as spin state transition in electrical conductivity. The composition of $x=0.75$ shows weak ferromagnetic behavior due to Co^{3+}-O^{2-}-Co^{4+} indirect superexchange interaction below 300 K (T_c) in the Sr^{2+} ion rich region.

The $SrCoO_{2.5}$ compound shows antiferromagnetic behavior with the plateau and the magnetic structure is the G-type in which near-neighbouring Co^{3+} ions have always opposite spins,[14,16] the Néel temperature (T_N) of the compound is about 550 K. Since Co^{3+} ions are only high spin state which results from the small crystal field (10Dq) due to the loose lattice, it is found that antiferromagnetic Co^{3+}-O^{2-}-Co^{3+} interaction represents the electrical and magnetic behaviors. Finally, the mixed valence of Co ions at B sites depending on the x-value and the spin transition between two Co ion states plays an important role in the physical properties of the $Dy_{1-x}Sr_xCoO_{3-y}$ system.

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Photolysis of Aqueous Ammonia in the Absence and the Presence of O_2

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The photochemical decomposition of aqueous ammonia in the absence (saturated with argon) and the presence of O_2 (saturated with air or oxygen) has been investigated using 184.9 nm UV light. The decomposition of ammonia depended on the concentration of oxygen in the solution. With increasing the concentration of oxygen, the decomposition of ammonia diminishes. Hydrazine is found the major product from the irradiation. In the presence of oxygen, hydrogenperoxide was also produced. The product yields depended also on the concentration of oxygen in the solution. The initial quantum yield of the products and of the ammonia decomposed were determined. Probable reaction mechanisms for the reaction were presented from the products analysis.

Introduction

Ammonia is produced in huge quantities worldwide for use as a primary source of nitrogen in the production of many commercial chemicals such as a fertilizer. However, ammonia with foul oder, generated from decomposition of a large amount of garbage, causes a serious environmental pollution. Therefore, it is interesting to study on the decomposition of ammonia. Photochemical or radiation-induced reaction can be used as a method. Earlier investigation on the decomposition of ammonia using a light was performed by Burtt and Zahlan.[1] The authors reported that NH_2, H, NH_3^+ and NH_2^+ are produced in alpha-induced decomposition of gaseous ammonia. Some years later, Okabe *et al.* studied on the photochemical reaction of gaseous ammonia using vacuum uv light.[2] Numerous studies on the photochemical decomposition of ammonia using ArF excimer laser were reported in order to understand the reaction mechanism.[3~9] Very recently Ponizovsky *et al.* reported on the removal through oxidation of ammonia in moist air by the use of pulse corona discharge.[10] So far, however, most of the investigations were carried out in gas phase. To our knowledge, there has been no report on the quantitative investigation of the photochemical decomposition of aqueous ammonia. In the present study, aqueous ammonia solution was irradiated with vacuum UV light of 184.9 nm in the absence and the presence of oxygen. In particular, the presence of oxygen during the irradiation of aqueous ammonia could be an important factor which may affect consecutive chemical reactions. Primary radicals, which would otherwise initiate decomposition, react with oxygen, forming peroxy radicals that cause eventually an oxidative degradation. The purpose of this study is to present quantitative results for photochemical reaction of aqueous ammonia and to investigate the effect of oxygen during the photochemical reaction.

Experimental

Lightsource and Actinometry. A low pressure mercury lamp (Osram HNS 12/oz) was used as the lightsource of UV light with 184.9 nm. The lamp was mounted in a quartz tube which was surrounded by the solution to be irradiated. The reaction vessel was made of Pyrex and was isolated from lamp by means of a quartz tube. The intensity (I_0) of the 184.9 nm light was determined by ethanol actinometer.[11,12] In order to perform the chemical actinometry, 5 M air-free aqueous ethanol was prepared and then it was irradiated as a function of the irradiation time. After that, the yield of hydrogen produced after irradiation of the solution was depicted as a function of the irradiation time. The lamp intensity was calculated by the slope of the curve as it passes through the origine using the known quantum yield, $Q\ (H_2)=0.40$.[11,12] and was found to be 7.77×10^{17} hν. mL^{-1}. min^{-1} at 25 ℃. It corresponds to about 27% of the intensity at 253.7 nm. No change in intensity of the lamp was observed over the period of the experiments. The yield of hydrogen produced after irradiation of air-free aqueous ethanol was measured by a thermal conductivity gas chromatography [Yanaco (Japan) Model G180-T; Molesieve 5A packed column; carrier gas: He]. The output of the gas chromatograph was integrated using integrator (Varian 4290).

