PHOTO-OXIDATION OF AMMONIA WITH AQUEOUS HYDROGEN PEROXIDE*

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Abstract

The reaction of ammonia with H_2O_2 in aqueous solution has been carried out either under irradiation or in the dark. For $pH > 9$, unprotonated ammonia NH_3 reacts with $HO\cdot$ generated from H_2O_2 under irradiation to give NO_2^-, NO_3^- and NH_2OH together with gaseous N_2, while in acidic solution the corresponding reaction of NH_4^+ with $HO\cdot$ is too slow to be observed. On the other hand, the reaction of NH_3 with H_2O_2 (HOO^-) in the dark leads to the same products as those under irradiation, but the reaction is much slower than that under irradiation. Probable mechanism for the oxidation of ammonia and the quantum yield for H_2O_2 decomposition are discussed.

Introduction

Hydrogen peroxide decomposes in the presence of iron(Ⅱ) ion or under irradiation to generate hydroxyl radical, which is known as an oxidant much more powerful than parent H_2O_2. The mixture (H_2O_2–Fe^{2+}) is known as Fenton's reagent and reactions with it have been reported for a large number of organic substances.[1] Also a series of studies in this laboratory have shown that irradiation of several substances with H_2O_2 leads to the complete oxidation; e. g., ethers[2], carboxylic acids[3,4] etc. Although $HO\cdot$ is known to oxidize organic substances by H-atom abstraction or addition to aromatic rings, studies on H-atom abstraction from N–H bonds by radicals with the exception of $HO\cdot$ generated by pulse radiolysis of water, are sparse and no information on the oxidation products is available. Therefore, we wish to report here some data on the reaction of ammonia with $HO\cdot$ generated by the u. v. photolysis of H_2O_2 and the nature of the oxidation products, because it consists solely of N–H bonds.

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Results and Discussion

To examine the effects of acidity and concentration of H_2O_2 on the decomposition of ammonia, the acidity of the solution containing NH_3 and H_2O_2 was controlled by the use of buffers; three solutions in which the ratio $[H_2O_2]_0/[NH_3]_0$ was adjusted to be 1.5, 5.0 and 10.0 were prepared, where $[\ ]_0$ represents initial concentration and $[NH_3]_0$ was always kept constant of 4.44×10^{-2}M. The value of 1.5 for $[H_2O_2]_0/[NH_3]_0$ means an equivalent amount ratio for the complete oxidation (eq 1).

$$2NH_3 + 3H_2O_2 \longrightarrow N_2 + 3H_2O \tag{1}$$

The solution thus prepared was photolyzed using the 254nm light from a 60W Hg lamp or allowed to react in the dark in a specially designed reaction vessel, where the evolved N_2 could be trapped. (see Experimental Section). For a ratio of 1.5 at pH 10.2, the decomposition of H_2O_2 under irradiation was complete after 3h, but 3 days were necessary in the dark. Fig. 1 shows the overall consumption of NH_3, when H_2O_2 was completely decomposed.

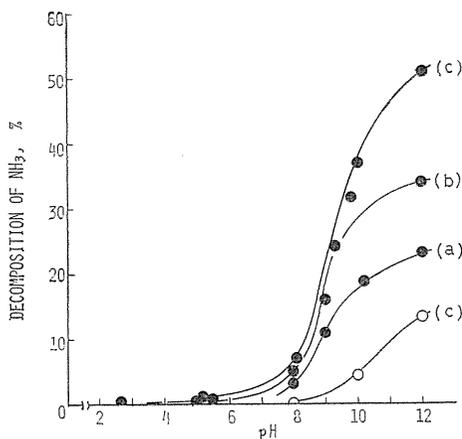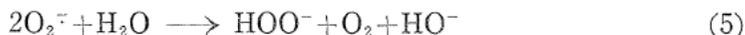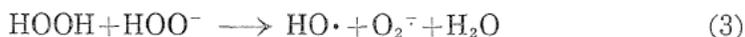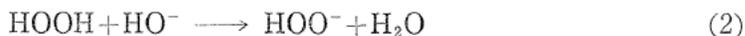

Fig. 1. Effect of pH on the decomposition of NH_3 in the presence of H_2O_2 at various molar ratio of reactants. (●), under irradiation; (○), in the dark. Initial concentration of NH_3 ($[NH_3]_0$) was 4.44×10^{-2}M. $[H_2O_2]_0/[NH_3]_0$ = 1.5, line(a); 5.0, line(b); 10.0, line(c).

