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# Mechanism of Chemiluminescence Reaction between Hypobromite and Ammonia or Urea

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The reaction kinetics, the chemiluminescence spectra, the products, and the lifetimes of emission species for the chemiluminescence reaction between hypobromite and ammonia or urea in an alkaline aqueous solution were investigated. Results show that the reaction mechanism for ammonia chemiluminescence is different from that for urea. The reaction of ammonia and hypobromite produces $NO_2$ in the gaseous phase and $NO_2^-$ in solution; however, the reaction of urea and hypobromite does not. For the reaction of ammonia and hypobromite, chemiluminescence intensity obeys 1.5 order kinetics for hypobromite concentration when ammonia is in excess, but the reaction of urea and hypobromite obeys second order kinetics for hypobromite when urea is in excess. The spectrum of the chemiluminescence from the ammonia and urea with hypobromite shows a maximum intensity at 710, and at 510 nm, respectively. The chemiluminescence lifetimes of the emission species were 0.056 and 0.092 s for the reaction of ammonia and the reaction of urea, respectively. The chemiluminescence species of the reaction between hypobromite and ammonia seems to be excited $NO_2$, that for urea seems to be excited $N_2$.

The reaction between ammonia and hypochlorite is well known due to importance in the process of disinfection of tap water[1] and in the manufacture of hydrazine.[2] It was reported that the products of the reaction of ammonia with hypochlorous acid were nitrogen trichloride, dichloramine, and monochloramine.[3] If the solution is strongly basic, the reaction between hypochlorite and ammonia produces molecular nitrogen ($N_2$). Therefore, this reaction was used to analyze ammonia by measuring the molecular nitrogen produced[4] or by a titrimetric method.[5,6] The reaction between hypobromite and ammonia is similar to that of hypochlorite, and produces monobromamine, dibromamine, and nitrogen tribromide in aqueous solution.[7,8] If the solution is strongly basic, the reaction between hypobromite and ammonia produces molecular nitrogen, as in the case for the reaction between hypochlorite and ammonia. Limited numbers of investigations on the mechanism of the reaction between urea and hypochlorite or hypobromite have been reported, and it has been found that the reactions produce nitrogen in alkaline solution.[9,10]

Recently, we found that the reaction between hypobromite and ammonium ion,[11] the reaction between hypobromite and urea,[12] and the reaction between hypobromite and humic acid[13] produce light emission. The intensity for the chemiluminescence between urea and hypobromite is almost 100 times higher than that for ammonia in the same concentration with urea. There were also some reports on the chemiluminescent detection of isoniazid[14] and derivatives of hydrazine[15] by oxidation with *N*-bromosuccinimide. *N*-bromosuccinimide contains a positively charged bromine atom and it is assumed that its oxidizing properties may result to produce hypobromous acid when *N*-bromosuccinimide is hydrolyzed. However, the reaction mechanism of chemiluminescence by the reaction of hypobromite or *N*-bromosuccinimide has not been identified yet. In this paper, the chemiluminescence spectra, the products, the kinetics, the species which emit the chemiluminescence, and the scheme of the chemiluminescence reaction are discussed.

## Experimental

**1. Apparatus and Procedure.** The chemiluminescence intensity was measured by the same chemiluminescence/flow injection analysis system as described in our previous study.[11] The time profiles of the chemiluminescences were measured using a stopped flow system,[11] mixing of two 0.100-$cm^3$ reagent solutions and tracing the change of chemiluminescence intensity.

To obtain a spectrum, the chemiluminescence was resolved by a grating spectrometer (Opto-Line 310.01/L) with 30-nm spectral resolution, and then detected by a photon counter (C1230 Hamamatsu Photonics K.K.) using a photomultiplier R-649 (Hamamatsu Photonics K.K.) as described in our previous study.[11] The chemiluminescence cell was a straight glass tube (i.d. 2 mm, o.d. 3 mm). The straight glass tube was placed just in front of the entrance slit of the spectrometer. A concentric double tube mixer, similar to the previous study,[11] is connected to the straight glass tube. Sodium hypobromite solution of 0.2 mol $dm^{-3}$ was used for the measurements of chemiluminescence spectra. The chemiluminescence intensities for the reactions between hypochlorite and ammonia or urea were so weak that the chemiluminescence spectra could not be measured by the equipment used in this investigation.