Reagents and General. Aqua ammonia (30% NH_3 in water, 99.99+ % NH_4OH) was purchased from Aldrich Chemical Co. and used as received. All other chemicals employed in this work were reagent grade and used without further purification. 1.0 M NH_4OH solution was prepared using quadruply distilled water, which was obtained by passing the distilled water through deionization system [Barnstead (U.S.A.) Nonopure II]. For air-free aqueous ammonia, each of the distilled water and aqua ammonia were first deaerated by bubbling about 60 min with high purity argon (99.999% pure) and then used to prepare 1.0 M NH_4OH solution. 80 mL of the freshly prepared solution was taken in an irradiation vessel and bubbled again about 3 min before the irradiation. The solution was then irradiated using low pressure Hg lamp. During the irradiation, the temperature was kept at 25±0.1 ℃ using a waterbath circulator. The UV spectrum of aqueous ammonia was recorded on a Hitachi Model 557 UV-spectrophotometer. The molar extinction coefficient (ε) of aqueous ammonia at 184.9 nm was obtained 500 $M^{-1}cm^{-1}$ by extrapolation. Aqueous ammonia did not absorb the simultaneously emitted light at 253.7 nm.

Analysis. In order to obtain MS spectra of the products in irradiated aqueous ammonia, two kinds of samples were made and used: one was used just as irradiated and the other was used after immediate extraction of the solution using dimethylether as an extractant. The samples prepared were analyzed using a GC-MS system (Varian saturn; DB-5 capillary column 50 m×0.25 μm, EI method); [product; m/z (rel. intensity), hydrazine; 17(10), 31(16), 32(100), hydroxylamine; 31(42), 33(78), 34(100)]. Identifications and determinations were made by comparison with fragmentation patterns of known amounts of the pure substances. The identified products from the MS spectra were reconfirmed by comparison with retention time of the separated GC peaks of the standard chemical, which was performed by the Varian Model 3700 gas chromatography. The amoumt of decomposed ammonia was determined by spectrophotometric method using aqueous $NiCl_2$ as a complexing reagent. In high concentration of ammonia (above 0.3 M), the blue color developed upon addition of nickel chloride to the aqueous ammonia. The develpoed color was characterized by the absorbance maximum at 590 nm. The remaining concentration of ammonia after irradiation was determined by comparison with a calibration curve. The amount of hydrazine produced was determined by spectrophotometric method.[13] An aliquot (1 mL) of the irradiated solutions were treated with p-dimethylaminobenzaldehyde as a complexing reagent. The molar extinction coefficient (ε) of colored complex was 66700 M^{-1} cm^{-1} at 458 nm in these experiments and it was not interfered by the presence of the other nitrogen-containing compounds such as hydroxylamine. Quantitative determination of hydroxylamine produced was also carried out spectrophotometrically by modified Csaky test.[14] The hydroxamic acids formed by oxidation of hydroxylamine with iodine has the maximum absorption at 540 nm and its molar extinction coefficient (ε) at this wavelength was calculated 9800 $M^{-1}cm^{-1}$. Spectrophotometric determination of hydrogen peroxide was performed by treatment with acidic $TiCl_4$ solution.[15] The developed color was characterized by the absorbance maximum at 414 nm and its molar extinction coefficient (ε) at this wavelength was 4430 $M^{-1}cm^{-1}$.

