International Journal of
Molecular Sciences

MDPI

Article

Hydrazine Radiolysis by Gamma-Ray in the N_2H_4–Cu^+–HNO_3 System

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Abstract: Radiolysis of chemical agents occurs during the decontamination of nuclear power plants. The γ-ray irradiation tests of the N_2H_4–Cu^+–HNO_3 solution, a decontamination agent, were performed to investigate the effect of Cu^+ ion and HNO_3 on N_2H_4 decomposition using a Co-60 high-dose irradiator. After the irradiation, the residues of N_2H_4 decomposition were analyzed by Ultraviolet-visible (UV) spectroscopy. NH_4^+ ions generated from N_2H_4 radiolysis were analyzed by ion chromatography. Based on the results, the decomposition mechanism of N_2H_4 in the N_2H_4–Cu^+–HNO_3 solution under γ-ray irradiation condition was derived. Cu^+ ions form $Cu^+N_2H_4$ complexes with N_2H_4, and then N_2H_4 is decomposed into intermediates. H^+ ions and $H^\bullet$ radicals generated from the reaction between H^+ ion and e_{aq}^- increased the N_2H_4 decomposition reaction. NO_3^- ions promoted the N_2H_4 decomposition by providing additional reaction paths: (1) the reaction between NO_3^- ions and $N_2H_4^{\bullet+}$, and (2) the reaction between $NO^\bullet$ radical, which is the radiolysis product of NO_3^- ion, and $N_2H_5^+$. Finally, the radiolytic decomposition mechanism of N_2H_4 obtained in the N_2H_4–Cu^+–HNO_3 was schematically suggested.

Keywords: radiolysis; γ-ray; irradiation; hydrazine; copper ion; nitrate ion

Citation: Chang, N.; Won, H.; Park, S.; Eun, H.; Kim, S.; Seo, B.; Kim, Y. Hydrazine Radiolysis by Gamma-Ray in the N_2H_4–Cu^+–HNO_3 System. *Int. J. Mol. Sci.* **2021**, *22*, 7376. https://doi.org/10.3390/ijms22147376

Academic Editor: Alexande Baykov

Received: 28 May 2021
Accepted: 30 June 2021
Published: 9 July 2021

1. Introduction

Hydrazine (N_2H_4) is commercially used to produce plastics, medicines, and textile dyes and to reduce the corrosion of a boiler in a thermal power plant [1,2]. In the nuclear field, N_2H_4 is added to the primary feed water to maintain the hydrogen concentration and to remove dissolved oxygen [3]. In addition, N_2H_4 can be applied as a chemical decontamination solution to remove radioactive nuclides in an oxide layer of a primary system in the nuclear power plant [4]. The decontamination solution containing N_2H_4 is developed to reduce the damage of the base metal and the secondary radioactive wastes compared with the decontamination using organic acid [5,6]. They are composed of N_2H_4 and inorganic acids such as HNO_3 and H_2SO_4 [5–7]. Furthermore, the metal ions can be added into the decontamination solution containing N_2H_4 for improving the decontamination performance [8]. For this reason, a N_2H_4–Cu^+–HNO_3 decontamination solution was suggested as the effective chemical decontamination solution [7]. The decontamination solution, however, can be decomposed under the high radiation field [9]. The radiolysis of the decontamination solution occurs by radionuclides in the primary system, such as Co-60 and Co-58, during the application. The decomposition of major compositions of the decontamination solution affects the decontamination performance. Therefore, it is necessary to analyze the radiolysis of N_2H_4, which is the major component of the N_2H_4–Cu^+–HNO_3 decontamination solution, during irradiation.

In this regard, a number of research studies concerning decomposition of N_2H_4 solution have been carried out. It is known that the decomposition of N_2H_4 under irradiation conditions can occur through a reaction with radiolysis products of water. Various radicals and products, such as e_{aq}^-, $^\bullet OH$, and H_3O^+, are generated by the radiolysis of water [10]. The radiolysis products of water as represented in Equation (1) [11].

$$H_2O \overset{\gamma-\text{radiation}}{\rightarrow} 0.27e_{aq}^-,\ 0.06\ H^\bullet,\ 0.26^\bullet OH,\ 0.045H_2,\ 0.08\ H_2O_2,\ 0.27H_3O^+ \quad (1)$$

The decomposition reaction mechanism of N_2H_4 in the aqueous solution by γ-ray irradiation can be found in the study of Buxton et al. [12]. They reported that radicals such as $N_2H_4^{\bullet+}$, $NH_2^\bullet$ and $N_2H_3^\bullet$, generated from N_2H_4, are decomposed into N_2 and NH_3. It is also shown that the NH_4^+ ion was produced by a reaction between $H^\bullet$ radical and $N_2H_5^+$. Garaix et al. studied the decay mechanism of the $NO_3^\bullet$ radical generated by the radiolysis of NO_3^- ions in the N_2H_4 solution using an electron beam [13]. They concluded that N_2H_4 exists mainly as $N_2H_5^+$ or $N_2H_6^{2+}$ in the acidic solution, both of which cause rapid consumption of $NO_3^\bullet$ radicals. Motooka et al. also reported that the deoxygenation reaction with radiolysis of N_2H_4 can be suppressed by salt in the water in the γ-radiation field [14]. In this way, the molecular structure of N_2H_4 after radiolysis and the decomposition mechanism of the N_2H_4 depend on the composition of the solution. However, there are few research studies about the N_2H_4 decomposition reaction in N_2H_4–Cu^+–HNO_3 solution. Therefore, it is necessary to study the decomposition reaction mechanism of the N_2H_4 in N_2H_4–Cu^+–HNO_3 solution during γ-ray irradiation to simulate the decontamination condition.

In this study, we evaluated the effects of Cu^+ ions and HNO_3 on N_2H_4 decomposition under the γ-radiation field. The study was performed by analyzing the concentration of remaining N_2H_4 and the concentration of the products in N_2H_4–Cu^+–HNO_3 solution after the irradiation. The decomposition mechanism of N_2H_4 in the solution containing Cu^+ ions and HNO_3 was also suggested.