It is apparent from Fig. 1 that the decomposition of NH_3 is closely related to the dissociation equilibrium of NH_3 (pK_a 9.3); i. e., in an acidic region, the rate of decomposition of NH_3 was very slow, while the decomposition of NH_3 is accelerated remarkably as the pH of the solution is increased from 8 to 10, and only slight acceleration of decomposition was observed for pH > 10, where most of the ammonia is unprotonated.

This observation suggests that unprotonated ammonia (NH_3) is oxidized much more easily than protonated ammonia (NH_4^+). This is consistent with the results obtained by the pulse radiolysis of aqueous ammonia[5] in the absence of H_2O_2.
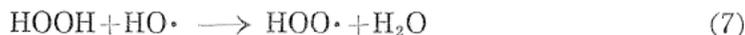
Upon comparing the decomposition under irradiation with that in the dark, it is evident that irradiation is effective for the decomposition of NH_3. This is explicable in terms of the difference of the concentration of active species. According

to the accepted scheme for the decomposition of H_2O_2[6], H_2O_2 decomposes in alkaline solution in the dark via eqs 2-5.

$$HOOH + HO^- \longrightarrow HOO^- + H_2O \tag{2}$$

$$HOOH + HOO^- \longrightarrow HO\cdot + O_2^- + H_2O \tag{3}$$

$$HO\cdot + O_2^- \longrightarrow HO^- + O_2 \tag{4}$$

$$2O_2^- + H_2O \longrightarrow HOO^- + O_2 + HO^- \tag{5}$$

The active species in the dark should be the hydroxyl radical, $HO\cdot$, because $HO\cdot$ (an electrophilic radical) is more reactive toward NH_3 (a nucleophile) than O_2^- (a nucleophilic radical). $HO\cdot$ is consumed by eq 4 and by reaction with NH_3.

On the other hand, both photolyses (eqs 6-9)[7] and alkaline decomposition (eqs 2-5) of H_2O_2 occur simultaneously under irradiation in alkaline solution. The active species in these cases may be $HO\cdot$ and $HOO\cdot$, of which the former should be more important, because the initial and main path for the photochemical decomposition of H_2O_2 is eq 6.[7]

$$HOOH \longrightarrow 2HO\cdot \tag{6}$$

$$HOOH + HO\cdot \longrightarrow HOO\cdot + H_2O \tag{7}$$

$$HOO\cdot + HOOH \longrightarrow HO\cdot + H_2O + O_2 \tag{8}$$

$$2HOO\cdot \longrightarrow HOOH + O_2 \tag{9}$$

About 3 days are necessary for the complete decomposition of H_2O_2 in the dark, while only about 3h are sufficient under irradiation for $[H_2O_2]_0/[NH_3]_0 = 1.5$. Therefore, the concentration of $HO\cdot$ under irradiation is much higher than that in the dark and hence the rate of H-atom abstraction from NH_3 should also be much higher.

The decomposition of NH_3 under these conditions gave N_2, NH_2OH, NO_2^- and NO_3^-, but hydrazine, NH_2NH_2, was not detected. Table 1 shows the product yields for a typical experiment under alkaline conditions. Here, evolving gaseous N_2 was collected in a gas buret and identified by GLC with TCD; the other products in solution were identfied and estimated by a colorimetric method (see Experimental Section).