Results and Discussion

First, the photolysis of 1.0 M deoxygenated aqueous ammonia solution was studied as a function of the number of

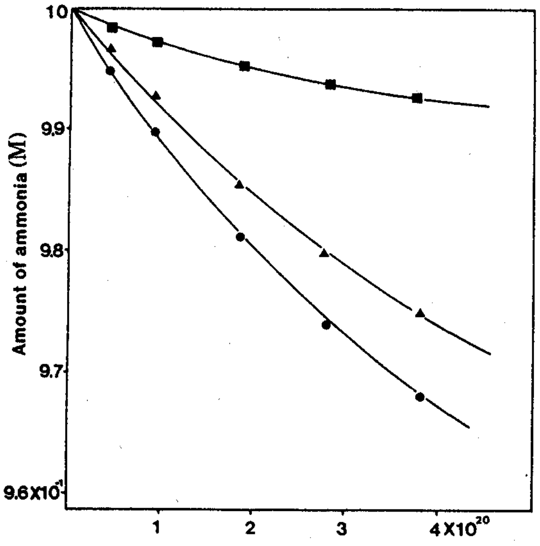

Figure 1. Amount of ammonia remained after irradiation of 1.0 M aqueous ammonia as a function of the number of quanta: (●) in the absence of O_2; (▲) in the saturation with air; (■) in the saturation with O_2.

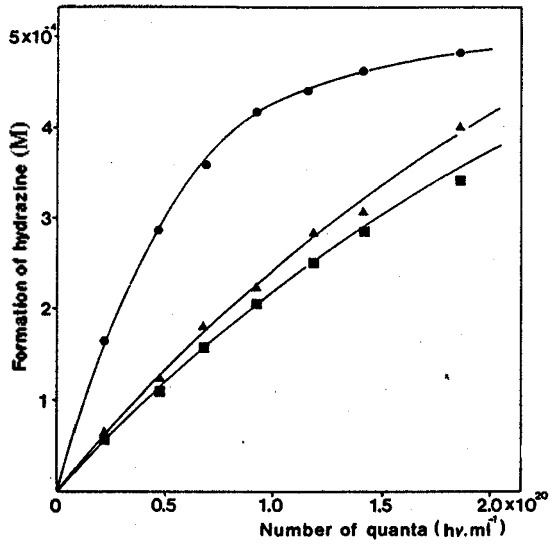

Figure 2. Formation of hydrazine after irradiation of 1.0 M aqueous ammonia as a function of the number of quanta: (●) in the absence of O_2; (▲) in the saturation with air; (■) in the saturation with O_2.

Table 1. Initial quantum yield (Q_i) of the compounds after irradiation (λ=184.9 nm) of 1.0 M aqueous ammonia in the absence and presence of O_2

Compounds	Q_i when saturated with		
	Ar	Air	O_2
Ammonia[a]	8.12×10^{-2}	4.51×10^{-2}	1.81×10^{-2}
Hydrazine	4.81×10^{-3}	1.76×10^{-3}	1.61×10^{-3}
Hydrogenperoxide	—	1.10×10^{-4}	1.32×10^{-4}
Hydroxylamine	$<10^{-5}$	$<10^{-5}$	$<10^{-5}$

[a] These values indicate the initial quantum yield of ammonia decomposed. The others indicate the initial quantum yield of the products.

quanta. After that, the solutions saturated with air or oxygen were investigated under the same experimental conditions. The results of the experiments were presented in Figure 1. During the irradiation of the solutions, hydrazine was produced mainly. The product yield as a function of the number of quanta is shown in Figure 2. No products were observed during the irradiation at 253.7 nm. As shown in Figure 1, the decomposition of ammonia depended on the number of quanta in all cases. The tendency of decomposition of ammonia as a function of the number of quanta was not linearly proportional to an equation of the first degree. This behavior indicates that a back reaction, which contributes to the formation of ammonia, occured in the system and that the obtained product was also decomposed by the absorption of the uv light or by an attack of the radicals formed during the photochemical reaction. Therefore the initial quantum yields (Q_i) are determined and summarized in Table 1.

