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Iodine Emission in the Presence of Humic Substances at the Water's Surface

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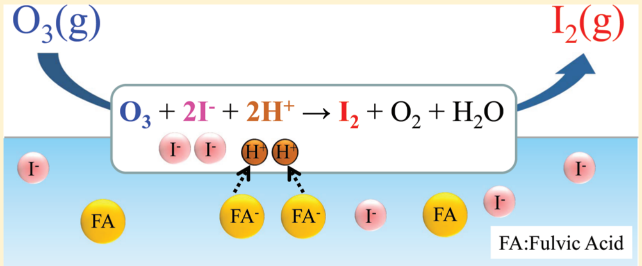

ABSTRACT: Humic substances that preferentially adsorb at the air/water interfaces of water or aerosols consist of both fulvic and humic acid. To investigate the chemical reactivity for the heterogeneous reaction of gaseous ozone, $O_3(g)$, with aqueous iodide, $I^-(aq)$, in the presence of standard fulvic acid, humic acid, or alcohol, cavity ring-down spectroscopy was used to detect gaseous products, iodine, $I_2(g)$ and an iodine monoxide radical, $IO(g)$. Fulvic acid enhanced the $I_2(g)$ production yield, but not the $IO(g)$ yield. Humic acid, *n*-hexanol, *n*-heptanol, and *n*-octanol did not affect the yields of $I_2(g)$ or $IO(g)$. We can infer that the carboxylic group contained in fulvic acid promotes the $I_2(g)$ emission by supplying the requisite interfacial protons more efficiently than water on its surface.

INTRODUCTION

Heterogeneous reaction at the air/water interface plays ubiquitous and fundamental roles in atmospheric chemistry involving reactive gas uptake on the aerosol/seawater surface. Since the hydrophobic components of humic substances are expected to be preferentially adsorbed at the air/water interfaces of water or aerosols with their hydrophobic parts pointing to the gas phase,[1−6] the chemical and physical properties (e.g., uptake, reaction rate, surface tension, and interfacial composition) of the surface should be affected by the surfactants.[5−12] Humic substances cannot be described in specific molecular terms because of their complex, multicomponent nature, but three fractions (humic acid (HUA), fulvic acid (FA), and humin) have been obtained on the basis of solubility characteristics. HUA is not soluble in water under acidic conditions ($pH < 2$) but is soluble at higher pH values. FA is soluble in water under all pH conditions. It remains in solution after removal of HUA by acidification. Humin is not soluble in either a strong base or a strong acid. The major functional groups in humic substances are carboxyl, phenolic hydroxyl, and alcoholic hydroxyl groups.[13−15] It is found in rivers, lakes, sea, groundwater, etc.[13] Fine aerosols, including FA and HUA, are generated by the wind and transported in the troposphere.[16,17]

Active halogen species in the air, such as halogen atoms and halogen monoxide radicals, affect the gaseous composition of the atmosphere, depleting ozone, controlling the HO_x/NO_x cycle, and producing cloud condensation nuclei in the atmosphere.[16,18−22] We have proposed on the basis of a stepwise mechanism of $I_2(g)$ and the iodine oxide radical, $IO(g)$, emission at the interface layers via rapid reaction of O_3 with $I^-(aq)$ under dark conditions using cavity ring-down spectroscopy (CRDS) combined with a gas−liquid interaction cell.[23−25]

$$I^- + O_3(\text{g or aq}) \rightarrow IOOO^- \tag{1}$$

$$IOOO^- \rightarrow IO^- + O_2 \tag{2a}$$

$$IOOO^- \rightarrow \rightarrow IO(g) + \text{products} \tag{2b}$$

$$IO^- + H^+ \rightleftarrows HOI(aq) \quad (pK_a = 10.8) \tag{3}$$

$$HOI(aq) + I^- + H^+ \rightleftarrows I_2(aq) + H_2O \tag{4}$$

$$I_2(aq) \rightarrow I_2(g) \tag{5}$$

In this study, we have studied the chemical reactivity of FA, HUA, and fatty alcohols at the air/water interface layers for the $O_3(g) + I^-(aq)$ reaction using CRDS detection of gaseous products $I_2(g)$ and $IO(g)$. The present results are compared with previously proposed production schemes for $I_2(g)$ and $IO(g)$.[23−25]

