

## Hypochlorite Oxidation of Ammonia. Effective Removal of Ammonia from Waste Water by UV-irradiation<sup>1)</sup>

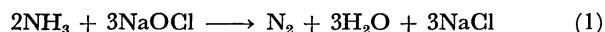
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The hypochlorite oxidation of ammonia giving rise to nitrogen evolution was carried out in the dark or under irradiation in order to study the reaction mechanism and application to waste water treatment. UV-irradiation accelerates remarkably the rate 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  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , the effect being a slight increase in  $\text{NO}_3^-$  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.



Another industrial application has recently been worked out for waste water treatment.<sup>2–4)</sup> 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.<sup>2–4)</sup> Generally, the oxidation rate is not high enough at low  $\text{NH}_3$  concentration as observed in ordinary waste water, so that unfavorable chlorinated products such as  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$  remain, depending on the pH as well as relative dosage of the oxidant to  $\text{NH}_3$ .<sup>2)</sup> As regards the elimination of chloramines, the active carbon is proposed because of its industrial availability.<sup>4)</sup>

On the other hand, hypochlorites are susceptible to light, decomposing to oxygen and chlorate along with chloride ion.<sup>5)</sup> Studies in this laboratory have shown that irradiation with hypochlorite enables complete oxidation of several organic substances which otherwise cannot be attained.<sup>6–8)</sup> 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  $\text{HOCl}$ .<sup>9)</sup> Into ice-cooled 0.20 M (1 M = 1 mol dm<sup>-3</sup>) 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  $\text{OCl}^-/\text{HOCl}$ ,  $\text{Cl}_2$ ,  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ ,  $\text{NCl}_3$ , and  $\text{NO}_2^-/\text{HNO}_2$ , but not  $\text{NO}_3^-/\text{HNO}_3$  nor  $\text{ClO}_3^-/\text{HClO}_3$ . Rapid titration was carried out for the sake of clear end point, since slow air oxidation causes regeneration of  $\text{HNO}_2$ .

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  $1.6 \times 10^3$  in the range 0.10—0.50 mM ammonia.

Concentrations of  $\text{NO}_2^-/\text{HNO}_2$  and  $\text{NO}_3^-/\text{HNO}_3$  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  $\text{HNO}_3$  to  $\text{HNO}_2$  after elimination of  $\text{HNO}_2$ . 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  $\text{NaClO}$ . 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  $\text{NH}_3$  (10 ml) mixed with a buffer solution (80 ml) was added 25, 30, or 35 mM aqueous  $\text{NaClO}$  (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. ( $\epsilon$ )  $\text{OCl}^-$ , 292 nm(392);  $\text{HOCl}$ , 235 (105);  $\text{Cl}_2$ , 315 (34);  $\text{NH}_2\text{Cl}$ , 245 (416);  $\text{NHCl}_2$ , 297 (265);  $\text{NCl}_3$ , 340 (255).<sup>10)</sup> The acidity constant of  $\text{HOCl}$  and hydrolysis constant of  $\text{Cl}_2$ <sup>9)</sup> 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  $\text{ClO}_3^-$ , zinc powder reducing  $\text{ClO}_3^-$  to  $\text{Cl}^-$  was added to the ir-

TABLE 1. RESIDUAL ACTIVE CHLORINE<sup>a)</sup> IN DARK REACTIONS<sup>b)</sup>

| $\frac{[\text{Ox}]}{[\text{NH}_3]}$ (mM) |    | 2.5/2.0 | 3.0/2.0 | 3.5/2.0 |
|------------------------------------------|----|---------|---------|---------|
| pH <sup>c)</sup>                         | 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  $\text{Cl}^-$  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  $\text{ClO}_3^-$  solutions, and calibrated with standard  $\text{Cl}^-$  solutions.

Comparative experiments between dark and irradiation reactions were carried out as follows. A buffer solution (320 ml) was mixed with a 20 mM  $\text{NH}_3$  solution (40 ml) and 25 or 30 mM aqueous  $\text{NaClO}$  (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  $\text{NH}_3$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ . 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:  $\text{NO}_2^-$ , 354 nm ( $\epsilon$  23);  $\text{HNO}_2$ , 371 (44);  $\text{NO}_3^-$ , 357 (12);  $\text{HNO}_3$ , 371 (19). Supplementary irradiation of 5.0 mM  $\text{NH}_3$  was conducted in the presence of  $\text{NaNO}_2$  (5.0 mM) or  $\text{NaNO}_3$  (5.0 mM) at various pH for 1 h, no significant decrease being observed in the concentration of  $\text{NH}_3$ ,  $\text{NO}_2^-$ , nor  $\text{NO}_3^-$ .