In the absence of oxygen. In aqueous ammonia solution, there are $NH_{3(aq)}$, $NH_4{}^+{}_{(aq)}$, $OH^-{}_{(aq)}$ and H_2O chemical species. These species absorb also the light of 184.9 nm. However, molar extinction coefficient (ε) of $NH_{3(aq)}$ at 184.9 nm was calculated 500 $M^{-1}cm^{-1}$ by extrapolation and these of $OH^-{}_{(aq)}$ and H_2O were reported to be 3600 $M^{-1}cm^{-1}$ and 0.032 $M^{-1}cm^{-1}$, respectively.[16,17] From the calculation using these values, it was found that most of the 184.9 nm (about 96.7%) was absorbed by aqueous ammonia and only a small part of the light (about 3.0%) was absorbed by $OH^-{}_{(aq)}$ ion in case of 1.0 M aqueous ammonia solution. The fraction of absorption by water was so small that it could be negligible. It is therefore expected that the photochemical decomposition of ammonia was carried out mainly by direct photolysis under the given concentration of aqueous ammonia.

In the photolysis of the gas-phase ammonia at 123.6 nm (*ca.* 10.03 eV) and 155.0 nm (*ca.* 8.00 eV), Okabe *et al.* reported that H_2 and NH radicals were produced mainly in contrast with H and NH_2 radicals were formed only about 16% of those radicals.[2] On the other hand, in the photolysis of gas phase ammonia using ArF excimer laser (193 nm, *ca.* 6.40 eV), it was reported that H and NH_2 radicals were produced mainly.[5-7,9] Since the light of 184.9 nm has relatively small photon energy (*ca.* 6.70 eV) and has closer energy to 193 nm, it is expected that the electronically excited ammonia by the absorption of 184.9 nm is splitted mainly into H and NH_2 radicals as presented in process (1). Futhermore, the fact that hydrazine was produced mainly by the irradiation of 184.9 nm supports such photofragmentation. The hydrogen atom produced by the process (1) can attack ammonia as in reaction (2). This reaction facilitates the decomposition of ammonia and thereby much more NH_2 radicals are reproduced. Although the hydrogen atom can react with each other to produce hydrogen molecules, the formation of NH_2 radicals in reaction (2) is superior because the reaction probability of the reaction defined by multiplication of concentration and rate constant is greater than that of reaction (3). To test this hypothesis, we tried to detect of hydrogen molecules produced by the irradiation. But the yield of hydrogen molecules formation was so small that it could be negligible.

This result supports that the hypothesis described above is reasonable.

$$NH_{3(aq)} \xrightarrow{h\nu} (NH_{3(aq)})^{*} \rightarrow H + \cdot NH_2 \qquad (1)$$

$$NH_{3(aq)} + H \rightarrow \cdot NH_2 + H_2 \quad (k = 1.1 \times 10^{8}\ M^{-1}s^{-1})^{18} \qquad (2)$$

$$H + H \rightarrow H_2 (k = 1 \times 10^{10}\ M^{-1}s^{-1})^{19} \qquad (3)$$

The NH_2 radicals produced react with each other. The formation of hydrazine could be explained by their dimerization process as in reaction (4a). Disproportionation process also occurred and NH_3 was produced as in reaction (4b). This process is a reason why the decomposition of ammonia as a function of the number of quanta was not proportional to an equation of the first degree.

$$2 \cdot NH_2 \longrightarrow N_2H_4 \qquad (4a)$$

$$ \longrightarrow \cdot NH + NH_3 \qquad (4b)$$

Dainton and Fowles proposed[16] that electronically excited hydroxide ion could be splitted into OH radical and so-called "solvated electron", e^{-}_{aq} as in reaction (5). Although a small part of the applied uv light (*ca.* 3%) was absorbed by $OH^{-}_{(aq)}$ in the given experimental conditions, the OH radicals produced by reaction (5) take part also in the decomposition process of ammonia as shown in reaction (6) and thereby NH_2 radicals are also produced. The formation of hydroxylamine could be interpreted by the combination of NH2 and OH radicals as shown in reaction (7). However, its amount was very small in this experimental condition as shown in Table 1. This is because not only small amount of OH radical was obtained by reaction (5) but also reactions (6), (7) and (8) competed with each other. Besides, hydrogenperoxide can also be produced during the reaction as byproducts. But the yield of hydrogenperoxide produced in the irradiation of air-free aqueous ammonia was so small that it can be negligible.