2. Theoretical Background

2.1. Radiolysis of Hydrazine in Acidic Solution

Hydrazine generally exists in the form of $N_2H_5^+$ by its reaction with H^+ ions in an acidic solution, as given in Equation (2) [13,15,16]. At pH 1, $N_2H_6^{2+}$ coexists with $N_2H_5^+$ through the reaction shown in Equation (3) [13,15,17]. Therefore, N_2H_4 exists in the forms of $N_2H_5^+$ and $N_2H_6^{2+}$ in the N_2H_4–HNO_3 system before irradiation.

$$N_2H_4 + H^+ \ 2194\ N_2H_5^+,\ pK \approx 7.9 \quad (2)$$

$$N_2H_5^+ + H^+ \leftrightarrow N_2H_6^{2+},\ pK \approx -1 \quad (3)$$

In an acidic solution, the same as the condition of this study, e_{aq}^-, $H^\bullet$, $OH^\bullet$, and H_2O_2 are generated as products after water radiolysis. It is possible that e_{aq}^- reacts with H^+ ions in the acidic solution and generates $H^\bullet$ as in the following Equation (4) [18]. The reactions between the water radiolysis products and the chemical species of N_2H_4 lead to the decomposition of N_2H_4.

$$e_{aq}^- + H^+ \rightarrow H^\bullet,\ k = 2.2 \times 10^{10}\ M^{-1}s^{-1} \quad (4)$$

The principal decomposition reactions and rate constants of the chemical species of N_2H_4 in the irradiation condition are listed in Equations (5)–(23). As shown in Equation (5), $N_2H_6^{2+}$ reacts with $OH^\bullet$ and produces N_2, the end product of N_2H_4 decomposition at pH 1 [19].

$$N_2H_6^{2+} + 4OH^\bullet \rightarrow N_2 + 4H_2O + 2H^+ \quad (5)$$

In addition, $N_2H_5^+$ is the main species form of N_2H_4 in the acidic solution. $N_2H_5^+$ reacts with the radiolysis products of water such as e_{aq}^-, $H^\bullet$, or $OH^\bullet$ as shown in

Equations (6)–(9) [12,20]. NH_4^+ ion, one of the end products of N_2H_4 decomposition, is produced by the reaction between $N_2H_5^+$ and $H^\bullet$, as indicated in Equation (7). The intermediates of $N_2H_5^+$ decomposition, N_2H_4, $NH_2^\bullet$, and $N_2H_4^{\bullet+}$, are generated by the reactions in Equations (6), (8) and (9). These intermediates cause the consecutive decomposition reactions of N_2H_4. In particular, N_2H_4 can also be hydrolyzed into $N_2H_5^+$ and $N_2H_6^{2+}$ as shown in Equations (2) and (3).

The consecutive decomposition reactions of N_2H_4 with $OH^\bullet$, $N_2H_4^{\bullet+}$, and H_2O_2 are listed in Equations (10)–(12) [12,20,21]. $N_4H_8^+$ is formed by the reaction between N_2H_4 and $N_2H_4^{\bullet+}$, as indicated in Equation (10). $^\bullet N_2H_3$ is generated by the reaction between N_2H_4 and $OH^\bullet$, as shown in Equation (11). The intermediates, $N_4H_8^+$ and $^\bullet N_2H_3$, participate in the other consecutive decomposition reactions of N_2H_4. However, N_2 is produced as the end product by the reaction between N_2H_4 and H_2O_2 (Equation (12)).

$NH_2^\bullet$ generated by the reaction in Equation (7) causes the reactions with $N_2H_5^+$ or N_2H_4, as represented in Equations (13) and (14) [12]. $N_2H_4^{\bullet+}$, $^\bullet N_2H_3$, and NH_3 are formed after the reactions shown in Equations (13) and (14). Among these products, $N_2H_4^{\bullet+}$ and $^\bullet N_2H_3$ cause the consecutive reactions because they are the reactive intermediates.

$N_2H_4^{\bullet+}$ produced by Equations (8), (9) and (13) participate in the consecutive reactions represented in Equations (15) and (16) [12]. As shown in Equation (15), $N_4H_9^{\bullet 2+}$ is generated after the reaction of $N_2H_4^{\bullet+}$ with $N_2H_5^+$. As indicated in Equation (16), $N_4H_9^{\bullet 2+}$ reacts with $N_2H_4^{\bullet+}$, and the reaction products are $N_4H_8^{2+}$ and $N_2H_5^+$. The $N_4H_8^{2+}$ is directly decomposed into N_2 and NH_3 in the ratio of 1 to 2. On the other hand, $N_2H_5^+$ is repeatedly decomposed into other forms, as represented in Equations (6)–(9), (13) and (15).

$^\bullet N_2H_3$ generated by Equations (11) and (14) is decomposed into various forms, as listed in Equations (17)–(22) [12]. The main end products of $^\bullet N_2H_3$ decomposition are N_2 and NH_3, as represented in Equations (19) and (20). The main intermediates, N_2H_4 and N_2H_2, are also generated from the decomposition reaction of $^\bullet N_2H_3$, as shown in Equations (17)–(22). N_2H_4 is hydrolyzed into $N_2H_5^+$ and $N_2H_6^{2+}$ in the acidic solution or causes consecutive decomposition reactions. N_2H_2 reacts with $H^\bullet$, and $^\bullet N_2H_3$ is produced as shown in Equation (23).

As mentioned above, it is expected that various intermediates are generated during the decomposition of the chemical species of N_2H_4. Therefore, the intermediates can affect the reaction with Cu^+ ions or NO_3^- ions in the N_2H_4–Cu^+–HNO_3 system.

$$N_2H_5^+ + {e_{aq}}^- \rightarrow H^\bullet + N_2H_4,\ k = 1.6 \times 10^8\ M^{-1}s^{-1} \quad (6)$$

$$N_2H_5^+ + H^\bullet \rightarrow NH_2^\bullet + NH_4^+,\ k = 1.0 \times 10^4\ M^{-1}s^{-1} \quad (7)$$

$$N_2H_5^+ + H^\bullet \rightarrow H_2 + N_2H_4^{\bullet+},\ k = 1.3 \times 10^5\ M^{-1}s^{-1} \quad (8)$$

$$N_2H_5^+ + OH^\bullet \rightarrow N_2H_4^{\bullet+} + H_2O,\ k = 8.2 \times 10^7\ M^{-1}s^{-1} \quad (9)$$

$$N_2H_4 + N_2H_4^{\bullet+} \leftrightarrow N_4H_8^{\bullet+},\ k_f = 6.0 \times 10^7\ M^{-1}s^{-1},\ k_b = 4.0 \times 10^5\ M^{-1}s^{-1} \quad (10)$$

$$N_2H_4 + OH^\bullet \rightarrow {}^\bullet N_2H_3 + H_2O,\ k = 5.4 \times 10^9\ M^{-1}s^{-1} \quad (11)$$