NO and $NO_2$ of gaseous products were measured by a chemiluminescent $NO_x$ detector (model-265P, Kimoto Electric Co., Ltd., Osaka, Japan). The schematic diagram of the experimental setup

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for detecting NO and $NO_2$ is shown in Fig. 1. After 10 $cm^3$ of 0.2 $mol\,dm^{-3}$ sodium hypobromite solution containing 0.5 $mol\,dm^{-3}$ sodium hydroxide was injected into the reactant solution (100 $cm^3$ of 1.0 $mol\,dm^{-3}$ ammonium chloride solution or 0.5 $mol\,dm^{-3}$ urea solution). The gases evolved were swept into a chemiluminescent $NO_x$ detector by continuous nitrogen carrier gas flow (0.5 $dm^3\,min^{-1}$). The analysis of anions produced in the solution phase were done as follows: 1.0 ml of 0.02 $mol\,dm^{-3}$ sodium hypobromite solution containing 0.2 $mol\,dm^{-3}$ sodium hydroxide was allowed to react with 10 ml of a solution of 0.002 $mol\,dm^{-3}$ ammonium sulfate or 0.001 $mol\,dm^{-3}$ urea solution in a test tube. After the reaction was completed, the pH of the solution was adjusted to about 7.5 with sulfuric acid solution and diluted to 50 ml with distilled water. Then analysis of the anion products was done using an ion chromatographic analyzer (Yokogawa IC-7000, Yokogawa Electronics Co., Tokyo, Japan).

Ultraviolet absorption of the reaction mixture were measured by a UV-1600 spectophotometer (Shimadzu Co., Kyoto, Japan) with a spectral resolution of 1 nm. Fluorescence spectra of the reaction mixture were measured by a Hitachi MPF-4 spectophotofluorometer. Measurements of pH were done with a glass electrode pH-meter (Cos pH-Meter/CP-1).

**2. Reagents.** Hypobromite solution was prepared by adding saturated bromine water or liquid bromine (99%) to cold sodium hydroxide solution. Hypochlorite solution was prepared by diluting commercially available hypochlorite solution with distilled water. The concentrations of hypobromite and hypochlorite were measured by the thiosulfate–iodide titrimetric method. Ammonium solution was obtained by dissolving ammonium chloride or ammonium sulfate into distilled water. Urea solution was prepared by dissolving urea into distilled water. All chemicals used were research grade, obtained from Wako Pure Chemicals Co., (Osaka, Japan) and used without further purification.

## Results and Discussion

**1. Hypobromite and Hypochlorite.** Hypohalite ions can be produced in principle by dissolving halogens in cold base according to the following general reaction scheme;

$$X_2 + 2OH^- = X^- + OX^- + H_2O \qquad (1)$$

and the equilibrium constants are all favorable to produce hypohalite ions. The constants for $Cl_2$ and for $Br_2$ at 25 °C are $7.5\times10^{15}$ and $2\times10^8$, respectively, and the reactions are rapid.[16] For saturated solutions of the halogens in water at 25 °C, the equilibrium concentrations of $[Cl_2]$ and $[Br_2]$ are 0.061 and 0.21 $mol\,dm^{-3}$, [HOCl] and [HOBr] are 0.030 and $1.15\times10^{-3}$ $mol\,dm^{-3}$ in aqueous solutions.[16] Hypochlorite, hypobromite, and their acids are good oxidizing agents, especially in acid solution, and this accounts for their ability to disinfect drinking water and for wide industrial use for bleaching and sterilizing.

