Hypochlorite Oxidation of Ammonia. Effective Removal of Ammonia from Waste Water by UV-irradiation[1]

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The hypochlorite oxidation of ammonia giving rise to nitrogen evolution was carried out in the dark or under irradiation in order to study the reaction mechanism and application to waste water treatment. UV-irradiation accelerates remarkably the rate of decomposition of unfavorable chloramines. The acceleration covers the pH region 2—12, where corresponding dark reactions are slow. The irradiation also affects the formation of by-products such as NO_2^- and NO_3^-, the effect being a slight increase in NO_2^- formation in the pH range 2—12. These results suggest an effective industrial application to avoid eutrophication in seas and lakes. The irradiation effect is discussed in relation to reaction mechanism, in which the irradiation possibly facilitates the N–N bond formation after chloramine formation.

Hypochlorite salt, especially sodium hypochlorite, oxidizes ammonia or ammonium ion in water. Though the oxidation is useful for hydrazine synthesis, it usually leads to rapid and quantitative evolution of nitrogen in the presence of excessive oxidant.

$$2NH_3 + 3NaOCl \longrightarrow N_2 + 3H_2O + 3NaCl \qquad (1)$$
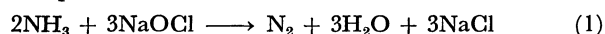
Another industrial application has recently been worked out for waste water treatment.[2-4] Ammonia together with related nitrogen compounds brings about serious eutrophication in seas and lakes, so that an effective industrial plan is required. This hypochlorite oxidation of ammonia is called break-point chlorination.[2-4] Generally, the oxidation rate is not high enough at low NH_3 concentration as observed in ordinary waste water, so that unfavorable chlorinated products such as NH_2Cl, $NHCl_2$, and NCl_3 remain, depending on the pH as well as relative dosage of the oxidant to NH_3.[2] As regards the elimination of chloramines, the active carbon is proposed because of its industrial availability.[4]

On the other hand, hypochlorites are susceptible to light, decomposing to oxygen and chlorate along with chloride ion.[5] Studies in this laboratory have shown that irradiation with hypochlorite enables complete oxidation of several organic substances which otherwise cannot be attained.[6-8] This article describes the effect of irradiation in the hypochlorite oxidation of ammonia, and the influencing factors such as pH and the molar ratio of hypochlorite to ammonia. A probable mechanism is discussed.

Experimental

Materials. Sodium hypochlorite was prepared by taking into account the dissociation constant for $HOCl$.[9] Into ice-cooled 0.20 M (1 M = 1 mol dm^{-3}) aqueous NaOH (1 l) was absorbed commercial chlorine gas until the solution showed 0.10 M by iodometry and pH 10 with a glass-electrode. After its pH was adjusted to 12 by addition of NaOH, the solution was stored in a refrigerator (stable at least for several months). An ammonia solution was prepared by dissolving a weighed amount of ammonium sulfate in distilled water. Buffer solutions except for preliminary experiments were prepared by mixing each 0.02 M phosphoric, boric and acetic acids with an appropriate amount of 0.10 M NaOH (Britton-Robinsons' buffer solution). Analytical reagents were used.

Instruments. UV and visible absorption measurements were carried out on a Hitachi 124 spectrophotometer in 1 cm cells. UV-irradiation reactions were conducted in a vessel equipped with a Halos 100 W high-pressure mercury lamp. Gas chromatograms were taken on a Yanaco 550 using a column of Molecular Sieves 5A.

Analysis. Iodometric titration was carried out according to the usual procedures to determine residual concentrations of oxidants such as $OCl^-/HOCl$, Cl_2, NH_2Cl, $NHCl_2$, NCl_3, and NO_2^-/HNO_2, but not NO_3^-/HNO_3 nor $ClO_3^-/HClO_3$. Rapid titration was carried out for the sake of clear end point, since slow air oxidation causes regeneration of HNO_2.

Ammonia was determined by Nessler's method according to JIS K 0101-1976. In order to attain distinct coloration, the resulting solution should be adjusted to pH 12. The calibration curve was based on the absorbance at 450 nm, its apparent molar coefficient being 1.6×10^3 in the range 0.10—0.50 mM ammonia.