$$N_2H_4 + 2H_2O_2 \rightarrow N_2 + 4H_2O,\ k = 2.4 \times 10^8\ M^{-1}s^{-1} \quad (12)$$

$$NH_2^\bullet + N_2H_5^+ \rightarrow N_2H_4^{\bullet+} + NH_3,\ k = 1.0 \times 10^6\ M^{-1}s^{-1} \quad (13)$$

$$NH_2^\bullet + N_2H_4 \rightarrow {}^\bullet N_2H_3 + NH_3,\ k = 1.0 \times 10^7\ M^{-1}s^{-1} \quad (14)$$

$$N_2H_4^{\bullet+} + N_2H_5^+ \leftrightarrow N_4H_9^{\bullet 2+},\ k_f = 6.0 \times 10^7\ M^{-1}s^{-1},\ k_b = 4.0 \times 10^5\ M^{-1}s^{-1} \quad (15)$$

$$N_2H_4^{\bullet+} + N_4H_9^{\bullet 2+} \rightarrow N_4H_8^{2+} + N_2H_5^+\ (N_4H_8^{2+} \rightarrow N_2 + 2NH_3),\ k = 4.0 \times 10^8\ M^{-1}s^{-1} \quad (16)$$

$${}^\bullet N_2H_3 + {e_{aq}}^- + H_2O \rightarrow N_2H_4 + OH^-,\ k = 7.0 \times 10^9\ M^{-1}s^{-1} \quad (17)$$

$${}^\bullet N_2H_3 + H^\bullet \rightarrow N_2H_4,\ k = 7.0 \times 10^9\ M^{-1}s^{-1} \quad (18)$$

$$^{\bullet}N_2H_3 + N_4H_8^{\bullet+} \rightarrow N_2H_4 + N_4H_7^{+} (N_4H_7^{+} \rightarrow N_2 + 2NH_3), \quad k = 1.0 \times 10^9\ M^{-1}s^{-1} \tag{19}$$

$$^{\bullet}N_2H_3 + N_4H_9^{\bullet 2+} \rightarrow N_2H_4 + N_4H_8^{2+} (N_4H_8^{2+} \rightarrow N_2 + 2NH_3), \quad k = 1.0 \times 10^9\ M^{-1}s^{-1} \tag{20}$$

$$^{\bullet}N_2H_3 + N_2H_4^{\bullet+} \rightarrow N_2H_2 + N_2H_5^{+}, k = 7.0 \times 10^8\ M^{-1}s^{-1} \tag{21}$$

$$^{\bullet}N_2H_3 + {}^{\bullet}N_2H_3 \rightarrow N_2H_2 + N_2H_4, k = 6.0 \times 10^8\ M^{-1}s^{-1} \tag{22}$$

$$N_2H_2 + H^{\bullet} \rightarrow {}^{\bullet}N_2H_3, k = 3.0 \times 10^9\ M^{-1}s^{-1} \tag{23}$$

2.2. Change of Copper Species during Irradiation

Copper ions in the solution would cause the decomposition of N_2H_4 during the irradiation. The redox reactions mainly occur between copper ions and radiolysis products of water such as e_{aq}^{-}, $H^{\bullet}$, and $OH^{\bullet}$, as listed in Equations (24)–(28) [22–25]. The equations show that copper ions coexist in the forms of Cu^0, Cu^+ ions and Cu^{2+} ions regardless of initial chemical species. In addition, Fenton reaction occurs in an acidic condition, as represented in Equation (29) [26,27]. The above reactions can affect the decomposition of N_2H_4 in the N_2H_4–Cu^+–HNO_3 system.

$$Cu^{+} + e_{aq}^{-} \rightarrow Cu^0 \tag{24}$$

$$Cu^{+} + H^{\bullet} \rightarrow Cu^0 + H^{+}, k = 5 \times 10^9\ M^{-1}s^{-1} \tag{25}$$

$$Cu^{+} + OH^{\bullet} \rightarrow Cu^{2+} + OH^{-}, k = (2\pm1) \times 10^{10}\ M^{-1}s^{-1} \tag{26}$$

$$Cu^{2+} + e_{aq}^{-} \rightarrow Cu^{+}, k = 3.5 \times 10^{10}\ M^{-1}s^{-1} \tag{27}$$

$$Cu^{2+} + H^{\bullet} \rightarrow Cu^{+} + H^{+}, k < 1.0 \times 10^6\ M^{-1}s^{-1} \tag{28}$$

$$H_2O_2 + Cu^{+} + H^{+} \rightarrow OH^{\bullet} + H_2O + Cu^{2+} \tag{29}$$

2.3. Radiolysis of Nitrate Ion

The principal reactions of NO_3^{-} ions during the irradiation are listed in Equations (30)–(38) [13,28–33]. The reactions can be classified by direct and indirect decomposition reactions. As shown in Equation (30), the NO_3^{-} ion is directly changed into $NO_3^{\bullet}$ and electron due to the γ-ray irradiation [13,28]. The NO_3^{-} ion is also changed into NO_3^{2-} ion or $NO_2^{\bullet}$ through the reactions with e_{aq}^{-} or $H^{\bullet}$, as can be seen in Equations (31) and (32) [29,30]. The $NO_3^{2-\bullet}$ reduces into $NO_2^{\bullet}$ in the water, as represented in Equation (33) [29,31]. During irradiation, $NO_2^{\bullet}$ reacts with the radiolysis products of water such as e_{aq}^{-}, $H^{\bullet}$, and $OH^{\bullet}$, and H^{+}, NO_2^{-} ion, and NO_3^{-} ions are produced as listed in Equations (34)–(36) [32]. On the other hand, $NO_2^{\bullet}$ reacts with water and generates NO_2^{-} and NO_3^{-} ions, as shown in Equation (37) [13,33]. As represented in Equation (38), NO_2^{-} ions generated from the reaction in Equations (34), (35) and (37) are changed into NO_3^{-} ions and $NO_2^{\bullet}$ through the reaction with $NO_3^{\bullet}$ [13,33]. The generated NO_2^{-} ions are directly consumed, and $NO_2^{\bullet}$ and NO_3^{-} ions are regenerated by the reaction indicated in Equation (38). As mentioned above, NO_3^{-} ions and their radicals generated from the radiolysis of NO_3^{-} can also participate in the decomposition reaction of N_2H_4 in the N_2H_4–Cu^+–HNO_3 system.