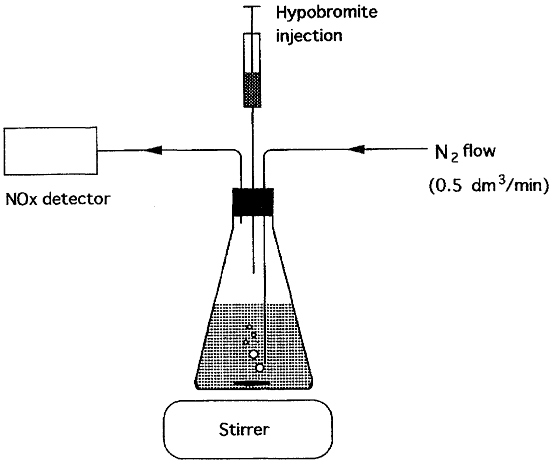

Fig. 1. Schematic diagram of reaction system for detecting products NO and $NO_2$.

**2. Relation of Ammonia Formation from the Hydrolysis of Urea and Chemiluminescence of Hypobromite with Urea.** Urea undergoes hydrolysis in the presence of base, acid, or enzyme, to produce ammonia or ammonium ion as described following equations:[10]

$$(NH_2)_2CO + 2OH^- \rightarrow 2NH_3 + CO_3^{2-} \qquad (2)$$

$$(NH_2)_2CO + 2H^+ + H_2O \rightarrow 2NH_4^+ + CO_2 \qquad (3)$$

$$(NH_2)_2CO + H_2O \xrightarrow{\text{urease}} 2NH_3 + CO_2 \qquad (4)$$

This implies that the chemiluminescence observed in the reaction of hypobromite and urea is perhaps caused by the chemiluminescent reaction of hypobromite and ammonia; urea is first converted into ammonia by hydrolysis, and then ammonia reacts with hypobromite to produce chemiluminescence. To examine this possibility, ammonia concentrations of urea solution in the pH range used in this study were measured by the indophenol spectrophotometric method.[17] The result is shown in Fig. 2. Relative chemiluminescence intensities of the reaction between urea and hypobromite in various concentrations of sodium hydroxide solutions are superimposed in Fig. 2 for comparison. Dependence of ammonia yields in the hydrolysis of urea to pH of the solution is different from that of the relative chemiluminescence intensities of the reaction between urea and hypobromite. Judging from this result, it is concluded that the chemiluminescence produced by the reaction between hypobromite and urea is not caused by formation of ammonia in the hydrolysis of urea.

**3. Lifetime of the Chemiluminescence.** Time profiles of the chemiluminescence from reaction $OBr^- + NH_3$ and reaction $OBr^- + (NH_2)_2CO$ were measured by the stopped flow system. Chemiluminescence intensity vs. reaction time after mixing of 0.2 $mol\,dm^{-3}$ ammonium chloride solution with 0.2 $mol\,dm^{-3}$ sodium hypobromite solution is shown in Fig. 3. Within 20 ms after the mixing, maximum chemiluminescence intensity was obtained, and the chemiluminescence was extinguished within 120 ms. For the reaction between hypobromite and urea, the chemiluminescence reached its maximum intensity at 70 ms and was extinguished within 400 ms as shown in Fig. 3. Differences of the rise and decay profiles of the chemiluminescence between urea and ammonia suggests that species emitting the chemiluminescence may be different for the two reaction systems. The lifetime of the emission species for the reaction between urea