EXPERIMENT

The principle of CRDS and the experimental details, including the present CRDS setup combined with a gas−liquid interaction cell, were presented in our previous publications.[23−26] Ozone was produced by O_2 with 1 sL min^{-1} (standard liter per minute) flowing through a high-pressure discharge ozonizer. Its concentrations were monitored by UV absorption with a 253.7 nm Hg lamp prior to the gas−liquid

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interaction cell. Gas flow rates were controlled by mass flow controllers so that the total flow rate was maintained at 3 sL min^{-1} with N_2 gas acting as a buffer. The typical concentration of $O_3(g)$ was 3.0×10^{15} molecules cm^{-3}. The product concentrations were monitored with a Nd^{3+}:YAG pumped dye laser (Lambda Physik, SCANmate) at 435.60 nm for the IO(g) band head of the $A\ ^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ ($v' = 3$, $v'' = 0$) transition and absorption cross section = 5.9×10^{-17} cm^2 $molecule^{-1}$.[27] The IO signal baseline was taken at 435.4 nm, a region in which there was no IO absorption. $I_2(g)$ concentration was monitored at 435.4 nm for the B–X band and calibrated by introducing a concentration-known $I_2(g)$ into the reaction cell with spectral fitting at 430–455 nm for the B–X band. The observed concentrations were $(1.2–1.5) \times 10^{11}$ molecules cm^{-3} for IO(g) and $(1.8–8.2) \times 10^{13}$ molecules cm^{-3} for $I_2(g)$.

The gas–liquid interaction cell was a Pyrex glass container (21 mm i.d. and 60 cm length). No secondary wall reactions occurred.[23,24] The cell was maintained at 100 torr by means of a rotary pump, a mechanical booster pump, and a $N_2(l)$ trap in tandem. NaI(aq) solution ([NaI] = 5 mM unless otherwise stated, volume = 20 mL) was poured 5 ± 1 mm above the bottom of the reaction cell. The CRDS detection region is 6 mm above the solution surface. The gas in the cell was completely replaced within a time interval of 0.70 s. Hence, the average contact time of $O_3(g)$ with the NaI(aq) solution was 0.70 s. To minimize possible secondary reactions, a freshly prepared solution was used to measure each data point, except for the concentration measurement as a function of reaction time (see below). FA (Standard II, International Humic Substances Society), HUA (Wako), malonic acid (Wako), hexanoic acid (Alfa Aesar), and sodium iodide (Sigma-Aldrich) were used. The solution or bulk pH was adjusted by adding HCl/KOH and measured using a pH meter.

The standard concentration of FA was 2.0 g L^{-1}, except for [FA]-dependence measurements (Figure 2). When HA or phenol were added, the concentrations were 4 and 1 mM, respectively. Corresponding to the ratio of charge density of the carboxylic and phenolic groups in FA, a mixture of 4 mM HA and 1 mM phenol was prepared, the details of which are described in the Discussion.

RESULTS

In the measurements of $I_2(g)$ concentration as a function of the measurement time, t, after introducing O_3 into the cell, the enhancement of $I_2(g)$ emission in the presence of FA or HA was observed during ozonolysis of a NaI solution, initially at pH 3.3, as shown in Figure 1. The $I_2(g)$ concentrations promptly increased upon introducing O_3 into the cell and then decayed asymptotically. The $I_2(g)$ concentration increased with [FA] at least from 0.5 up to 2.0 g L^{-1} at the initial pH 3.3 when $I_2(g)$ signals were monitored at t = 15 s, as shown in Figure 2. At t = 3 min, the pH of the reacted solution slightly changed from the initial value of 3.3 to an end value of 3.7 (with 2.0 g L^{-1} FA), appreciably from 3.3 to 5.1 with 4 mM HA, and greatly from 3.3 to 10.3 without acids. In the case of 3 min ozonolysis of FA solution without NaI, any 434–435 nm light-absorbing species did not appear, and a pH change from the initial value did not occur.