## 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.<sup>2–4)</sup> The breakpoint lies at the molar ratio 3/2, hypochlorite (Ox) to ammonia ( $\text{Ox}/\text{NH}_3$ ), 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  $\text{pH} > 8$  and  $\text{pH} < 4$  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  $\text{Ox}/\text{NH}_3$ .

In order to examine the influence of pH on residual

TABLE 2. COMPARISON BETWEEN DARK AND IRRADIATION REACTIONS<sup>a)</sup>

| $\frac{[\text{Ox}]}{[\text{NH}_3]}$ (mM) | pH | Dark (mM)                 |                               |                             | Irradiation (mM)          |                               |                             |
|------------------------------------------|----|---------------------------|-------------------------------|-----------------------------|---------------------------|-------------------------------|-----------------------------|
|                                          |    | $[\text{NH}_3] \times 10$ | $[\text{NO}_2^-] \times 10^2$ | $[\text{NO}_3^-] \times 10$ | $[\text{NH}_3] \times 10$ | $[\text{NO}_2^-] \times 10^2$ | $[\text{NO}_3^-] \times 10$ |
| 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  $\text{Ox}/\text{NH}_3$  adjusted around the stoichiometric ratio of 3/2 (Table 1).

When a sufficient amount of hypochlorite ( $\text{Ox}/\text{NH}_3 > 3/2$ ) is used in the pH region 4–10, oxidation is completed within at least 1 h. When  $\text{Ox}/\text{NH}_3$  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  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$ <sup>10</sup> instead of  $\text{OCl}^-$ ,  $\text{HOCl}$ , and  $\text{Cl}_2$ , apart from contamination of  $\text{OCl}^-$ ,  $\text{HOCl}$ , and  $\text{Cl}_2$  formed readily from sodium hypochlorite (see Experimental). The type of chloramines formed depends not only on pH,<sup>2,10</sup> but also on  $\text{Ox}/\text{NH}_3$ . UV measurements on various ratios of  $\text{Ox}/\text{NH}_3$  (0.5–3.0) were carried out at several pH. At pH 12.0, the absorption of  $\text{NH}_2\text{Cl}$  alone took place up to *ca.* 1.0 of  $\text{Ox}/\text{NH}_3$ , while two absorptions of  $\text{NH}_2\text{Cl}$  and  $\text{OCl}^-$  appeared over 1.0 of  $\text{Ox}/\text{NH}_3$ . Solutions of pH 9.5 gave an absorption indicating overlap of  $\text{NH}_2\text{Cl}$  and  $\text{HOCl}$  up to 1.3 of  $\text{Ox}/\text{NH}_3$ , the absorption at 290 nm becoming distinct with an increase in  $\text{Ox}/\text{NH}_3$ . Since aqueous sodium hypochlorite at pH 9.5 exists as a form of  $\text{HOCl}$ , the absorption at 290 nm may be assigned to  $\text{NHCl}_2$  rather than  $\text{OCl}^-$ . 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  $\text{NCl}_3$  and/or  $\text{Cl}_2$ . These chloramines undergo rapid interconversion as well as nitrogen evolution, determination of their equilibrium constants being unsuccessful.

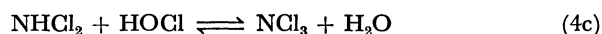
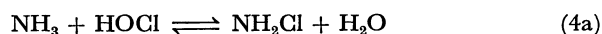
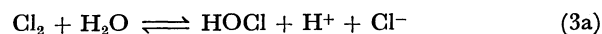
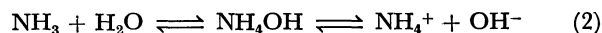
**Effect of Irradiation.** The iodometric titer decreased very rapidly when solutions containing  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ ,  $\text{NCl}_3$  or their equilibrated species (*vide infra*) were irradiated with UV light of wavelength  $> 290$  nm. Consumption of the oxidant was completed 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-decomposition 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  $\text{NaClO}$  assuming that the irradiation is also expressed as in Eq. 1. In order to estimate  $\text{ClO}_3^-$  which is formed in *ca.* 40% yield on irradiation of aqueous  $\text{NaClO}$  alone,<sup>5</sup> several attempts on  $\text{Cl}^-$  determination were made after treatment with zinc powder which reduced  $\text{ClO}_3^-$  to  $\text{Cl}^-$ . But no significant increase in  $\text{Cl}^-$  concentration was observed with this reduction treatment.

