

# Supporting Information of

## Direct emission of I<sub>2</sub> molecule and IO radical from the heterogeneous reactions of gaseous ozone with aqueous potassium iodide solution

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### SI text

#### *Experimental details*

The cavity ring-down mirrors (Research Electro-Optics, 7.8 mm dia. and 1 m curvature) had a specified maximum reflectivity of 0.9994 and were mounted 1.04 m apart. Light leaking from the end mirror was detected by a photomultiplier tube (Hamamatsu Photonics, R212UH) through a band pass filter. The ring-down signal of the light intensity was recorded in a personal computer. The decay of the light intensity is represented by equation (I)<sup>1</sup>;

$$I(t) = I_0 \exp(-t/\tau) = I_0 \exp(-t/\tau_0 - \sigma Nctl/L), \quad (\text{I})$$

where  $I_0$  and  $I(t)$  are the light intensities at time 0 and  $t$ , respectively.  $\tau_0$  is the cavity ring-down time without any absorbed species (about 20  $\mu\text{s}$  at 435 nm),  $\tau$  the measured cavity ring-down time with absorbed species,  $c$  the velocity of light,  $l$  and  $L$  are the length of the reaction surface where absorbers are considered to be present ( $l = 70 \pm 10$  cm) and the length between mirrors ( $L = 104$  cm),  $N$  and  $\sigma$  are the concentration and absorption cross section of the species of interest, respectively. Each ring-down trace was digitized with a time resolution of 100 MHz. The digitized traces were transferred to a personal computer and averaged over 16 runs to calculate the ring-down rate,  $\tau^{-1}$ .

Note that the reaction system is under dark condition. We confirmed that the effect of interior roof lamps was negligible. Furthermore, when the probe light intensity, measured before the entrance of a mirror, was changed between 0.25 to 0.50 mJ, the IO(g) and I<sub>2</sub>(g) yields were constant within 2%. Thus, the influence of the probe CRD beam intensity in the cavity was negligible to photolyze/activate any reactions. It should be noted that the diameter change from 2.1 to 9.6 cm did not influence on the results, such as the IO(g) and I<sub>2</sub>(g) yields. This means that no any wall-reactions are important under the present conditions. The scattering effect of water vapor on the CRD signal was below 3%. A freshly prepared KI(aq) solution was used for the every measurement, that is, each data point in the present figures was obtained with newly prepared solution to reduce the effect of the accumulative products in the solution. We confirmed that the IO(g) and I<sub>2</sub>(g) signal intensities were the same by O<sub>3</sub>(g) exposure for total solution-gas contact time for at least 120 s. Thus, no solution-aging was observed during the ozonation under the present condition. For each data point of the figures, at least three experiments were performed and confirmed the reproducibility.

KI, I<sub>2</sub>, and KBr were obtained from Nacalai Tesque (> 99.5 %), Wako pure chemical industries (> 99.9 %), and Nacalai Tesque (> 99 %), respectively, and diluted by ultra-purity deionized water. N<sub>2</sub> (> 99.999%, Teisan) and UHP O<sub>2</sub> (> 99.995%, Teisan) were used without further purification.

#### *Measurement of the effective uptake coefficient for O<sub>3</sub>(g) on KI(aq) solution*

The effective uptake coefficient,  $\gamma_{\text{eff}}$ , for O<sub>3</sub>(g) on the KI solution was obtained by measurements of the decrease of [O<sub>3</sub>(g)] during the average contact time,  $t = 0.70$  s. The  $\gamma_{\text{eff}}$  is determined as follows. Since the first-order rate constant  $k_r$  (s<sup>-1</sup>) for the heterogeneous reaction is related to the number of collisions s<sup>-1</sup> on the KI(aq) surface and the fraction of those collisions that go to uptake,  $\gamma_{\text{eff}}$ , the concentration of O<sub>3</sub>(g) removed at the KI(aq) surface per second is given by:

$$\frac{d[O_3(g)]}{dt} = k_r[O_3(g)] = \gamma_{\text{eff}} \frac{A(u_{\text{av}}/4)}{V}[O_3(g)] \quad (\text{II})$$