Concentrations of NO_2^-/HNO_2 and NO_3^-/HNO_3 were determined by Gries' method involving diazotization of acidified aniline and the subsequent azo-dye development with 1-naphthylamine. The determination involves the reduction of HNO_3 to HNO_2 after elimination of HNO_2. Both procedures were carried out according to JIS K 010-1976.

Dark Reaction. Examination of breakpoint was carried out in buffered 2.0 mM ammonia solutions of pH 9.5, 7.9, 7.3, 6.9, 5.1, 2.6, and 1.6 by adding an appropriate amount of aqueous NaClO. After 15 min, concentrations of residual active chlorine were determined iodometrically.

The influence of pH on reaction rate was examined as follows. To a solution of 20 mM NH_3 (10 ml) mixed with a buffer solution (80 ml) was added 25, 30, or 35 mM aqueous NaClO (10 ml) with stirring. The reaction solution was kept standing in the dark for 1 h, and an aliquot (10 ml) was titrated iodometrically. The results are given in Table 1.

Identification of chloramines formed initially is based on the following UV spectra; absorption max. (ε) OCl^-, 292 nm(392); $HOCl$, 235 (105); Cl_2, 315 (34); NH_2Cl, 245 (416); $NHCl_2$, 297 (265); NCl_3, 340 (255).[10] The acidity constant of $HOCl$ and hydrolysis constant of Cl_2[9] were taken into consideration for assigning the species in the reaction solutions.

Irradiation Reaction. Irradiation was carried out at room temperature in the air. For the product analysis of evolved gas, it was performed under helium with the system connected to a gas burette. For detection of ClO_3^-, zinc powder reducing ClO_3^- to Cl^- was added to the ir-

TABLE 1. RESIDUAL ACTIVE CHLORINE[a] IN
DARK REACTIONS[b]

$\dfrac{[Ox]\ (mM)}{[NH_3]\ (mM)}$	2.5/2.0	3.0/2.0	3.5/2.0
pH[c] 12	2.22	1.55	1.81
11	1.93	0.95	0.65
10	1.43	0.25	0.30
9	1.34	0.35	0.20
8	1.26	0.70	0.04
7	1.18	0.85	0.00
6	1.51	1.30	0.30
5	1.76	1.55	0.00
4	1.81	1.00	0.50
3	1.88	1.70	2.30
2	1.86	1.81	2.35

a) Concentration; mM. b) Reaction time; 1 h at 30 °C.
c) Britton-Robinsons' buffer solution.

radiated solutions adjusted at pH 5, and the concentration of resulting Cl^- was determined by colorimetry of iron(III) thiocyanate after addition of ammonium iron(III) sulfate and mercury(II) thiocyanate. The color development was checked with ClO_3^- solutions, and calibrated with standard Cl^- solutions.

Comparative experiments between dark and irradiation reactions were carried out as follows. A buffer solution (320 ml) was mixed with a 20 mM NH_3 solution (40 ml) and 25 or 30 mM aqueous $NaClO$ (40 ml) was added with stirring. Half of the resulting solution was irradiated for 5—20 min until the iodometric titer became constant. Aliquots were diluted to an appropriate concentration and adjusted to neutral to make test solutions for analysis of NH_3, NO_2^-, and NO_3^-. Their standard calibration curves

were checked from time to time. The other half of the solution was kept standing in the dark for 5—10 d in a stoppered flask, then worked up by a similar analytical procedure. The results are given in Table 2.

UV absorptions of species: NO_2^-, 354 nm (ε 23); HNO_2, 371 (44); NO_3^-, 357 (12); HNO_3, 371 (19). Supplementary irradiation of 5.0 mM NH_3 was conducted in the presence of $NaNO_2$ (5.0 mM) or $NaNO_3$ (5.0 mM) at various pH for 1 h, no significant decrease being observed in the concentration of NH_3, NO_2^-, nor NO_3^-.

Results

Dark Reaction.   At 2 mM concentration of ammonia, the dark reaction of ammonia with hypochlorite proceeds rapidly to a considerable extent at room temperature. The change is readily followed by iodometric titration, on addition of an appropriate amount of aqueous sodium hypochlorite to buffered ammonia solutions. Studies on breakpoint chlorination show that a plot of residual active chlorine *vs.* the amount of the oxidant added gradually reaches a maximum and then drops sharply to a minimum (breakpoint), increasing again.[2-4] The breakpoint lies at the molar ratio 3/2, hypochlorite (Ox) to ammonia (Ox/NH_3), or slightly above, which corresponds to Eq. 1. The reaction was examined over a wide range of pH at a reaction time of 15 min. Such a breakpoint was observed in the pH range 4—8. However, a solution at pH>8 and pH<4 gave no breakpoint. A curve for pH 9.5 is located at a little lower than the expected line for no ammonia oxidation. At pH 2.6, a slightly distinct minimum was observed at about 2.0 of Ox/NH_3.