Several breakpoint chlorination studies reveal that  $\text{NO}_2^-$  and  $\text{NO}_3^-$  are accompanied as by-products in the reaction in alkaline media.<sup>2</sup> 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  $\text{Ox}/\text{NH}_3$  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  $\text{NH}_3$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  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  $\text{Ox}/\text{NH}_3$  as well as pH of the solution. UV spectra show transient existence of chloramines such as  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$ . The type of chloramine formed depends on pH,<sup>2,10</sup> *viz.*, alkaline or neutral solution gives  $\text{NH}_2\text{Cl}$ , while  $\text{NCl}_3$  is favored at pH below 4, the relatively unstable  $\text{NHCl}_2$  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  $\text{NH}_3$  (Eq. 1), the chloramine formation should also depend on  $\text{Ox}/\text{NH}_3$ . One mol of  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$  requires 1, 2, and 3 mol of hypochlorite, respectively.  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$  are then in equilibrium with each other and even with  $\text{OCl}^-$ ,  $\text{HOCl}$ , and  $\text{Cl}_2$ . Possible equilibria in the system of ammonia and sodium hypochlorite are as follows.



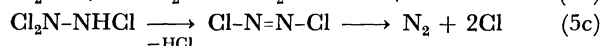
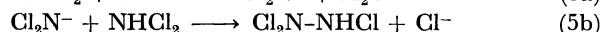
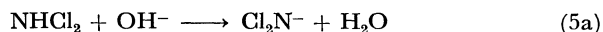
By taking advantage of the low reactivity of  $\text{NH}_2\text{Cl}$  (slow nitrogen evolution) in a high alkaline solution, the equilibrium constant for  $\text{NH}_2\text{Cl} + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{OCl}^-$  was estimated to be  $1.6 \times 10^{-3}$  at 15 °C,<sup>12</sup> showing the preference of  $\text{NH}_2\text{Cl}$  to free  $\text{NH}_3$ . According to our preparative attempts, generation of  $\text{NCl}_3$  requires a highly acidic solution to suppress the nitrogen evolution and to enable ultimate chlorination of  $\text{NH}_3$ . Though  $\text{NHCl}_2$  requires the ratio  $\text{Ox}/\text{NH}_3$  of 2, a maximum amount of  $\text{NHCl}_2$  is generated under the conditions where  $\text{Ox}/\text{NH}_3$  is slightly lower than 3/2 at pH 4.0–4.5. In any event, the formation of chloramines such as  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$  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  $\text{Ox}/\text{NH}_3$  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<sup>4</sup> because of the applicability at various pH.

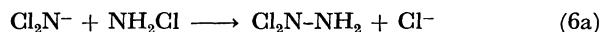
The dark and irradiation reactions give essentially the same products, though the amount of by-product  $\text{NO}_2^-$  in the irradiation is larger than that in the dark. The similarity in products is of interest, since species  $\text{OCl}^-$ ,  $\text{HOCl}$  and  $\text{Cl}_2$  equilibrated with  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and  $\text{NCl}_3$  (Eq. 2) might decompose into oxygen or chlorate ion on irradiation.<sup>5</sup> Our results suggest that  $\text{NH}_3$  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  $\text{NO}_2^-$ . Solutions of  $\text{NO}_2^-$ ,  $\text{HNO}_2$ ,  $\text{NO}_3^-$ , and  $\text{HNO}_3$  possess very weak absorptions at wavelength  $< 400$  nm (see Experimental). However, the irradiation of these species in the presence of  $\text{NH}_3$  or  $\text{NH}_4^+$  gave rise to neither significant evolution of nitrogen nor change in concentration of  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . 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.*<sup>13)</sup> reported in their study on the side-reaction of  $\text{NHCl}_2$  that the following condensation takes place between two mol of  $\text{NHCl}_2$ , leading to nitrogen, as an explanation for chlorinated products of ethers.



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  $\text{NHCl}_2$  and  $\text{NCl}_3$ . 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  $\text{NHCl}_2$ , since irradiation enables nitrogen evolution from  $\text{NH}_2\text{Cl}$  in an alkaline solution or from  $\text{NCl}_3$  in an acidic solution. Thus the following kinds of condensation are possible:



Even the intervention of hydrazine may be possible, since the reaction of aqueous  $\text{NaOCl}$  with  $\text{NH}_3$  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.<sup>15)</sup> 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.<sup>16)</sup> 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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