Figure 3 shows the $I_2(g)$ concentrations (monitored at t = 15 s) with/without FA or HA as a function of initial pH. The $I_2(g)$ concentrations increased up to 5-fold below pH ~ 5 in the presence of FA or HA. On the other hand, the IO(g) concentrations remain constant (within 20%) in the entire pH range 3–10.

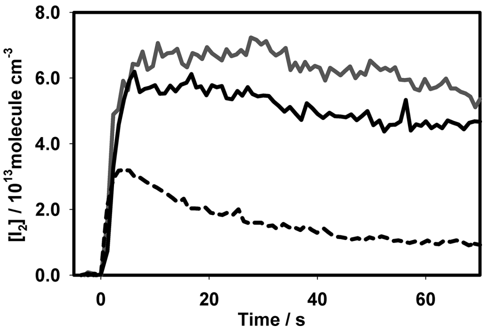

Figure 1. Gaseous iodine concentrations $[I_2(g)]$ during ozonolysis of 5 mM aqueous NaI solutions in the absence/presence of added fulvic acid or hexanoic acid: dashed line, pH 3.3; solid line, in the presence of 2.0 g L^{-1} fulvic acid at pH = 3.3; solid gray line, in the presence of 4 mM hexanoic acid at pH = 3.3.

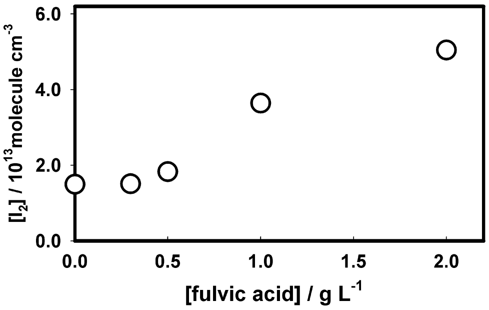

Figure 2. Gaseous iodine concentrations, $[I_2(g)]$, as a function of fulvic acid concentration in ozonolysis of 5 mM NaI solutions at initial bulk pH 3.3, which are measured 15 s after the introduction of 3.0×10^{15} molecules cm^{-3} $O_3(g)$.

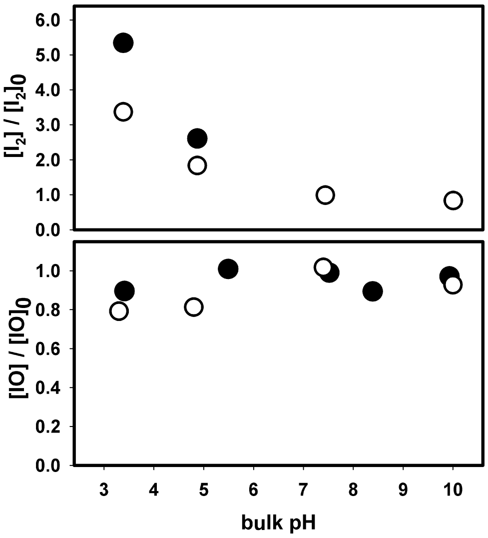

Figure 3. Effects of bulk pH on the yields of I_2 (upper panel) and IO (lower panel) in ozonolysis of 5 mM NaI solutions, which are measured 15 s after $O_3(g)$ introduction as a function of initial bulk pH. $[I_2]$ and [IO] in the presence of 2.0 g L^{-1} fulvic acid (open circle) or 4 mM hexanoic acid (solid circle); $[I_2]_0$ and $[IO]_0$ in the absence of added acids.