In order to examine the influence of pH on residual

TABLE 2. COMPARISON BETWEEN DARK AND IRRADIATION REACTIONS[a]

$\dfrac{[Ox]\ (mM)}{[NH_3]\ (mM)}$	pH	Dark (mM)			Irradiation (mM)		
		$[NH_3] \times 10$	$[NO_2^-] \times 10^2$	$[NO_3^-] \times 10$	$[NH_3] \times 10$	$[NO_2^-] \times 10^2$	$[NO_3^-] \times 10$
2.5/2.0	12	7.3	0.2	0.2	4.0	6.4	0.2
	11	6.8	0.4	0.4	4.7	5.6	0.3
	10	6.8	0.4	0.9	4.0	2.4	0.2
	9	5.8	0.3	0.5	3.8	3.3	0.4
	8	6.5	0.1	2.3	4.3	2.0	0.4
	7	6.8	0.1	1.4	3.7	2.0	0.3
	6	5.8	0.1	2.3	0.3	2.0	0.4
	5	6.5	0.1	1.7	3.2	2.7	0.9
	4	6.5	0.3	1.1	4.5	2.5	0.8
	3	6.5	0.1	0.5	5.7	0.7	1.4
3.0/2.0	12	3.2	12.7	0.5	3.8	19.5	0.6
	11	2.1	0.0	0.5	3.9	10.5	0.5
	10	1.9	0.0	0.8	2.8	6.0	0.3
	9	2.2	0.0	1.8	3.0	7.0	0.4
	8	1.6	0.0	1.9	2.4	7.0	0.5
	7	1.3	0.0	1.7	2.6	6.5	0.4
	6	1.8	0.0	3.4	3.4	4.5	0.6
	5	2.5	0.0	1.7	3.4	2.0	1.7
	4	1.6	0.6	0.8	3.2	3.8	0.8
	3	1.4	0.6	1.0	3.6	2.0	1.9
	2	0.9	1.4	0.7	3.6	1.8	2.5

a) Reaction time; dark 5-10 d, irradiation 20 min (a 100 W high-pressure mercury lamp).

active chlorine, a series of runs were conducted in buffer solutions with three values of the ratio Ox/NH_3 adjusted around the stoichiometric ratio of 3/2 (Table 1).

When a sufficient amount of hypochlorite $(Ox/NH_3 >$ 3/2) is used in the pH region 4—10, oxidation is completed within at least 1 h. When Ox/NH_3 is lower than 3/2, oxidation takes place sluggishly. Thus, a deviation from the neutral solution causes insufficient oxidation, even with excess oxidant.