$$NO_3^{-} \overset{\text{radiation}}{\rightarrow} NO_3^{-}* \rightarrow NO_3^{\bullet} + e^{-} \tag{30}$$

$$NO_3^{-} + e_{aq}^{-} \rightarrow NO_3^{2-\bullet}, k = 9.7 \times 10^9\ M^{-1}s^{-1} \tag{31}$$

$$NO_3^{-} + H^{\bullet} \rightarrow NO_2^{\bullet} + OH^{-}, k = 1.0 \times 10^7\ M^{-1}s^{-1} \tag{32}$$

$$NO_3^{2-\bullet} + H_2O \rightarrow NO_2^{\bullet} + 2OH^{-}, k = 1.0 \times 10^3\ M^{-1}s^{-1} \tag{33}$$

$$NO_2^{\bullet} + e_{aq}^{-} \rightarrow NO_2^{-}, k = 1.0 \times 10^{10}\ M^{-1}s^{-1} \tag{34}$$

$$NO_2^{\bullet} + H^{\bullet} \rightarrow H^+ + NO_2^-, k = 1.0 \times 10^9\ M^{-1}s^{-1} \quad (35)$$

$$NO_2^{\bullet} + {}^{\bullet}OH \rightarrow H^+ + NO_3^-, k = 1.0 \times 10^{10}\ M^{-1}s^{-1} \quad (36)$$

$$2NO_2^{\bullet} + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+, k = 4.5 \times 10^8\ M^{-1}s^{-1} \quad (37)$$

$$NO_3^{\bullet} + NO_2^- \rightarrow NO_2^{\bullet} + NO_3^-, k = 4.4 \times 10^9\ M^{-1}s^{-1} \quad (38)$$

3. Results

3.1. Effect of Copper Ions on Hydrazine Decomposition

In order to investigate the effect of copper ions on the N_2H_4 decomposition, γ-ray was irradiated to the N_2H_4–Cu^+–HNO_3 solution and N_2H_4–HNO_3 solution at pH 3. The absorbed dose was varied from 0 to 20 kGy, and the $[N_2H_4]_0$ in the solutions was equal to 50 × [N2H4]0 in the solutions was equal to 50 × 10^{-3} mol dm^{-3}. The pH of the solution was adjusted to 3using HNO_3. Figure 1 shows the change in the concentration of N_2H_4 as a result of the γ-irradiation. The decomposed portion of N_2H_4 increased with the increase in the absorbed dose regardless of the presence of the Cu^+ ions. This result indicates that the amount of radiolysis products of water participating in the N_2H_4 decomposition was enhanced when the absorbed dose was increased. At the same absorbed dose, the decomposed portion of N_2H_4 was higher when the copper ions existed than that when the copper ions were absent, as indicated in Figure 1. In particular, 12.48 × 10^{-3} mol dm^{-3} of N_2H_4 in the solution containing Cu^+ ions was decomposed after the 20 kGy of γ-irradiation. When the Cu^+ ions were absent in the solution, 9.05 × 10^{-3} mol dm^{-3} of N_2H_4 was decomposed. Moreover, the G-values for the N_2H_4 decomposition were calculated for 20 kGy of absorbed dose and listed in Table 1. G(–N_2H_4), for the solution containing Cu^+ ions, was higher than that of the solution not containing Cu^+ ions.

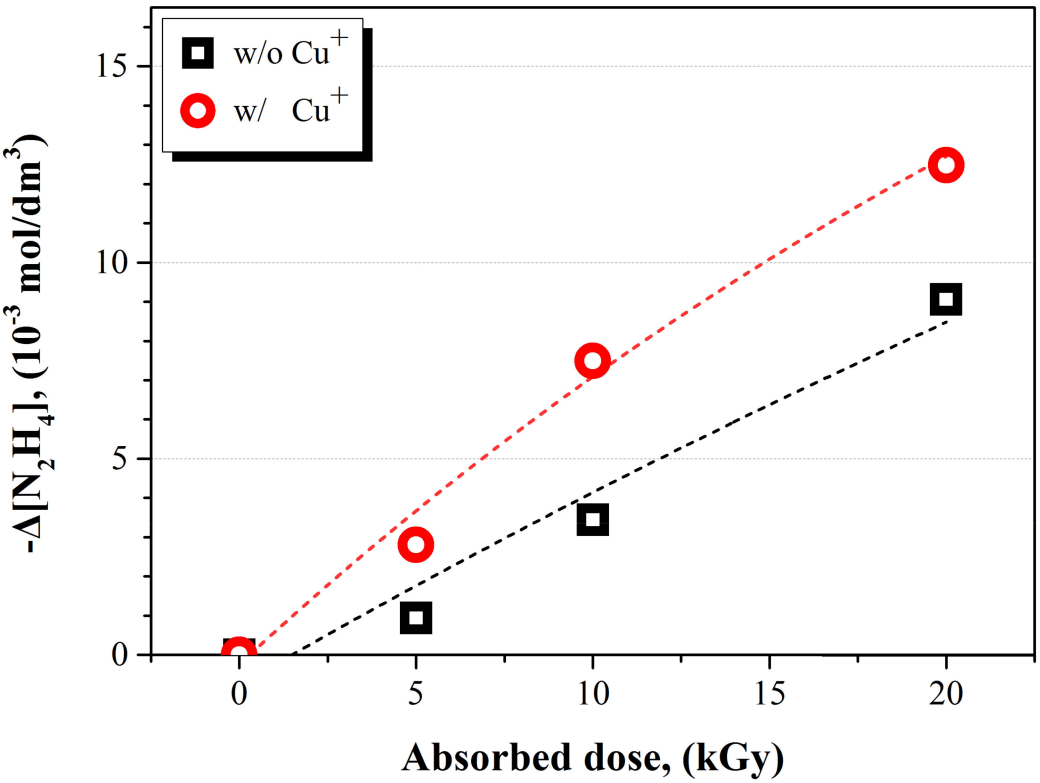

Figure 1. Dependence of N_2H_4 decomposition on Cu^+ ions after γ-irradiation on the solution of which $[N_2H_4]_0$ = 50 × 10^{-3} mol dm^{-3} at pH 3.

Table 1. G(–N_2H_4) values in the N_2H_4–HNO_3 and N_2H_4–Cu^+–HNO_3 solutions of which $[N_2H_4]_0 = 50 \times 10^{-3}$ mol dm^{-3} at 20 kGy of absorbed dose.