Figure 4(A–D) shows the ratios of IO(g) and $I_2(g)$ concentrations after ozonolysis of NaI solution in the

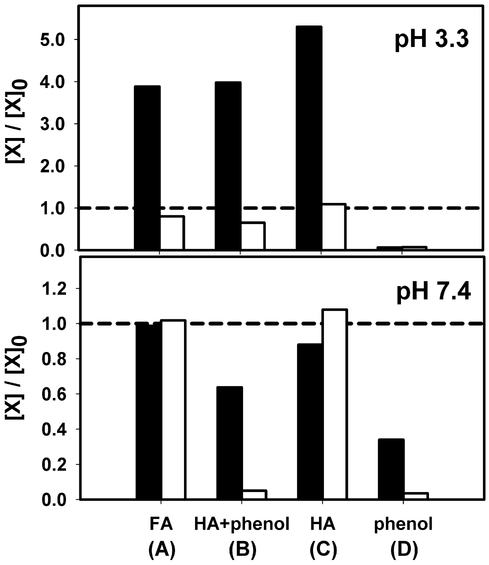

Figure 4. Effects of acids and bulk pH on the yields of I_2 (black bar) and IO (white bar) in ozonolysis of 5 mM NaI solutions, measured 15 s after $O_3(g)$ introduction at an initial pH of 3.3 (upper panel) and 7.4 (lower panel). [X] represents $[I_2]$ or [IO] in the presence of (A) 2.0 g L^{-1} fulvic acid, (B) 4 mM hexanoic acid and 1 mM phenol mixture, (C) 4 mM hexanoic acid, and (D) 1 mM phenol; $[X]_0$ represents $[I_2]_0$ or $[IO]_0$ in the absence of added acids and phenols.

absence/presence of (A) FA, (B) a mixture of HA and phenol, (C) HA, and (D) phenol at pH 3.3 and pH 7.4. Under acidic conditions, the $I_2(g)$ emission was enhanced in the cases of A–C, but was suppressed by the addition of phenol in D. The IO(g) emission was suppressed in B and D, but not in A or C. Under neutral conditions, the $I_2(g)$ and IO(g) emission were not affected in A and C, but were suppressed in B and D. In addition, the unchanged concentrations for $I_2(g)$ and IO(g) were observed at pH = 10.0 in A. The addition of HUA (~3.0 g L^{-1}) or fatty alcohols (~10 mM) to the NaI solution also did not affect the $I_2(g)$ emission in the pH range of 3.3–10. Table 1 summarizes the effects of various cosolutes on the formation of IO(g) and $I_2(g)$ during ozonolysis of NaI solutions in the absence/presence of humic substances, phenols, weak acids, and alcohols. Phenols suppressed the $I_2(g)$ and IO(g) emission, and weak acids enhanced it.

To investigate the reduction of I_2/I^- and I_3^-/I^- by FA, we prepared a 2.0 g L^{-1} solution and an I_2 saturated NaI solution.[29] Three hours after mixing the two solutions at pH 5.8, no appreciable change in the pH was found.

■ DISCUSSION

Our previous study reported suppression of $I_2(g)$ and IO(g) emission in the presence of phenols at pH > 3 as a result of fast proton transfer at the air/water interface.[24] Interfacial reactions of $I^-(aq) + O_3(g)$ and subsequent reactions consume protons, resulting in a changing interfacial pH from acidic/neutral to basic via reactions 3 and 4. Phenol (pK_a = 10.0), *p*-methoxyphenol (10.3), or *p*-cresol (10.2) suppressed the $I_2(g)$ and IO(g) emission as a result of the acid dissociation of phenols and rapid reaction of phenolates with O_3 at the interface layer.[30,31]