$$OH^{-}_{aq} \xrightarrow{h\nu} (OH^{-}_{aq})^{*} \rightarrow \cdot OH + e^{-}_{aq} \qquad (5)$$

$$NH_{3(aq)} + \cdot OH \rightarrow \cdot NH_2 + H_2O \cdot \quad (k = 3.6 \times 10^{7}\ M^{-1}s^{-1})^{20} \qquad (6)$$

$$\cdot NH_2 + \cdot OH \rightarrow NH_2OH \quad (k = 9.5 \times 10^{9}\ M^{-1}s^{-1})^{21} \qquad (7)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (k = 5.0 \times 10^{9}\ M^{-1}s^{-1})^{22} \qquad (8)$$

The produced solvated electron, e^{-}_{aq} is combined with ammonium ion dissolved in solution as in reaction (9). The H atoms formed by reaction (9) can also take part in the decomposition of ammonia as in reaction (2).

$$NH_4{}^{+}{}_{(aq)} + e^{-}_{aq} \rightarrow NH_{3(aq)} + H \qquad (9)$$

As shown in Figure 2, the yield of hydrazine produced as a function of number of quanta was not proportional to an equation of the first degree. The reason for this can be explained as follows; one is because hydrazine absorbs also light at 184.9 nm with increasing number of quanta and it is decomposed. The other is because hydrazine is also attacked by H atoms and OH radicals very rapidly as in reactions (10) and (11). Getoff reported that H attack to the hydrazine occurs very rapidly.[23]

$$N_2H_4 + H \rightarrow H_2 + N_2H_3 \qquad (10)$$

$$N_2H_4 + \cdot OH \rightarrow H_2O \cdot + N_2H_3 \quad (k = 1.4 \times 10^{10}\ M^{-1}s^{-1})^{24} \qquad (11)$$

In the presence of oxygen. In the irradiation of 1.0 M aqueous ammonia saturared with air, the decomposition of ammonia and the formation of hydrazine decreased compared with in the case of air-free aqueous ammonia as shown in Figures 1 and 2, respectively. These behaviors can be interpreted that oxygen affects the decomposition process of aqueous ammonia. Decomposition of ammonia was carried out mainly both by its direct photolysis and by H attack to ammonia as described above. In the presence of oxygen, however, the produced H atoms participate not only in the reaction (2) but also in the combination with oxygen very rapidly as in reaction (12). Therefore, ammonia saturated with air was less decomposed than air-free solution.

$$H + O_2 \rightarrow HO_2 \cdot \quad (k = 2.5 \times 10^{10}\ M^{-1}s^{-1})^{25} \qquad (12)$$

Because reactions (2) and (12) are a competition reaction, the NH_2 radicals in the irradiation of aqueous ammonia saturated with air are less produced than in that of air-free ammonia, leading that the hydrazine formed by its dimerization process gives the lower yield. Furthermore, as shown in Figures 1 and 2, the result that the least decomposition of ammonia and the least formation of hydrazine were carried out in the presence of oxygen supports the postulate described above. The HO_2 radical formed in reaction (12) is so unstable that it is converted into hydrogenperoxide and oxygen through disproportionation process as in reaction (13). The oxygen molecules produced by this reaction react also with H atoms again as in the reaction (12). This chain reaction is a reason why ammonia was much more decomposed in the presence of O_2.

$$2HO_2 \cdot \rightarrow H_2O_2 + O_2 \quad (2k = 3.7 \times 10^{6}\ M^{-1}s^{-1})^{26} \qquad (13)$$