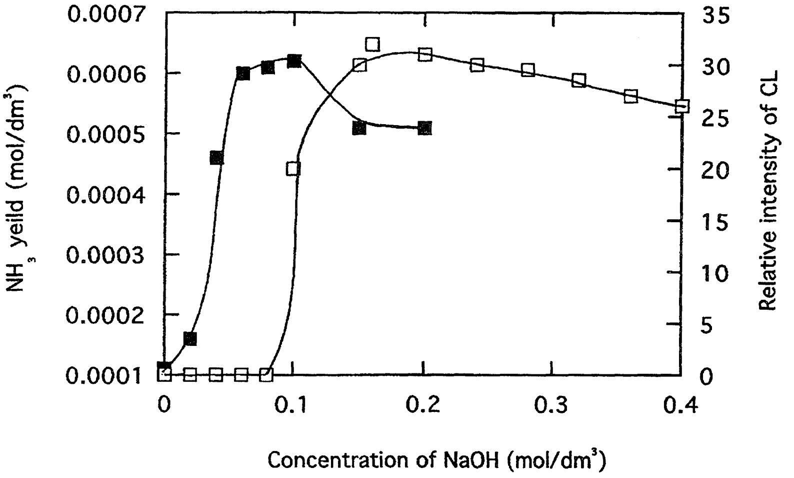

Fig. 2. Comparison of ammonia yield by the hydrolysis of urea with the chemiluminescence intensity in the reaction between hypobromite and urea under various concentrations of sodium hydroxide solution. Filled square: Ammonia yields by the hydrolysis of 0.050 mol dm$^{-3}$ urea. Open square: Relative chemiluminescence intensity 0.010 mmol dm$^{-3}$ urea reacted with 0.040 mol dm$^{-3}$.

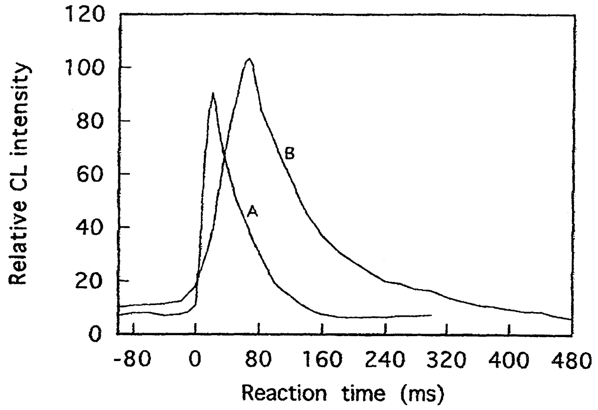

Fig. 3. Time profile of the chemiluminescence from the reaction between ammonia and hypobromite and the chemiluminescence from the reaction between urea and hypobromite. Curve A: ammonium chloride, 0.2 mol dm$^{-3}$; sodium hypobromite, 0.2 mol dm$^{-3}$; sodium hydroxide, 1.0 mol dm$^{-3}$. Curve B: urea, 0.05 mol dm$^{-3}$; sodium hypobromite, 0.04 mol dm$^{-3}$; sodium hydroxide, 0.2 mol dm$^{-3}$.

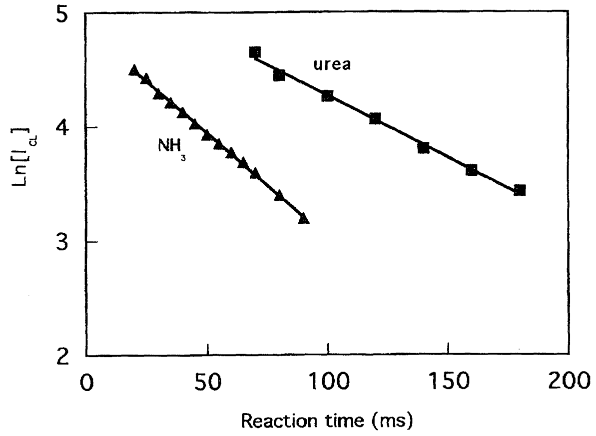

Fig. 4. Logarithmic plot of the chemiluminescence intensity vs. reaction time for the reaction of hypobromite with ammonia or urea. Triangle: ammonia + hypobromite; ammonium chloride, 0.2 mol dm$^{-3}$; sodium hypobromite, 0.2 mol dm$^{-3}$; sodium hydroxide, 1.0 mol dm$^{-3}$. Square: urea + hypobromite; urea, 0.2 mol dm$^{-3}$; sodium hypobromite, 0.04 mol dm$^{-3}$, sodium hydroxide, 0.2 mol dm$^{-3}$. Solid line: Linear regression of each plots, $\log[I_{CL}]=4.86-0.0183t$ for ammonia and $\log[I_{CL}]=5.36-0.0109t$ for urea ($t$: the reaction time in ms).

and hypobromite is longer than that for the reaction between ammonium ion and hypobromite. Drawing the ln [$I_{CL}$] ($I_{CL}$ represents the chemiluminescence intensity, the same hereinafter) vs. time plot for both chemiluminescence reactions as shown in Fig. 4, the constants of decay of the chemiluminescence were obtained to be 18.3 and 10.9 s$^{-1}$, and the chemiluminescence lifetimes of the emission species were 0.056 and 0.092 s for the reaction $OBr^- + NH_3$ and the reaction $OBr^- + (NH_2)_2CO$, respectively.