$$C_6H_5OH \rightarrow C_6H_5O^- + H^+ \tag{6}$$

$$C_6H_5O^- + O_3(\text{g or aq}) \rightarrow C_6H_5O + O_3^- \tag{7}$$

$$C_6H_5OH + O_3(\text{g or aq}) \rightarrow \text{products} \tag{8}$$

By contrast, the $I_2(g)$ emission is enhanced via the efficient interfacial proton transfer in the presence of organic weak acids when the initial pH is adjusted to the individual pK_a[25]

$$IO^- + HA \rightleftarrows HOI(aq) + A^- \tag{9}$$

$$HOI(aq) + I^- + HA \rightleftarrows I_2(aq) + H_2O + A^- \tag{10}$$

The surface-active acids, for example, HA or octanoic acid (OA), by situating their C(O)OH groups closer to the interface[5−11] provide accessible proton donors to IO^-/HOI at the air/water interface and more effectively enhance the $I_2(g)$ emission. Hayase et al. measured ratios of $I_2(g)$ concentrations in the presence of 4 mM HA, OA, and acetic acid (AA) over those measured in their absence.[25] They found that these ratios, *R*, follow in the order of *R*(OA) > *R*(HA) ≫ *R*(AA), which represents direct evidence that the heterogeneous ozonation of I^- proceeds mainly in the air/water interfacial layers, since the

Table 1. Effects of Cosolutes on the Formation Rates of IO(g) and $I_2(g)$ in the Reaction of I^- with O_3(g or aq)

	cosolute	concn (mM)	pK_a[2,28]	$k_{O_3}/M^{-1}s^{-1}$[30,44]	IO[a]	I_2[a]	ref
humic substances	fulvic acid	0.5–2.0 g L^{-1}	*d*		N	E[b]	this work
3 < pH < 10	humic acid	3.0 g L^{-1}			N	N	this work
phenols	phenol	0.2–1.0	10	1.3×10^3	S	S	24
3 < pH < 11	*p*-cresol	0.5	10.3	3.0×10^4	S	S	24
	p-methoxyphenol	0.5	10.2	3.0×10^4	S	S	24
acids	hexanoic acid	1–25	4.8	$\leq 0.48 \times 10^{-3}$	N	E	25
3 < pH < 5	octanoic acid	4–10	4.8	$\leq 2.5 \times 10^{-3}$	N	E	25
	malonic acid	4–10	2.9[e]	7	N	E[c]	25
	acetic acid	4–10	4.8	$\leq 3 \times 10^{-3}$	N	N	25
alcohols	*n*-butyl alcohol	5	17.1	0.58	N	N	24
3 < pH < 10	*tert*-butyl alcohol	100	17.2	3.0×10^{-3}	N	N	24
	n-hexyl alcohol	1–10	*f*		N	N	this work
	n-heptyl alcohol	1–10	*f*		N	N	this work
	n-octyl alcohol	1–10	*f*	≤ 0.8	N	N	this work

[a] E, S, and N stand for enhancement, suppression, and no effect, respectively. [b] 3.3 < pH < 4.8. [c] 3 < pH < 6. [d] pK_1 ~ 1.8, pK_2 ~ 3.4, pK_3 ~ 4.2, and pK_4 ~ 5.7. [e] pK_{a2} is 5.7. [f] These values are estimated to be larger than 17.2 on the basis of the fact that acids with the larger alkyl groups weaken acidity.

more tensioactive acids, by placing their CO(O)H groups closer to the interface and providing proton donors accessible to IO^-/HOI at the air/water interfacial layers in the pH range where water itself is a poorer donor, should enhance $I_2(g)$ concentrations.