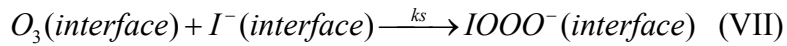
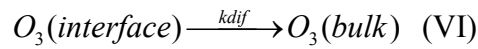
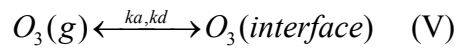
where  $A$  (cm<sup>2</sup>) is the KI(aq) surface area,  $u_{\text{av}}$  is the mean thermal speed of the O<sub>3</sub>(g),  $(8RT/\pi m)^{0.5} \sim 3.6 \times 10^4$  cm s<sup>-1</sup>, and  $V$ (cm<sup>3</sup>) is the volume of gas over the KI(aq) solution. Thus, the measured loss rate of O<sub>3</sub>(g) is first order with respect to [O<sub>3</sub>(g)] and therefore obeys following the relationship:

$$\ln\left(\frac{[O_3(g)]_i}{[O_3(g)]_f}\right) = \gamma_{eff} \frac{A(u_{av}/4)}{V} t \quad (III)$$

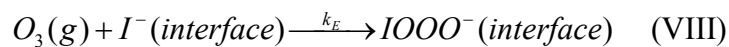
thus,  $\gamma_{eff}$  is given by,

$$\gamma_{eff} = \frac{\ln([O_3(g)]_i/[O_3(g)]_f)}{A/V(u_{av}/4)t} \quad (IV)$$

where  $[O_3(g)]_i$  and  $[O_3(g)]_f$  are the initial concentration of  $O_3(g)$  measured by Hg-lamp at before entrance and the concentration over the KI(aq) solution measured by CRDS, respectively, and  $t$  is the reaction time. The values used for calculation are  $270 \text{ cm}^3$  for  $V$  and  $100 \text{ cm}^2$  for  $A$ , respectively. Normally, the concentration of  $O_3(g)$  after the reaction cell should be used as  $[O_3(g)]_f$  for  $\gamma_{eff}$  measurement. Unfortunately, the accumulative  $I_2$  contamination on the wall of down-stream cell interferes the accurate  $[O_3(g)]_f$  measurement. Hence, we use the concentration in the gas/liquid interaction cell measured by CRDS which must be approximately twice of the actual  $[O_3(g)]_f$ . Figures 5A and 5B show the  $\gamma_{eff}$  plot as a function of  $[O_3(g)]$  and  $[KI]$ , respectively. In this reaction, two  $O_3$  uptake mechanisms are considered. One is a Langmuir-Hinshelwood mechanism, in which  $O_3(g)$  is once adsorbed on the water surface, then  $O_3(interface)$  reacts with  $I^-$ .



The other one is an Eley-Rideal mechanism, in which  $O_3(g)$  directly reacts with  $I^-$  on the interface.



Here, we consider that O<sub>3</sub> uptake proceeds via a Langmuir-Hinshelwood mechanism,<sup>2</sup> rather than Eley-Rideal mechanism. If an Eley-Rideal mechanism could happen, the  $\gamma_{eff}$  plot as a function of [O<sub>3</sub>(g)] should be independent of [O<sub>3</sub>(g)],<sup>2</sup> which is disaccord with the present observation in Fig. 5A. A log-log plot of Fig. 5A yields a linear line, implying a Langmuir-Hinshelwood mechanism is more likely than an Eley-Rideal mechanism (see Fig. 6 in Ref.2).<sup>2</sup>

We can obtain the uptake coefficient for a Langmuir-Hinshelwood mechanism by dividing the net loss on the surface by the gas-surface collision rate, [O<sub>3</sub>(g)]  $u_{av}/4$ .