**4. Products of Chemiluminescence Reactions.** It is well known that ammonia or urea is oxidized by hypobromite to produce nitrogen gas in alkaline solution. To discover the role of nitrogen compounds in this reaction, the nitrogen containing products of the reactions in solution phase or gaseous phase were measured. Ion chromatographic analysis of the products in the reaction between hypobromite with ammonium sulfate or urea demonstrated that the reaction between ammonium ion and hypobromite forms nitrite and small amounts of nitrate and that the reaction between urea and hypobromite forms an unidentified anion and small amounts of nitrite. Typical ion chromatogram of products in the ammonia reaction is shown in Fig. 5. Measurement of gaseous products of the reactions also showed the difference between the two chemiluminescence reactions. Nitrogen dioxide and small amounts of nitrogen monoxide were detected in the gaseous products of the reaction between hypobromite and ammonium ion, while very small amounts of nitrogen dioxide and no nitrogen monoxide were detected in the gaseous products of the reaction between hypobromite and urea. Analytical results of gaseous products are summa-

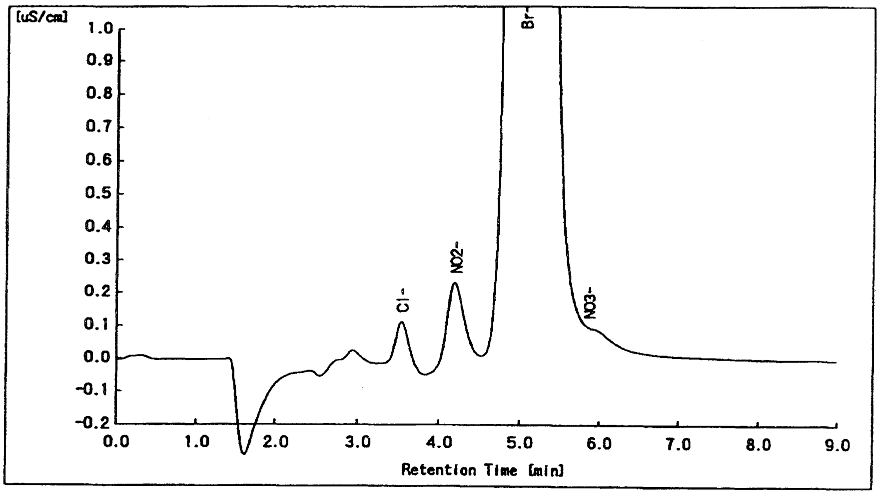

Fig. 5. Ion chromatogram of the reaction mixture of ammonium sulfate and hypobromite.

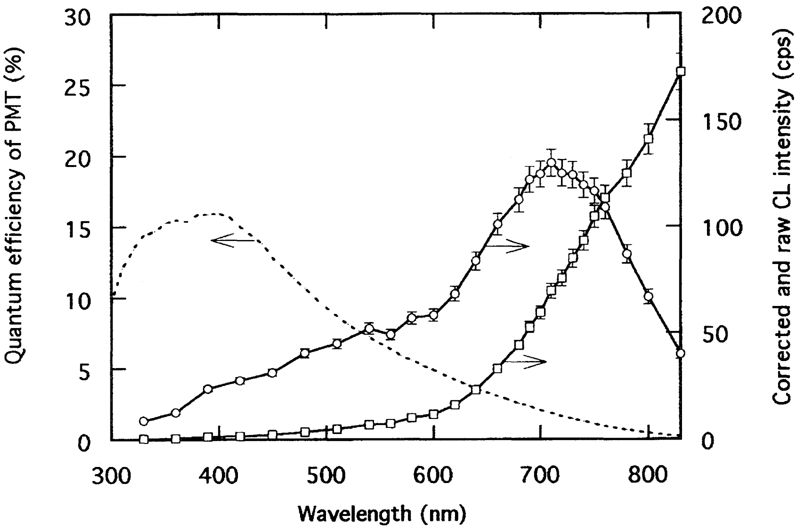

Fig. 6. Chemiluminescence spectra by the reaction $NH_3+OBr^-$. Open circle: Raw spectrum from the reaction of 1.0 mol dm$^{-3}$ of ammonium chloride + 0.2 mol dm$^{-3}$ of sodium hypobromite containing 1.0 mol dm$^{-3}$ sodium hydroxide. Open square: Spectrum corrected for a bias due to the quantum efficiency of the photomultiplier tube R-649. Broken line: quantum efficiency of the R-649 photomultiplier.

rized in Table 1.