As apparent from Table 1, the decomposition of NH_3 in Run 10 was 51.0% (photolysis), but only 13.4% in Run 12 (dark); therefore, irradiation is effective for the oxidative decomposition of NH_3. As the concentration of oxidant increases, the yield of NH_2OH decreases, while that of N_2 increases but the increase in the yields of NO_2^- and NO_3^- were small. These results may be explained by secondary oxidation of NH_2OH, NH_2NH_2 and NO_2^-.

Aqueous 0.05M NH_2OH was photolyzed at pH 10.2 for 20h, giving quantitatively gaseous N_2 as a sole product (eq 10). Under the same conditions, photolysis in the presence of 0.075M H_2O_2 gave N_2 and O_2 as gaseous products, and NO_2^- and NO_3^- in solution. In this photolysis, NH_2OH was completely converted to N_2, NO_2^-, and NO_3^- and the yields of these products were 70%, 27%, and 3%, respectively (eq 11). The same solution containing NH_2OH and H_2O_2 was in turn kept

Table 1. Product yields from the phtolysis of NH_3–H_2O_2 mixtures after complete consumption of H_2O_2[a]

Run No.	pH	$[H_2O_2]_0/[NH_3]_0$	[decompd NH_3] %	N_2	Product Yield,[b] %		
					NH_2OH	NO_2^-	NO_3^-
1	8.1	10.0	6.9	10	69	20	0.3
2	9.0	1.5	10.1	15	72	13	0.8
3	9.0	5.0	15.9	19	61	19	1.2
4	9.3	10.0	24.2	20	60	17	1.1
5	10.2	1.5	18.9	23	61	15	1.7
6	9.8	5.0	31.8	30	50	17	1.6
7	10.0	10.0	37.1	37	43	17	2.7
8	12.0	1.5	23.3	42	36	19	2.3
9	12.0	5.0	34.1	53	31	14	1.4
10	12.0	10.0	51.0	65	23	16	2.8
11	12.0[c]	5.0	9.0	76	19	3	0.3
12	12.0[c]	10.0	13.4	80	13	5	0.4

[a] Initial concentration of NH_3 ($[NH_3]_0$) 4.44×10^{-2}M. 3–4 h were required for complete decomposition of H_2O_2.

[b] The yield is based on the amount of NH_3 decomposed. The accuracy of the yields was always better than $\pm 10\%$ for N_2 and NH_2OH, $\pm 5\%$ for NO_2^- and NO_3^-.

[c] Dark reaction, 3 days.

standing in the dark for 24h. In this case, NH_2OH was also converted quantitatively into N_2 (92%), NO_2^- (8%), and NO_3^- (trace) (eq 12).

$$NH_2OH \xrightarrow[20h]{h\nu} N_2 \quad (100\%) \tag{10}$$

$$NH_2OH \xrightarrow[2h]{H_2O_2,\ h\nu} N_2 + NO_2^- + NO_3^- \atop (70\%) \ (27\%) \ \ (3\%) \tag{11}$$

$$NH_2OH \xrightarrow[24h]{H_2O_2,\ dark} N_2 + NO_2^- + NO_3^- \atop (92\%) \ (8\%) \ \ (trace) \tag{12}$$
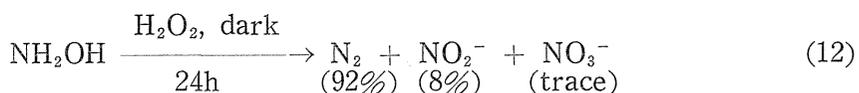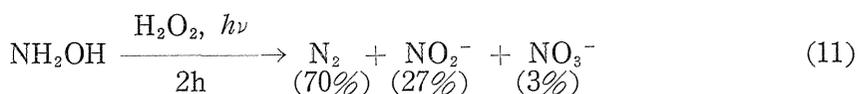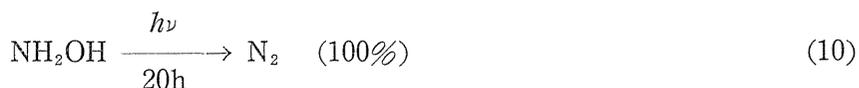
Hydrazine, NH_2NH_2, which was not detected in this photolysis, was easily oxidized by H_2O_2 to N_2 alone both under irradiation (15 min) and in the dark (150 min) (eq 13). Therefore, the fact that NH_2NH_2 was not detected during the photolysis of NH_3–H_2O_2 mixtures may be due to its complete consumption by the rapid reaction with H_2O_2 (or HO·).