To test this expectation, the amount of hydrogenperoxide formed by the irradiation of aqueous ammonia was analyzed. In contrast to the results on the decomposition of ammonia and on the production of hydrazine, the formation of hydrogenperoxide in the irradiation of aqueous ammonia saturated with oxygen was greater than in that saturated with air. In the irradiation of air-free aqueous ammonia, hydrogenperoxide was not detected by the analytical method used in this study. This result indicates that reaction (12) plays an important role in the formation of hydrogenperoxide. Its initial quantum yield was calculated and presented in Table 1. But the values are very small. It is because the formation of HO_2 radical is also small. In addition to H atom, it might be postulated that NH_2 radical can also combine with oxygen as in reaction (14), because oxygen reacts generally with radicals very well.[27] As a result, so-called aminoperoxide radicals, NH_2OO can be produced. This radical is so unstable that it can be converted to hydroxylamine through the reactions (15)-(17).

$$\cdot NH_2 + O_2 \rightarrow NH_2OO \cdot \qquad (14)$$

$$NH_2OO \cdot + NH_3 \rightarrow 2\ NH_2O \cdot + H \qquad (15)$$

$$NH_2O \cdot + NH_3 \rightarrow NH_2OH + \cdot NH_2 \qquad (16)$$

$$NH_2O \cdot + H \rightarrow NH_2OH \qquad (17)$$

Despite the expectation to produce a large amount of hydroxylamine in the irradiation of aqueous ammonia saturated with air or with oxygen, the amount of hydroxylamine produced remains unchanged in compared with the case of air-free ammonia. From the result, it might be deduced that reaction (14) proceeds very slowly. Consequently, its formation could be interpreted only as a result of the combination of NH_2 and OH radicals as in reaction (7).

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A Mechanistic Study on Reactions of Aryl Benzoates with Ethoxide, Aryloxides and Acetophenone oximates in Absolute Ethanol

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Second-order rate constants have been measured spectrophotometrically for the reactions of aryl benzoates ($X\text{-}C_6H_4CO_2C_6H_4\text{-}Y$) with EtO^-, $Z\text{-}C_6H_4O^-$ and $Z\text{-}C_6H_4C(Me){=}NO^-$ in absolute ethanol at 25.0 ℃. All the reactions have been performed in the presence of excess 18-crown-6 ether in order to eliminate the catalytic effect shown by alkali metal ion. A good Hammett correlation has been obtained with a large ρ^- value (-1.96) when σ^- (Z) constant was used for the reaction of *p*-nitrophenyl benzoate (PNPB) with $Z\text{-}C_6H_4O^-$. Surprisingly, the one for the reaction of PNPB with $Z\text{-}C_6H_4C(Me){=}NO^-$ gives a small but definitely positive ρ^- value ($+0.09$). However, for reactions of $C_6H_5CO_2C_6H_4\text{-}Y$ with EtO^-, correlation of log *k* with σ^- (Y) constant gives very poor Hammett correlation. A significantly improved linearity has been obtained when σ^o (Y) constant was used, indicating that the leaving group departure is little advanced at the TS of the RDS. For reactions of $X\text{-}C_6H_4CO_2C_6H_4\text{-}4\text{-}NO_2$ with EtO^-, $C_6H_5O^-$ and $C_6H_5C(Me){=}NO^-$, correlations of log *k* with σ (X) constants for all the three nucleophile systems give good linearity with large positive ρ values, *e.g.* 2.95, 2.81 and 3.06 for EtO^-, $C_6H_5O^-$ and $C_6H_5C(Me){=}NO^-$, respectively. The large ρ values clearly suggest that the present reaction proceeds *via* a stepwise mechanism in which the formation of the addition intermediate is the RDS.

Introduction

Acyl-transfer reactions have been known to be one of the most important chemical reactions occurring in living bodies, and numerous studies have been performed to investigate the reaction mechanism using many kinds of model sys-