**5. Chemiluminescence Spectra.** Spectra of the chemiluminescence produced by the reaction between hypobromite and ammonium ion and by the reaction between hypobromite and urea are illustrated in Figs. 6 and 7, respectively. The quantum efficiency of the photomultiplier tube R-649 used in this experiment to the wavelength is also illustrated in Figs. 6 and 7. For the wavelength over 800 nm, uncertainty of the measurement is large due to low PMT sensitivity. Therefore, discussion here is limited to 800 nm and below. The spectrum of the chemiluminescence from ammonium ion reaction shows a broad band spreading from 600 nm to more than 800 nm with a peak at about 710 nm. The spectrum of the chemiluminescence produced by the urea reaction shows a broad band from 400 to 700 nm with a structure. The maximum emission of urea was at 510 nm.

As reported, the spectrum of the CL between NO and $O_3$ is also a broad emission from 600 to 3000 nm with a peak at 1200 nm.[18,19] The quantum efficiency of the photomultiplier tube used in this investigation is very poor after 800 nm as shown in Figs. 6 and 7. The raw spectra (open circles) of the chemiluminescence reactions were corrected by the quantum efficiency of the photomultiplier. It can be seen that the corrected chemiluminescence spectrum (open squares) between hypobromite and ammonium ion is very similar with the chemiluminescence spectrum of the reaction between NO and $O_3$ in the range from 600 to 800 nm.

**6. Relationship between Chemiluminescence Intensity and the Reactant Concentrations.** The relationship between the chemiluminescence intensity and the reactant concentrations was investigated using the flow injection analysis system. By exchanging streams of hypobromite solution and carrier solution and controlling the reactant concentrations, hypobromite can be produced in excess of ammoni-

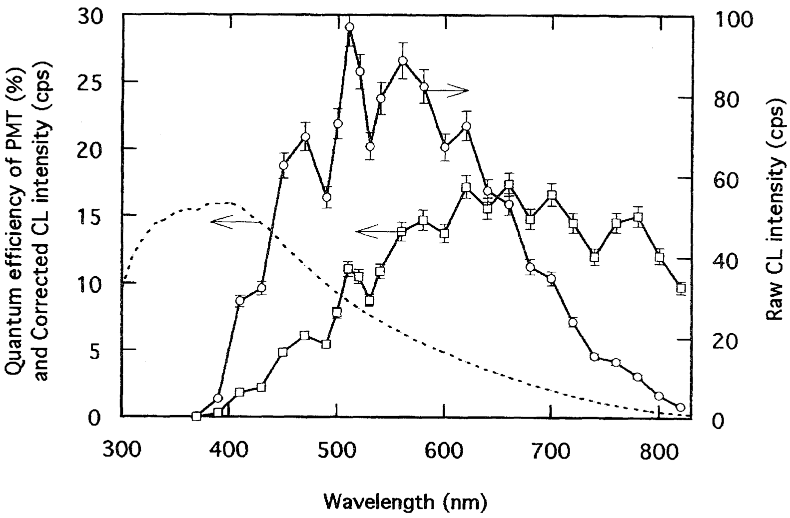

Fig. 7. Chemiluminescence spectrum by reaction $(NH_2)_2CO+OBr^-$. Open circle: Raw spectrum from the reaction of 0.2 mol dm$^{-3}$ of urea + 0.2 mol dm$^{-3}$ of sodium hypobromite containing 0.2 mol dm$^{-3}$ sodium hydroxide. Open square: Spectrum corrected for a bias due to the quantum efficiency of the photomultiplier tube R-649. Broken line: quantum efficiency of the photomultiplier tube R-649.