$$NH_2NH_2 + H_2O_2 \xrightarrow[\text{or dark (150 min)}]{h\nu\ (15\ min)} N_2 + H_2O \tag{13}$$
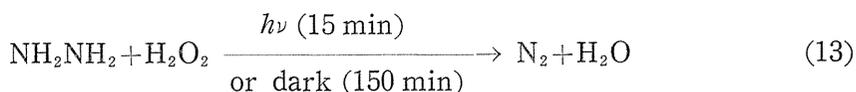
On the other hand, nitrite ion NO_2^- in alkaline solution (pH 10.2) was not oxidized even in the presence of H_2O_2 either under irradiation or in the dark (eq 14). Therefore, NO_3^- was not formed via NO_2^-.

$$NO_2^- + H_2O_2 \xrightarrow{\quad h\nu \text{ or dark} \quad} \text{no reaction} \tag{14}$$
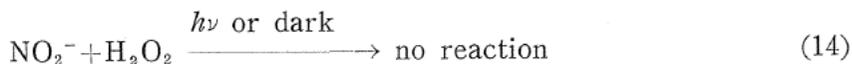
The results of auxiliary studies show that the oxidation of NH_2OH with H_2O_2 in the dark yields mainly N_2, but under irradiation produces NO_2^-, accompanied by N_2. Therefore, the difference in the product distribution between irradiation and dark conditions may be due to either the effect of irradiation on the oxidation rate or to the contribution of an active species $(HOO\cdot)$ formed upon irradiation.

The quantum yield for the decomposition of H_2O_2 was determined at pH 10.2. The quantum yield was 15 in the absence of NH_3 and 24 in the presence of NH_3 for $[H_2O_2]_0/[NH_3]_0 = 1.5$. A variety of quantum yields has been reported[8,9] for the photolysis of H_2O_2 in aqueous solution, e. g., Sethuram and Rao reported[10] values of $1.87 \pm 0.5([H_2O_2]_0 = 5 \times 10^{-2}M)$ at pH 4.45, and 14.5 ± 0.5 in the presence of $NH_2OH([NH_2OH]_0 = 1.5 \times 10^{-4}M)$ at the same pH. The quantum yields obtained here are of the same order of magnitude as theirs, but the value in the presence of NH_3 is ca. 1.5 times greater than that in H_2O_2 alone. This fact suggests that active species other than $HO\cdot$ and $HOO\cdot$ may take part in the decomposition of H_2O_2.

Mechanism

As stated above, protonated ammonia(NH_4^+) reacts only very slowly, if at all, with $HO\cdot$, but unprotonated ammonia (NH_3) readily reacts with $HO\cdot$ to give observed products. This is consistent with the electrophilic nature of $HO\cdot$[11].
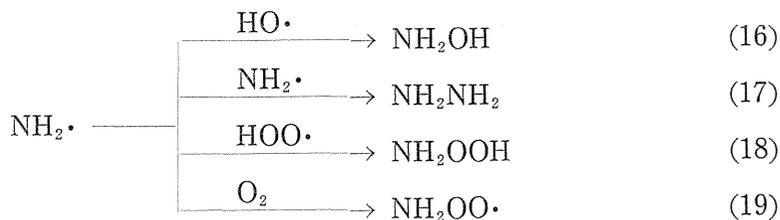
Although the oxidation of NH_3 proceeds under alkline conditions, the efficiency of H_2O_2 in promoting the decomposition of NH_3 is low both under irradiation and in the dark. This suggests a low reactivity of NH_3 toward $HO\cdot$ and the rapid self-decomposition of H_2O_2 under irradiation (eqs 6–9) or alkaline dark condition (eqs 2–5).