Total Dose (kGy)	G(–N_2H_4) Value (10^{-7} mol/J)	
	w/o Cu^+ Ions	w/Cu^+ Ions
20	4.52	6.24

There are several explanations for the effect of copper ions on the decomposition of N_2H_4: (1) a catalyzed reaction of H_2O_2 occurs [34], (2) copper ions lower the energy barrier of N-H bonds cleavage in the gas phase [35], and (3) the formation of $Cu^+N_2H_4$ occurs [36,37]. The experimental condition of Zhong and Lim is similar to that of this study [36,37]. They suggested that $Cu^+N_2H_4$ complex acts as a scavenger and it increases the decomposition reaction of N_2H_4. The predicted mechanism is given in Equations (39)–(41). N_2H_4 reacts with Cu^+ ion and forms the $Cu^+N_2H_4$ complex, as shown in Equation (39). This complex can react with H_2O_2 and produces N_2H_2, as indicated in Equation (40). The reaction between the $Cu^+N_2H_4$ complex and N_2H_2 causes the generation of $Cu(^\bullet N_2H_3)_2$ that decomposes into Cu^+ ion and $^\bullet N_2H_3$, as represented in Equation (41).

$$Cu^+ + N_2H_4 \leftrightarrow Cu^+N_2H_4 \quad (39)$$

$$Cu^+N_2H_4 + H_2O_2 \rightarrow Cu^+ + N_2H_2 + 2H_2O, \text{(slow)} \quad (40)$$

$$Cu^+N_2H_4 + N_2H_2 \leftrightarrow Cu^+(^\bullet N_2H_3)_{2,\ cage} \rightarrow Cu^+ + 2^\bullet N_2H_3, \text{(slow)} \quad (41)$$

N_2H_4 was considered to be reproduced as the intermediate during radiolysis in this study; however, the hydrazine was hydrolyzed into $N_2H_5^+$ or $N_2H_6^{2+}$ in acidic conditions. The N_2H_4 could form the $Cu^+N_2H_4$ complex with the Cu^+ ion through the reaction, as indicated in Equation (39). As can be seen in Equations (40) and (41), it was possible that the $Cu^+N_2H_4$ complex was separated into Cu^+ ion, N_2H_2, and water after reacting with H_2O_2 generated from the radiolysis of water. The N_2H_2 could react with $H^\bullet$ and generate $^\bullet N_2H_3$ according to the Equation (23). Moreover, N_2H_2 could also cause a reaction with the $Cu^+N_2H_4$ complex and form $Cu^+(N_2H_3^\bullet)_2$. $Cu^+(N_2H_3^\bullet)_2$ was directly decomposed into $^\bullet N_2H_3$ and Cu^+ ion following the reaction in Equation (41). $^\bullet N_2H_3$ was decomposed into N_2 or NH_3 during the γ-ray irradiation, as listed in Equations (19) and (20). The Cu^+ ion regenerated from the reactions shown in Equations (40) and (41) repeatedly formed the $Cu^+N_2H_4$ complex and caused the decomposition reaction of N_2H_4 again. Therefore, these two reactions offered new decomposition reaction paths of N_2H_4 where the Cu^+ ion acted as the catalyst.

The electrochemical characterization, under the same conditions as this experiment, was also performed by Yang et al. [38]. Figure 2 shows the cyclic voltammograms using an ITO (Indium-Tin Oxide) electrode in solutions of 3 mM N_2H_4, 0.3 mM $Cu(NO_3)_2$, 0.1 M $NaNO_3$, and 3 mM N_2H_4 + 0.3 mM $Cu(NO_3)_2$. All the test solutions were adjusted to pH 3 using HNO_3. The oxidation peak of the N_2H_4 near 0.3 V increased significantly with the addition of $Cu(NO_3)_2$. The peak is quite different from that of N_2H_4 alone or $Cu(NO_3)_2$ alone. This result implies that Cu^+ ions make coordination compounds with N_2H_4, as listed in reaction Equation (39). Therefore, it is inferred that Cu^+ ions affect the N_2H_4 decomposition by formation of the $Cu^+N_2H_4$ complex in the N_2H_4–Cu^+–HNO_3 system.

3.2. Effect of HNO_3 on Hydrazine Decomposition

HNO_3 affects the decomposition of N_2H_4 in two ways: (1) the effect of H^+ ions and (2) the effect of NO_3^- ions. In order to investigate the effect of H^+ ions and NO_3^- ions on N_2H_4 decomposition, the concentration of the chemical species of N_2H_4 was analyzed according to the pH change under the radiation field. The pH of each solution was adjusted to 1, 3, and 5 by adding HNO_3, respectively. Every sample solution included 50×10^{-3} mol dm^{-3} of N_2H_4 and 0.5×10^{-3} mol dm^{-3} of Cu^+ ions. As a result, the concentration of chemical species of N_2H_4 decreased with a decreasing pH

at the same absorbed dose, as shown in Figure 3. The concentrations of decomposed N_2H_4 were 29.96 × 10^{-3} mol dm^{-3} (pH = 1), 15.92 × 10^{-3} mol dm^{-3} (pH = 3), and 13.42 × 10^{-3} mol dm^{-3} (pH = 5) at 40 kGy, respectively. The decomposed portion of N_2H_4 significantly increased as the solution's pH decreased from 3 to 1. At the same time, the G(–N_2H_4) at pH 1 was 7.49 × 10^{-7} mol J^{-1} for 40 kGy of absorbed dose, as shown in Table 2. The G(–N_2H_4) at pH 3 and 5 were 3.98 × 10^{-7} mol J^{-1} and 3.35 × 10^{-7} mol J^{-1} for 40 kGy of absorbed dose, respectively. Based on this result, it was confirmed that the G-values for the decomposition of N_2H_4 increased with the decreasing of the pH.