Table 1. NO and $NO_2$ Measured in the Gas Phase Products

| | For $NH_4^+ + OBr^-$ | | For $(NH_2)_2CO + OBr^-$ | |
|---|---|---|---|---|
| Reaction time | NO | $NO_2$ | NO | $NO_2$ |
| min | ($\times 10^9$) mol/mol | | ($\times 10^9$) mol/mol | |
| 0 | 0 | 0 | 0 | 0 |
| 1 | 0 | 42 | 0 | 3 |
| 2 | 11 | 406 | 0 | 4 |
| 3 | 16 | 209 | 0 | 3 |
| 4 | 16 | 88 | 0 | 2 |
| 5 | 17 | 46 | 0 | 4 |
| 6 | 18 | 30 | 0 | 6 |
| 7 | 19 | 25 | 0 | 5 |
| 8 | 21 | 21 | 0 | 6 |
| 9 | 21 | 19 | 0 | 7 |
| 10 | 21 | 18 | 0 | 9 |
| 11 | 21 | 18 | 0 | 10 |
| 12 | 21 | 16 | 0 | 12 |
| 13 | 21 | 16 | 0 | 13 |
| 14 | ND[a] | ND | 0 | 14 |
| 15 | ND | ND | 0 | 15 |

a) Not determined.

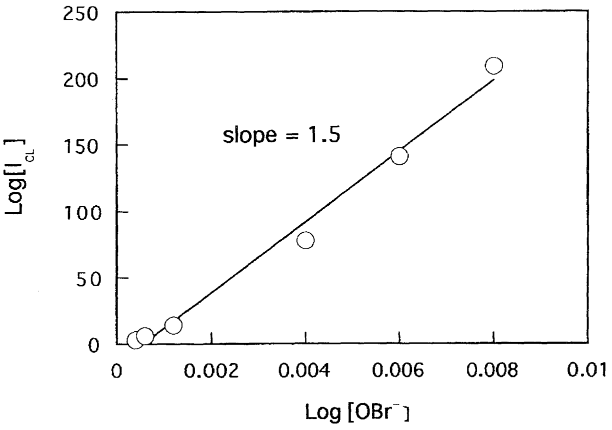

Fig. 8. Relationship between chemiluminescence intensity and hypobromite concentration when ammonium ion concentration is in excess. Sodium hydroxide: 1.0 mol dm$^{-3}$. Ammonium chloride: 0.1 mol dm$^{-3}$.

um or urea, or in a reverse manner. Results show that the chemiluminescence intensities relate to the concentrations of ammonium ion or urea by first order when hypobromite is in excess of ammonium or urea. On the other hand, on average, the chemiluminescence intensity shows 1.5 order dependence on the hypobromite concentration when ammonium ion is in excess of hypobromite (slopes of Log [$I_{CL}$] against Log [$OBr^-$] plot are 1.42, 1.56, 1.50, and 1.53 for four repetitive experiments), and second order on the concentration of hypobromite when urea is in excess of hypobromite (slopes of the same plot are 2.07, 1.98, 1.86, 2.15, and 1.90). One of the experimental results for the ammonium reaction and the urea reaction is shown in Figs. 8 and 9, respectively. This suggest that the rate of formation of the emission species for the reaction of hypobromite with ammonium ion or urea obeys 1.5 and second order kinetics with respect to hypobromite concentration, respectively, while it obeys first order kinetics with respect to the concentration of reactants, ammonium ion or urea, for both reactions.

**7. Chemiluminescence Reactions of Hypobromite or Hypochlorite with Other Compounds Similar to Ammonia or Urea.** It is of mechanistic interest to investigate whether reactions between hypobromite or hypochlorite and some other reducing reagents analogous to urea, ammonia and humic acid, produce chemiluminescence or not. In general, the reaction of hypobromite gives a stronger chemiluminescence than that of hypochlorite. The reaction between hypochlorite and ammonium ion, urea, or humic acid produce very weak chemiluminescence. On the contrary, reaction between hypobromite and hydrazine does not produce chemiluminescence, while hypochlorite does. Also, it