The progress of reaction was followed by UV spectroscopy. Immediate measurements on addition of aqueous hypochlorite to buffered ammonia showed new absorptions corresponding to NH_2Cl, $NHCl_2$, and NCl_3[10] instead of OCl^-, $HOCl$, and Cl_2, apart from contamination of OCl^-, $HOCl$, and Cl_2 formed readily from sodium hypochlorite (see Experimental). The type of chloramines formed depends not only on pH,[2,10] but also on Ox/NH_3. UV measurements on various ratios of Ox/NH_3 (0.5—3.0) were carried out at several pH. At pH 12.0, the absorption of NH_2Cl alone took place up to ca. 1.0 of Ox/NH_3, while two absorptions of NH_2Cl and OCl^- appeared over 1.0 of Ox/NH_3. Solutions of pH 9.5 gave an absorption indicating overlap of NH_2Cl and $HOCl$ up to 1.3 of Ox/NH_3, the absorption at 290 nm becoming distinct with an increase in Ox/NH_3. Since aqueous sodium hypochlorite at pH 9.5 exists as a form of $HOCl$, the absorption at 290 nm may be assigned to $NHCl_2$ rather than OCl^-. At pH 5.1, the result was similar to that at pH 9.5. At pH 2.6, the third absorption appeared at 340 nm, and was assigned to NCl_3 and/or Cl_2. These chloramines undergo rapid interconversion as well as nitrogen evolution, determination of their equilibrium constants being unsuccessful.
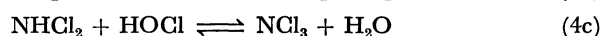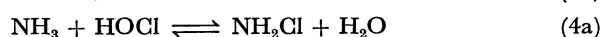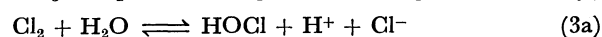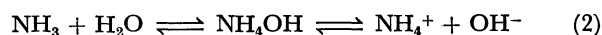
Effect of Irradiation. The iodometric titer decreased very rapidly when solutions containing NH_2Cl, $NHCl_2$, NCl_3 or their equilibrated species (*vide infra*) were irradiated with UV light of wavelength > 290 nm. Consumption of the oxidant was completed after 5—20 min by internal irradiation with a 100 W high-pressure mercury lamp. UV study of the resulting solutions showed transparency at 210—370 nm, indicating photo-decomposion of chloramines. The gas evolved was confirmed to be nitrogen by gas chromatography. The volumetric determination of evolved nitrogen gave an over 80% yield on the basis of NaClO assuming that the irradiation is also expressed as in Eq. 1. In order to estimate ClO_3^- which is formed in ca. 40% yield on irradiation of aqueous NaClO alone,[5] several attempts on Cl^- determination were made after treatment with zinc powder which reduced ClO_3^- to Cl^-. But no significant increase in Cl^- concentration was observed with this reduction treatment.

Several breakpoint chlorination studies reveal that NO_2^- and NO_3^- are accompanied as by-products in the reaction in alkaline media.[2] Such a side reaction was also observed in the irradiation reaction. Comparative experiments between dark and irradiation reactions (Table 2) were conducted by changing the ratio Ox/NH_3 as well as pH. For completion of the reaction, 5—10 d were required in the dark, while only 20 min was sufficient under irradiation. The

concentrations of residual NH_3, NO_2^-, and NO_3^- were determined.

Discussion

We see from residual active chlorine in dark reactions (Table 1) that the rate of reaction depends on the relative ratio of Ox/NH_3 as well as pH of the solution. UV spectra show transient existence of chloramines such as NH_2Cl, $NHCl_2$, and NCl_3. The type of chloramine formed depends on pH,[2,10] *viz.*, alkaline or neutral solution gives NH_2Cl, while NCl_3 is favored at pH below 4, the relatively unstable $NHCl_2$ being formed in the pH range 4.5—5.0. This was confirmed by our observation. Since nitrogen evolution requires 3/2 mol of hypochlorite for 1 mol of NH_3 (Eq. 1), the chloramine formation should also depend on Ox/NH_3. One mol of NH_2Cl, $NHCl_2$, and NCl_3 requires 1, 2, and 3 mol of hypochlorite, respectively. NH_2Cl, $NHCl_2$, and NCl_3 are then in equilibrium with each other and even with OCl^-, $HOCl$, and Cl_2. Possible equilibria in the system of ammonia and sodium hypochlorite are as follows.

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^- \qquad (2)$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (3a)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (3b)$$

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O \qquad (4a)$$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \qquad (4b)$$
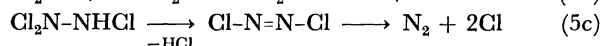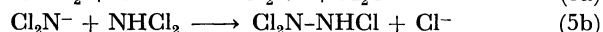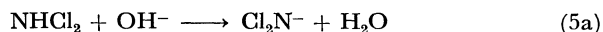
$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O \qquad (4c)$$

By taking advantage of the low reactivity of NH_2Cl (slow nitrogen evolution) in a high alkaline solution, the equilibrium constant for $NH_2Cl+OH^- \rightleftharpoons NH_3+OCl^-$ was estimated to be 1.6×10^{-3} at 15 °C,[12] showing the preference of NH_2Cl to free NH_3. According to our preparative attempts, generation of NCl_3 requires a highly acidic solution to suppress the nitrogen evolution and to enable ultimate chlorination of NH_3. Though $NHCl_2$ requires the ratio Ox/NH_3 of 2, a maximum amount of $NHCl_2$ is generated under the conditions where Ox/NH_3 is slightly lower than 3/2 at pH 4.0—4.5. In any event, the formation of chloramines such as NH_2Cl, $NHCl_2$, and NCl_3 is a rapid process, influencing the whole oxidation mechanism at the initial stage.