In the presence of FA, the enhancement of $I_2(g)$ emissions was also observed during ozonolysis of a NaI solution via a similar reaction mechanism in the presence of organic weak acids.

$$IO^- + FA \rightleftarrows HOI(aq) + FA^- \tag{11}$$

$$HOI(aq) + I^- + FA \rightleftarrows I_2(aq) + H_2O + FA^- \tag{12}$$

FA and HUA have a range of apparent molecular weights, solubilities and acid strengths.[14,15,32,33] Charge density analysis enables us to estimate the amounts of dissolved carboxylic and phenolic groups in FA or HUA.[14] Charge densities (meq g^{-1} C^{-1}) of both the carboxylic and phenolic groups were determined by the titration technique.[34] The charge density of carboxylic groups was measured at pH 8.0, and that of phenolic groups were 2 times the change in charge density between pH 8.0 and 10.0.[34] According to the acidic functional group analysis of the standard FA, Standard II, charge densities of the carboxylic and phenolic groups are 11.17 and 2.84 meq g^{-1} C^{-1}, respectively. $I_2(g)$ emission from the ozonolysis of NaI solutions in the presence of 4 mM HA and 1 mM phenol, which is a ratio similar to the charge density of the carboxylic and phenolic groups in FA, is enhanced in acidic conditions (pH 3.3) because the HA dissociation via reactions 9 and 10 is preferable to the phenol dissociation via reaction 6 (Figure 4B). In neutral/basic conditions, the emission of $I_2(g)$ and IO(g) are suppressed, since O_3 is consumed by phenolate and phenol via reactions 7 and 8 and HA cannot provide accessible interfacial protons (Figure.4B).

At pH 7.4, there will be a combination of phenol and phenolate, which can react with O_3. These aqueous rate constants with O_3 are $k_8 = 1.3 \times 10^3$ M^{-1} s^{-1} for phenol and $k_7 = 1.4 \times 10^9$ M^{-1} s^{-1} for phenolate. The total aqueous rate constant at pH 7.4 is $\sim 10^7$ M^{-1} s^{-1}, which depends on how much of each form is present and the respective rate constants. The aqueous rate constant of I^- with O_3 is $k_1 = 2 \times 10^9$ M^{-1} s^{-1}.[35] Under the conditions of Figure 4, the concentrations of I^- and phenol are 5 and 1 mM, respectively. Therefore, the ozone loss rates of $O_3(aq)$ with $I^-(aq)$ and phenol(aq) are 1×10^7 and 1×10^4 s^{-1} at pH 7.4, respectively, and hence, the reaction of I^- with O_3 dominates. Note that these are bulk phase kinetics.

In contrast, the phenolic group of FA does not suppressed IO(g) or $I_2(g)$ emission under neutral/basic conditions (Figure.4A), whereas the enhancement effect of the carboxylic group is observed at an initial bulk pH < 5. The experimental results suggest that the enhancement and suppression effects depend not only on the charge densities of the carboxylic and phenolic groups, but also on other physical or chemical properties. No suppression effects on IO(g) or $I_2(g)$ emission by the phenolic groups in FA may be caused by reactivity of ozone toward aromatic compounds, which is known to be highly dependent on the charge density of the compounds.[36] Since the structures of large phenolic compounds in humic substances vary, unlike simple phenols, their respective reactivities toward ozone could also vary. Moreover, for large macromolecules, the reaction rate constants of ozone with reactive sites are limited because of the steric hindrance effect. IO(g) concentrations remain constant (within 20%), as shown in Figure 3. The results imply that the proton, H^+, is not involved in IO(g) emission, since reaction 2b may involve several steps.[23]

Unchanged $I_2(g)$ and IO(g) concentrations caused by HUA addition were observed in the pH range of 3.3−10. The dissolution rate of HUA is strongly dependent on the pH. The dissolution rate, even at pH 4 and 5, is very slow, and it may take several years to achieve equilibration.[37] HUA does not promptly provide a proton.