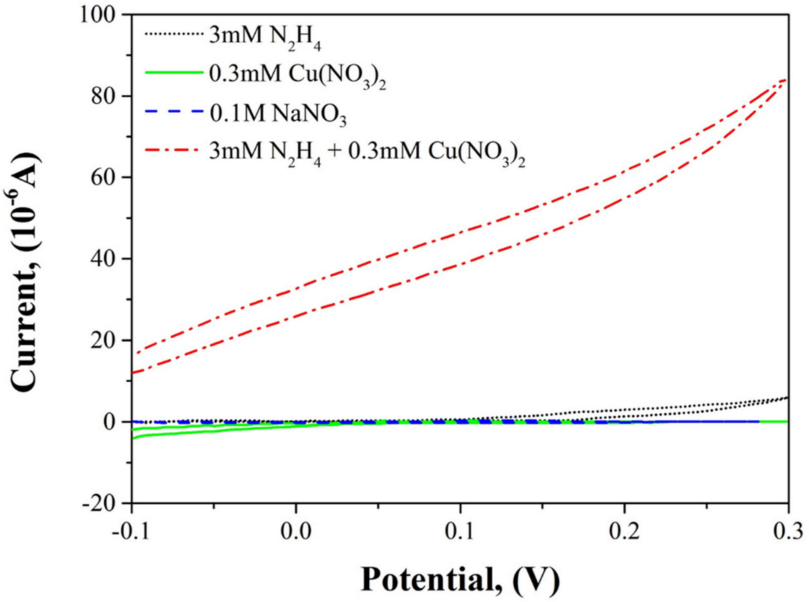

Figure 2. Cyclic voltammograms of 3 mM N_2H_4, 0.3 mM $Cu(NO_3)_2$, 0.1 M $NaNO_3$, and 3 mM N_2H_4 + 0.3 mM $Cu(NO_3)_2$ solutions at scan rate of 20 mV/s. Adapted with permission from [38] Haesik Yang.

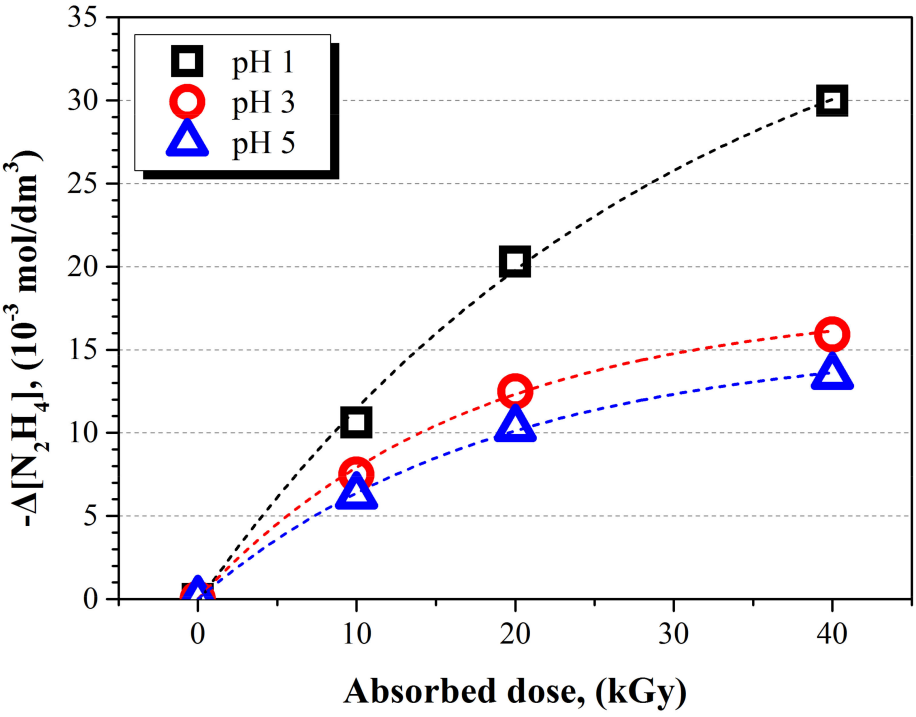

Figure 3. Concentration change of chemical species of N_2H_4 according to the absorbed dose under various pHs condition.

Table 2. G(–N_2H_4) values in the different pH of N_2H_4–Cu^+–HNO_3 solutions of which $[N_2H_4]_0 = 50 \times 10^{-3}$ mol dm^{-3} at 40 kGy of absorbed dose.

Total Dose (kGy)	G(–N_2H_4) Value (10^{-7} mol/J)		
	pH 1	pH 3	pH 5
40	7.49	3.98	3.35

Firstly, the above results can be explained by the effect of the H^+ ion on N_2H_4 decomposition. As mentioned above, the reaction between the H^+ ion and e_{aq}^- caused the generation of $H^\bullet$, as represented in Equation (4). The increase in $H^\bullet$ promoted the reaction between $H^\bullet$ and the intermediates of N_2H_4 decomposition, such as $N_2H_5^+$, $N_2H_3^\bullet$, and N_2H_2, listed in Equations (7), (8), (18) and (23). When the reactions shown in Equations (7), (8) and (23) occurred, NH_4^+ ions or the intermediates such as $^\bullet NH_2$, $N_2H_4^{\bullet+}$, and $^\bullet N_2H_3$ were produced. As represented in Equation (18), N_2H_4 is recovered through the reaction between $^\bullet N_2H_3$ and $H^\bullet$. This N_2H_4 could be decomposed after hydrolysis into $N_2H_5^+$ or be decomposed directly through the reactions listed in Equations (10)–(12). On the other hand, it was possible to form the $Cu^+N_2H_4$ complex with copper ions and cause a decomposition reaction of N_2H_4 using Equations (40) and (41). In particular, N_2H_4 and $^\bullet N_2H_3$ generated from the reactions shown in Equations (18) and (23) have a high reaction rate, which are 7.0×10^9 $M^{-1}s^{-1}$ and 3.0×10^9 $M^{-1}s^{-1}$, among the reactions concerned $H^\bullet$. The N_2H_4 and $^\bullet N_2H_3$ are mostly decomposed into N_2 and NH_3, as mentioned above.

Secondly, the increase in the decomposition reaction of N_2H_4 with the lowering of the pH of the N_2H_4–Cu–HNO_3 solution could also be explained by the effect of the NO_3^- ion. When the NO_3^- ion reacts with $NH_4^{\bullet+}$, which is the chemical species of N_2H_4, N_2H_2 and $^\bullet NO_2$ are produced due to the reaction, as represented in Equation (42) [39]. As listed in Equation (23), the N_2H_2 reacts with $H^\bullet$, and $^\bullet N_2H_3$ is generated. As mentioned above, $^\bullet N_2H_3$ normally decomposes into N_2 and NH_3, leading to N_2H_4 decomposition. $^\bullet NO_2$ participates in the reaction with radiolysis products of water, and finally NO_3^- is formed by the reaction shown in Equations (34)–(38). On the other hand, $NO_3^\bullet$ generated during the radiolysis of NO_3^- ions also affects N_2H_4 decomposition. When $NO_3^\bullet$ reacts with $N_2H_5^+$, $N_2H_4^{\bullet+}$ and HNO_3 are produced, as shown in Equation (43) [13,39]. $N_2H_4^{\bullet+}$ is consecutively decomposed not only by the reaction listed in Equations (15) and (16) but also by the reaction shown in Equation (42). NO_3^- ions recovered from the reaction shown in Equation (43) participate in the decomposition reaction of the chemical species of N_2H_4. Therefore, the increase in HNO_3 in the N_2H_4–Cu^+ solution accelerated the decomposition of N_2H_4 by increasing the occurrence of reaction concerned with $H^\bullet$ and adding new decomposition reaction paths, including that of the NO_3^- ion.