The reaction time in the dark is shortened by a factor of over 100 for the present systems, where the ratio Ox/NH_3 is less than that of stoichiometry (Table 2). The acceleration effect due to UV-irradiation would provide an effective industrial design in waste water treatment, where thermal acceleration cannot be applied. The UV-irradiation may also have an advantage over active carbon[4] because of the applicability at various pH.
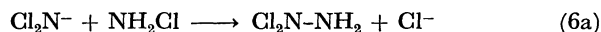
The dark and irradiation reactions give essentially the same products, though the amount of by-product NO_2^- in the irradiation is larger than that in the dark. The similarity in products is of interest, since species OCl^-, $HOCl$ and Cl_2 equilibrated with NH_2Cl, $NHCl_2$, and NCl_3 (Eq. 2) might decompose into oxygen or chlorate ion on irradiation.[5] Our results suggest that NH_3 can be oxidized in accordance with Eq. 1. The

reason is not clear why the dark and irradiation reactions differ in the by-product formation of NO_2^-. Solutions of NO_2^-, HNO_2, NO_3^-, and HNO_3 possess very weak absorptions at wavelength <400 nm (see Experimental). However, the irradiation of these species in the presence of NH_3 or NH_4^+ gave rise to neither significant evolution of nitrogen nor change in concentration of NO_2^- and NO_3^-. Thus, irrespective of by-product formation, the irradiation reaction should proceed via a path analogous to the dark reaction.

The mechanism of nitrogen evolution, in particular the process after the rapid formation of chloramines, has not been clarified. Schmitz et al.[13] reported in their study on the side-reaction of $NHCl_2$ that the following condensation takes place between two mol of $NHCl_2$, leading to nitrogen, as an explanation for chlorinated products of ethers.

$$NHCl_2 + OH^- \longrightarrow Cl_2N^- + H_2O \tag{5a}$$

$$Cl_2N^- + NHCl_2 \longrightarrow Cl_2N\text{-}NHCl + Cl^- \tag{5b}$$

$$Cl_2N\text{-}NHCl \xrightarrow[-HCl]{} Cl\text{-}N\text{=}N\text{-}Cl \longrightarrow N_2 + 2Cl \tag{5c}$$

The postulate involves deprotonation with base (Eq. 5a). On the basis of UV spectra, stepwise chlorination occurs to a greater extent with lowering in pH to give $NHCl_2$ and NCl_3. As a result, the postulate might be in line with the fact that the dark reaction is more rapid in neutral solution than in solutions of higher or lower pH (Table 1). However, species undergoing N–N bond formation do not seem to be restricted to $NHCl_2$, since irradiation enables nitrogen evolution from NH_2Cl in an alkaline solution or from NCl_3 in an acidic solution. Thus the following kinds of condensation are possible:

$$Cl_2N^- + NH_2Cl \longrightarrow Cl_2N\text{-}NH_2 + Cl^- \tag{6a}$$

$$Cl_2N^- + NCl_3 \longrightarrow Cl_2N\text{-}NCl_2 + Cl^- \tag{6b}$$

Even the intervention of hydrazine may be possible, since the reaction of aqueous NaOCl with NH_3 gives hydrazine which is readily oxidized to nitrogen.

As regards acceleration by irradiation, in the case of N-chlorinated organic compounds irradiation causes their homolytic N–Cl bond cleavage because of its low bond energy.[15] It might affect the step of decomposition of chlorinated hydrazine (Eqs. 5c and 6), assuming that it is rate-determining. The rate-deter-

mining step for nitrogen evolution might be N–N bond formation (Eq. 5a, 5b, or 6) rather than decomposition (Eq. 5c), since chloramines are detected instead of unstable chlorinated hydrazines. Irradiation can change the acid dissociation constants of phenols or amines.[16] The change of basicity of chloramines by irradiation is probable in this case. Photoexcitation energy might be changed to molecular thermal energy, e.g., vibrational energy, facilitating N–N bond formation (Eqs. 5a, 5b and 6).

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