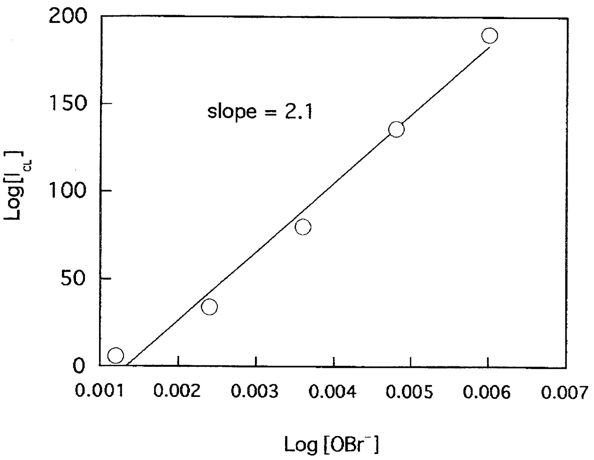

Fig. 9. Relationship between chemiluminescence intensity and hypobromite concentration when urea concentration is in excess. Sodium hydroxide: 0.2 mol dm$^{-3}$. urea: 0.05 mol dm$^{-3}$.

is noteworthy that reaction between formamide and hypobromite does not produce chemiluminescence in spite of the similarity in its chemical bond structure to urea.

**8. Tentative Scheme of the Chemiluminescence Reaction.** According to the previous investigations mentioned above (3,7,8), the reaction between hypobromite and ammonia or urea produces bromamines in solution phase and molecular nitrogen in gas phase under alkaline solution. One may assume that the emission species of the chemiluminescence reaction between hypobromite and ammonia or urea could be bromamines or molecular nitrogen. To investigate whether bromamines are responsible for the chemiluminescence or not, the fluorescence spectrum was measured after hypobromite had reacted with ammonium ion or urea. Excitation wavelengths from 250 to 350 nm were used. However, no fluorescence was detected, suggesting that bromamines may not be the emission species.

The results discussed above suggest that the chemiluminescence reaction for ammonium ion and hypobromite is different from that for urea and hypobromite. For the reaction of $NH_3+OBr^-$, the chemiluminescence spectrum is consistent with that from the reaction of $NO+O_3$ although the spectrum was measured only in a quite limited wavelength range of the $NO+O_3$ chemiluminescence. At this moment, it is reasonable to assign the emission species to electronically excited $NO_2$. For the reaction $(NH_2)_2CO+OBr^-$, the emission species is apparently different from that for the reaction of $NH_3+OBr^-$, namely excited $NO_2$. Judging from the products reported for this reaction so far, molecular nitrogen ($N_2$), is another potential candidate for the emission species. Nitrogen is known to have a visible emission (2nd positive band) in the wavelength region longer than 337 nm,[20] accompanied by a structure resulting from vibrational progressions. We could not resolve the structure in the chemiluminescence from the reaction between hypobromite and urea due to the poor resolution of the spectrometer used in this study. Therefore, although the spacing of the structure must be identified to assign the emission species, nitrogen is the probable species for the emission species. According to the discussion above, we tentatively propose the scheme for the chemiluminescence reactions as follows:

For the reaction between ammonia and hypobromite:

$$NH_3+OBr^- \rightarrow NO+Br^- \tag{5}$$

$$NO+OBr^- \rightarrow NO_2^* \tag{6}$$

$$NO_2^* \rightarrow NO_2+h\nu \tag{7}$$

For the reaction between urea and hypobromite:

$$(NH_2)_2CO+2OBr^- \rightarrow N_2^*+2Br^- \tag{8}$$

$$N_2^* \rightarrow N_2+h\nu \tag{9}$$

However, for the reaction of $NH_3+OBr^-$, it can't be denied that molecular nitrogen is one of the possible emission species. For future investigations, it will be useful to systematically study the kinetics, products, and CL spectra of other compounds similar to ammonia or urea, such as $HCONH_2$, $NH_2NH_2$, $NH_2COCONH_2$, $NH_2Br$, $NH_2OH$ etc., and the responsibility of CL intensities with the yields of $N_2$, NO, and $NO_2$.

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