$$N_2H_4^{\bullet+} + NO_3^- \rightarrow N_2H_2 + H_2O + {}^\bullet NO_2,\ k = 2.5 \times 10^7\ M^{-1}s^{-1} \quad (42)$$

$$N_2H_5^+ + NO_3^\bullet \rightarrow N_2H_4^{\bullet+} + NO_3^- + H^+,\ k = 1.3 \times 10^9\ M^{-1}s^{-1} \quad (43)$$

Moreover, the decomposed portion of N_2H_4 increased rapidly at pH 1 compared to at pH 3 and 5, when the absorbed doses increased at the rates shown in Figure 3. This was caused by $H^\bullet$ and $NO_3^\bullet$ being generated by irradiation. Since the amount of HNO_3 added at pH 1 was larger than at pH 3 and 5, the amount of $H^\bullet$ and $NO_3^\bullet$ produced was larger at pH 1 than at pH 3 and 5. The increase in $H^\bullet$ and $NO_3^\bullet$ promoted the decomposition of N_2H_4 through the reactions, as mentioned above.

In order to investigate the anionic effect, the remaining concentration of N_2H_4 in the NO_3^- ion system was compared with that of the SO_4^{2-} ion system at pH 3. Quantities of 10, 20, and 40 kGy of the absorbed doses were irradiated to each solution. The initial concentration of N_2H_4 in each solution was 50×10^{-3} mol dm^{-3}. As shown in Figure 4, the decomposed concentration of N_2H_4 increased when the absorbed dose increased regardless of the type of acid added. At the same absorbed dose, three times higher concentrations of N_2H_4 in the NO_3^- ion system were decomposed as compared to the

SO_4^{2-} ion system. As indicated in Table 3, the G-value for the decomposition of N_2H_4 at 40 kGy was 3.98×10^{-7} mol J^{-1} when the acid added in the solution was HNO_3. G(–N_2H_4) was 1.25×10^{-7} mol J^{-1} when the acid injected in the solution was H_2SO_4. From these results, we found that the NO_3^- ions facilitated the decomposition of N_2H_4 in the solution.

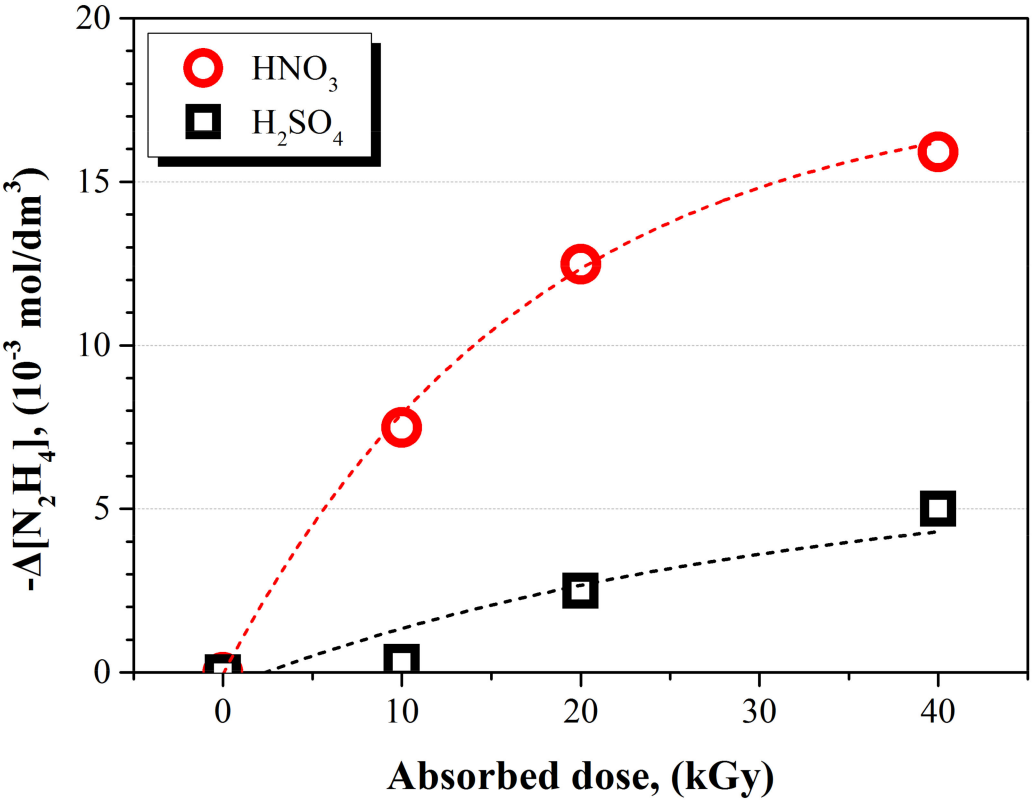

Figure 4. Concentration change of chemical species of N_2H_4 according to the absorbed dose under different acid conditions.

Table 3. G(–N_2H_4) values of N_2H_4–Cu^+–HNO_3 and N_2H_4–Cu^+–H_2SO_4 solutions of which $[N_2H_4]_0 = 50 \times 10^{-3}$ mol dm^{-3} at 40 kGy of absorbed dose.