The oxidation of NH_3 begins with H-atom abstraction by $HO\cdot$ to give the amino radical $NH_2\cdot$ (eq 15) under both conditions.

$$NH_3 + HO\cdot \longrightarrow NH_2\cdot + H_2O \tag{15}$$

$NH_2\cdot$, thus formed, reacts with $HO\cdot$ to give NH_2OH or with $NH_2\cdot$ to give NH_2NH_2. Here, the yield of NH_2NH_2 is expected to be much lower than that of NH_2OH because the concentration of $NH_2\cdot$ is lower than that of $HO\cdot$ and/or because NH_2NH_2 (a reductant) reacts rapidly with H_2O_2 to give N_2 and H_2O. This expectation is consistent with observation.

As mentioned above, the different yields of products between the photolytic and dark reactions may be due to the participation of $HOO\cdot$ in the former case, because $HOO\cdot$ is the only different active species under irradiation in comparison with those involved in the alkaline decomposition of H_2O_2. It is anticipated that the formation of $HOO\cdot$ would be considerably enhanced because of the high rate of induced decomposition of H_2O_2 by $HO\cdot$ (eqs 6–9). Therefore, the observed higher yield of NO_2^- under irradiation compared with those in the dark may be due to the formation of NH_2OOH (eq 18).

$$NH_2 \cdot \underbrace{\begin{array}{l} \xrightarrow{\quad HO \cdot \quad} NH_2OH \\ \xrightarrow{\quad NH_2 \cdot \quad} NH_2NH_2 \\ \xrightarrow{\quad HOO \cdot \quad} NH_2OOH \\ \xrightarrow{\quad O_2 \quad} NH_2OO \cdot \end{array}} \qquad \begin{array}{r} (16) \\ (17) \\ (18) \\ (19) \end{array}$$

As to a probable mechanism for the formation of the final products, the following pathways are conceivable; (a) the primary product, NH_2OH, which is formed via eq 16, undergoes further reaction to give N_2, NO_2^- and NO_3^-; (b) NH_2NH_2 (eq 17) is oxidized to N_2; (c) active species NH_2OOH (eq 18) may be photochemically decomposed to $NH_2O \cdot$ and $HO \cdot$; (d) $NH_2OO \cdot$ (eq 19) undergoes bimolecular decomposition to $NH_2O \cdot$ and O_2 and then the radical $NH_2O \cdot$ is oxidized to give the final products, NO_2^- and NO_3^-. Some of the active radical species formed in the above processes (a)–(d) react with H_2O_2 to give $HO \cdot$ and $HOO \cdot$, thus causing the quantum yield to increase in the presence of NH_3.

Experimental

Materials

Aqueous 90% hydrogen peroxide of guaranteed grade was purchased from Mitsubishi Gas Chem. Co. Aqueous 28% ammonia was of commercial guaranteed grade and other analytical reagents were used without further purification.

Apparatus

U. v. and visible spectra were measured on a Hitachi 124 spectrophotometer. U. v. irradiation was performed with a Halos 60W low-pressure Hg lamp at 20°C in a quartz vessel. The vessel was attached to a bottle filled with aqueous alkaline pyrogallol and the bottle was connected to a gas buret, where all connections were made with capillary tubes in order to minimize a dead volume.

