_{(aq)}$  at pH 5.6, DO 7.8 mg L<sup>-1</sup>, and ambient temperature. The solid line is the linear least-squares fits.



Figure S5. The plot of the concentrations of  $I_{3^{-}(aq)}$  formed from the photooxidation of iodide ions by the 375-nm LED (~2.0 × 10<sup>15</sup> photons cm<sup>-2</sup> s<sup>-1</sup>) as a function of the irradiated photon fluence in the case of using artificial seawater (pH 8.0, DO 7.0 mg L<sup>-1</sup>) as the solvent. The solid line is the linear least-squares fits for the data after induce period.