$$\gamma_{eff} = \frac{4(k_s[I^-(interface)] + k_{dif})[O_3(interface)]}{u_{av}[O_3(g)]} \quad (IX)$$

where  $k_s$  is the reaction rate on the surface between [I<sup>-</sup>(interface)] and [O<sub>3</sub>(g)] and  $k_{dif}$  is the diffusion rate to the bulk. Under steady-state condition, the rate of adsorption can be equated to the net rate of desorption, reaction on the surface and diffusion to the bulk. Then, a Langmuir equilibrium for O<sub>3</sub> adsorption onto the surface is obtained by:

$$k_a[O_3(g)](1 - \theta) = (k_d + k_s[I^-(interface)] + k_{dif})\theta / \sigma \quad (X)$$

then,

$$\theta = \frac{K[O_3(g)]}{1 + K[O_3(g)]} \quad (XI)$$

where  $\theta = [O_3(interface)]\sigma$  means the ratio of occupied sites of water surface by O<sub>3</sub>, and  $\sigma$  is the surface area occupied by one O<sub>3</sub> molecule. The Langmuir constant,  $K$ , is given by:

$$K = \frac{k_a\sigma}{k_d + k_s[I^-(interface)] + k_{dif}} \quad (XII)$$

Using eqn.(XVIII) and (XIX), eqn (XVI) can be rearranged to

$$\gamma_{eff} = \frac{4(k_s[I^-(interface)] + k_{dif})K}{u_{av}\sigma(1 + K[O_3(g)])} \quad (XIII)$$

Assuming  $K[O_3(g)] \gg 1$ ,  $\gamma_{eff}$  can be modified as

$$\gamma_{eff} \approx \frac{4(k_s[I^-(interface)] + k_{dif})}{u_{av}\sigma} \frac{1}{[O_3(g)]} \quad (XIX)$$

The solid line in Fig. 5A shows a fitting of the data to an eqn (XIX), and the data is well fitted with the curve. Here, we assume that  $[\Gamma(interface)]$  is in equilibrium with  $[\Gamma(bulk)]$ , so that  $[\Gamma(interface)]$  is not linear to  $[\Gamma(bulk)]$  due to surface-segregation effects. Then, a Langmuir equilibrium for  $\Gamma$  segregation onto the surface is obtained by:

$$k_a'[I^-(bulk)](1 - \theta') = k_d'\theta' / \sigma' \quad (XX)$$

then,

$$\theta' = \frac{K'[I^-(bulk)]}{1 + K'[I^-(bulk)]} \quad (XXI)$$

where  $\theta' = [\Gamma(interface)]\sigma'$  means the ratio of occupied sites of water surface by  $\Gamma$ , and  $\sigma'$  is the surface area occupied by one  $\Gamma$  ion.  $[O_3(aq)]$  estimated from the Henry constant is much smaller than  $[\Gamma(bulk)]$  and  $[\Gamma(interface)]$ . Thus, in eqn. (XX), attribution of the reaction of  $\Gamma(interface) + O_3(interface)$  to equilibrium is assumed to be negligible. The Langmuir constant,  $K'$ , is given by:

$$K' = \frac{k_a'\sigma'}{k_d'} \quad (XXII)$$

Using eqn.(XXI) and (XXII), eqn (XIX) can be rearranged to:

$$\gamma_{eff} \approx \frac{4k_s}{u_{av}\sigma\sigma'[O_3(g)]} \left( \frac{K'[I^-(bulk)]}{1 + K'[I^-(bulk)]} \right) + \frac{4k_{dif}}{u_{av}\sigma[O_3(g)]} \quad (XIII)$$

The solid line in Fig. 5B shows a fitting of the data to an eqn. (XIII), and the data is well fitted with the curve again.

## References

1. Enami, S.; Hoshino, Y.; Ito, Y.; Hashimoto, S.; Kawasaki, M.; Wallington, T. J., *J. Phys. Chem. A* **2006**, 110, 3546-3551.
2. McCabe, J.; Abbatt, J. P. D., *J. Phys. Chem. C* **2009**, 113, 2120-2127.