Analysis

Iodometric titration for estimating the H_2O_2 concentration was carried out according to the usual procedure. Rapid titration was necessary whenever NO_2^- was present, since NO_2^- might interfere by reacting with I^-. Ammonia was determined by colorimetric method using Nessler's reagent according to JIS K 0101-1976. The calibration curve was based on the absorbance at 440nm, ε 1.9×10^3 (pH 12). The concentration of NO_2^- was determined by Gries' method[12] which involves diazotization of acidified aniline and subsequent azo-dye development with 1-naphthylamine, $\lambda_{max} = 530$nm in H_2O, ε 3.3×10^4. The concentration of NO_3^- was determined as NO_2^- by means of the above Gries' method after reducing NO_3^- to NO_2^- with zinc powder.[13] In the presence of NO_2^-, the reduction of NO_3^- was carried out after decomposing HNO_2 as diazo compound by heating. The concentration of NH_2OH was measured by a colorimetric method based on Fishbein's report[14] (ε 1.7×10^3 at λ_{H_2O} 460nm). The concentration of NH_2NH_2 was also determined by a colorimetric method after condensation of p-dimethylaminobe-

nzaldehyde with NH_2NH_2 (λ_{max}458nm, ε 2.8×10^4 in lN HCl).

Reaction of NH_3 with H_2O_2

A buffer solution (500 ml) was mixed with 0.533M aqueous ammonia (50ml) and 0.800, 2.67, 5.33M aqueous H_2O_2 (50ml) was added after the air in the vessel was replaced with gaseous helium. The buffer solutions used were 0.1M KH_2PO_4 +0.1M NaOH for pH 6–8; 0.1M H_3PO_4+0.1M NaOH for pH 8–10; 0.05M $NaHCO_3$ +0.1M NaOH for 9.6–12; HCl for pH < 6. Photolyses were carried out in the apparatus described above at 20°C. The evolved gas was collected in the gas buret after passing through aqueous alkaline pyrogallol to eliminate oxygen and then the volume of the gas was estimated. The gas in the buret was analyzed by GLC (TCD) using two columns packed with Porapak QS and Molecular Sieve 5A and identified to be nitrogen. The products in aqueous solution were analyzed according to the procedures as described above. In the case of the dark reactions of NH_3 with H_2O_2, the preparation of the reactant solution and the analytical methods of the products were the same as described in the irradiation reaction.

Reaction of NH_2OH

Aqueous 0.05M NH_2OH (250ml) was irradiated at pH 10.2 until NH_2OH could not be detected (20h). A mixture of aqueous NH_2OH and aqueous H_2O_2 ([NH_2OH]=0.05M, [H_2O_2]=0.075M, total volume 500ml) was also irradiated at pH 10.2 until H_2O_2 was consumed completely. The same mixture was kept standing in the dark and it took 24 h for the complete decomposition of NH_2OH. Product analyses were carried out by the same procedures as in the reaction of NH_3.

Reaction of NH_2NH_2 with H_2O_2

A mixture (300ml) of aqueous 5.8×10^{-3}M hydrazine sulfate and aqueous 1.1×10^{-2}M H_2O_2 was photolyzed at pH 10.2 for 15 min, giving quantitatively N_2. On the other hand, the dark reaction of the same mixture needed 150 min for 88% consumption of NH_2NH_2 and the product was also N_2 alone.

Reaction of NO_2^- with H_2O_2

The reaction of an equimolar mixture (200 ml) of $NaNO_2$ and H_2O_2 (0.01M) was carried out at pH 10.2 under irradiation and in the dark. No decrease of the concentration of NO_2^- was observed in both conditions after H_2O_2 was completely consumed.

Determination of quantum yield for the decomposition of H_2O_2

Quantum yields were determined using a potassium ferrioxalate actinometer.[15] Aqueous 0.067M H_2O_2 (22.5ml) was irradiated at pH 10.2 for 80 min at 20°C. The average quantum yield for the decomposition of H_2O_2 was 15. A solution of the same concentration of H_2O_2 was also irradiated in the presence of NH_3 (0.067M H_2O_2 and 0.044M NH_3) at pH 10.2 for 80 min. The quantum yield was 24.

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