With the addition of 2.0 g L^{-1} FA, the bulk pH slightly changed from the original 3.3 to the final 3.7 during the experiment because the acid provides H^+ in the I_2 formation processes to prevent proton depletion. The bulk pH of the NaI solution mixed with FA is supposed to be maintained by the rich amount of carboxylic groups, apparent in the charge density study.[14] To investigate the buffering capacity of FA, we prepared a 2.0 g L^{-1} solution and an I_2-saturated NaI solution. Although the reaction of the I_2/I_3^- reduction by FA was reported to generate I^- and H^+,[29] no appreciable change in the bulk pH was observed by mixing the saturated I_2/I_3^- solution with a 2.0 g L^{-1} FA solution. FA has many functional groups, which may act as buffer solutions, to keep a certain pH level nearly constant during the reduction. No bulk pH change was observed in the heterogeneous experiment of $O_3(g)$ with 2.0 g L^{-1} FA only, which means that the reaction products during ozonolysis of FA do not change the bulk pH. These results imply that FA effectively buffers the system in these time scales under the present experimental conditions.

By assuming a universal neutralization rate constant value of $k(X^- + H^+)_{aq} \sim 1 \times 10^{10}$ M^{-1} s^{-1}, the rate constants for the reverse acid dissociations become: $k_d \sim 1 \times 10^{10-pKa}$ M^{-1} s^{-1}. Acid dissociation rates in the presence of the Armadale Horizons Bh fulvic acid are 1.6×10^8 s^{-1} for pK_1, 4.0×10^6 s^{-1} for pK_2, 6.3×10^5 s^{-1} for pK_3, and 2.0×10^4 s^{-1} for pK_4,[16] which are comparable with that of HA $k_d \sim 1.6 \times 10^5$ s^{-1}. This is consistent with the present experimental results that the presence of FA at the air/water interface effectively buffers the system to prevent proton depletion and sustain the $I_2(g)$ production rate.

As for atmospheric implications, organic compounds that coexist with I^- in the aqueous phase should be taken into account for estimation of iodine emission toward the atmosphere, as summarized in Table 1. The presence of organic compounds may change the air−water interfacial property; surface-active organics (e.g., fatty acids and alcohols) are known to significantly retard the evaporation of water and penetration of atmospheric gases through the interface.[5−11] However, the IO(g) and $I_2(g)$ concentrations were unaffected by the addition of octanol that coats the solution surface. The results summarized in Table 1 for organic compounds imply that the interfacial rapid reaction of I^- with gaseous O_3 depends on chemical reaction processes such as the competitive reaction with O_3 or H^+ provision for the $I_2(g)$ formation pathways as well as the physical state of the surface.

■ CONCLUSION

Humic substances, which consist of carboxylic and phenolic groups, are widely distributed in estuaries and coastal regions where biogenic-produced iodide is also richly contained.[15,17,38−40] Fulvic acid enhances the $I_2(g)$ concentrations via interfacial proton transfer in the interfacial reaction of $I^-(aq)$ with O_3(g or aq). The proposed enhancement mechanism is similar to that of the weak organic acids in the heterogeneous reaction of I^- with ozone in the pH range of 3−5.[25] However, humic acid does not affect this. This difference is due to the fact that humic acid precipitates under acidic conditions.

The atmospheric precipitation study indicates that typical atmospheric aerosols are mildly acidic as a result of the uptake of acidic gas, such as carbon dioxide and nitric acid, or acidified in situ by the oxidation of dissolved S(IV), even in clean marine air. Moreover, aerosols are expected to be strongly acidified in urban areas where polluted with acidic gases, such as nitrogen oxide or sulfur oxide.[41−45] The enhancement of the $I_2(g)$ concentrations by the undissociated carboxylic group in the pH range from 3 to pK_a and suppression of the IO(g) and $I_2(g)$ emission occur in ambient atmospheric air as a result of the high reactivity of simple phenols with O_3 at pH > 3.[30,31] The widely distributed aqueous fulvic acid accelerates the $I_2(g)$ emission in the pH range of 3−5. Thus, the acidity of I^- containing aerosols and chemical species control iodine transfer between water and air.

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Notes

The authors declare no competing financial interest.

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