Total Dose (kGy)	G(–N_2H_4) Value (10^{-7} mol/J)	
	Containing HNO_3	Containing H_2SO_4
40	3.98	1.25

3.3. Decomposition Mechanism of Hydrazine in N_2H_4–Cu^+–HNO_3 System

The decomposition reactions of the N_2H_4 in N_2H_4–Cu^+–HNO_3 system are schematically shown in Figure 5. N_2H_4 in the acidic solution is hydrolyzed and coexists as $N_2H_5^+$ or $N_2H_6^{2+}$. These species are decomposed into intermediates such as $N_2H_4^{\bullet+}$, $^{\bullet}N_2H_3$, and $NH_2^{\bullet}$ under irradiation conditions. N_2H_4 can decompose into NH_4^+ ion, N_2, or NH_3. However, it was verified that the end products were mainly formed with N_2 or NH_3. In addition, N_2H_4 decomposition was promoted by the influence of the Cu^+ ion, H^+ ion, and NO_3^- ion in the N_2H_4–Cu^+–HNO_3 system, as explained in Sections 3.1 and 3.2. As represented in green line in Figure 5, Cu^+ ions form the $Cu^+N_2H_4$ complex with N_2H_4. The $Cu^+N_2H_4$ complex participates in the reactions, as shown in Equations (40) and (41). The complex decomposes into $^{\bullet}N_2H_3$ and further decomposes into the end products through the consecutive reactions, as listed in Equations (17)–(22). The recovered Cu^+ ion from the complex repeatedly forms an N_2H_4 complex that acts as a catalyst to accelerate the decomposition of N_2H_4. $H^{\bullet}$ was produced through the reaction between the H^+ ion and e_{aq}^-. Therefore, the decomposition reaction of N_2H_4 by $H^{\bullet}$ was promoted as the concen-

tration of the H^+ ion increased. As shown in the orange line in Figure 5, NO_3^- ions or $NO_3^\bullet$ radicals accelerate the N_2H_4 decomposition by providing the additional reaction paths to change $N_2H_5^+$ into $N_2H_4^{\bullet+}$. They also cause $N_2H_4^{\bullet+}$ to decompose into N_2H_2. NO_3^- ion and $NO_3^\bullet$ were regenerated by the radiolysis of $NO_2^\bullet$ and $NO_3^\bullet$, as shown in Equations (34)–(38), and they participated in the N_2H_4 radiolysis reaction again. Consequently, N_2H_4 decomposition was promoted in the N_2H_4–Cu^+–HNO_3 system through the mechanism shown in Figure 5.

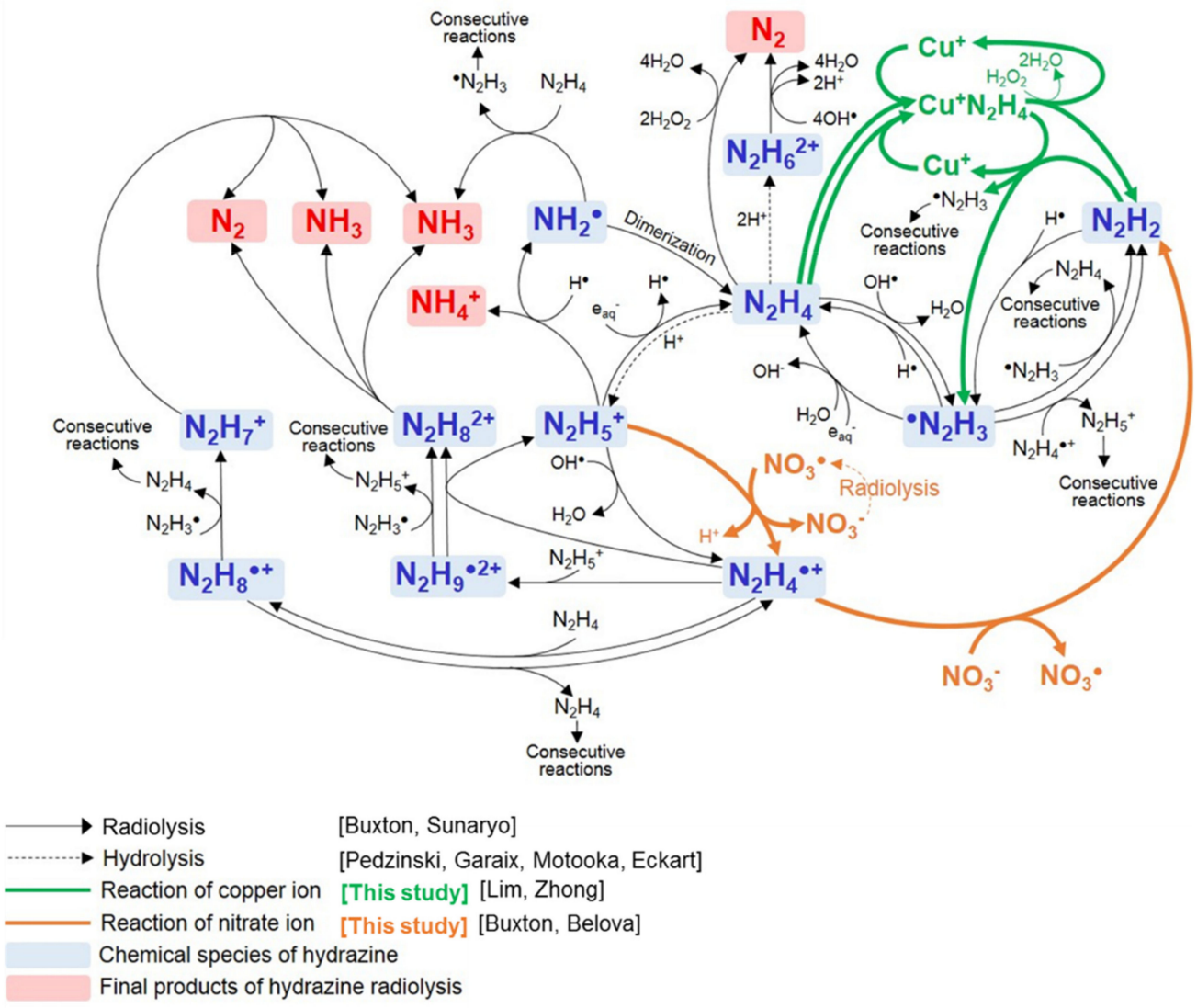

Figure 5. Schematic diagram of radiolysis of N_2H_4 in N_2H_4–Cu^+–HNO_3 system.

In order to verify the effect of Cu^+ ions on the decomposition mechanism of N_2H_4 in the N_2H_4–HNO_3 solution, the fraction of N_2H_4 and end products were analyzed after irradiation with 20 kGy of the absorbed dose. The initial concentrations of N_2H_4 in the solution were 50×10^{-3} mol dm^{-3}, and the pH of the solution was adjusted to 3. The results were compared with and without Cu^+ ions in the solution, as represented in Figure 6. Through the above reactions, it was verified that N_2H_4 in the N_2H_4–Cu^+–HNO_3 solution was finally decomposed into N_2, NH_3, and NH_4^+ ion under an irradiation condition by the reactions with radiolysis products of water or consecutive decomposition reactions. For this reason, the fraction of N_2 and NH_3 in the solution after γ-ray irradiation was calculated by subtracting the amount of remaining chemical species of N_2H_4 and NH_4^+ ions produced after irradiation from the initial amount of N_2H_4.

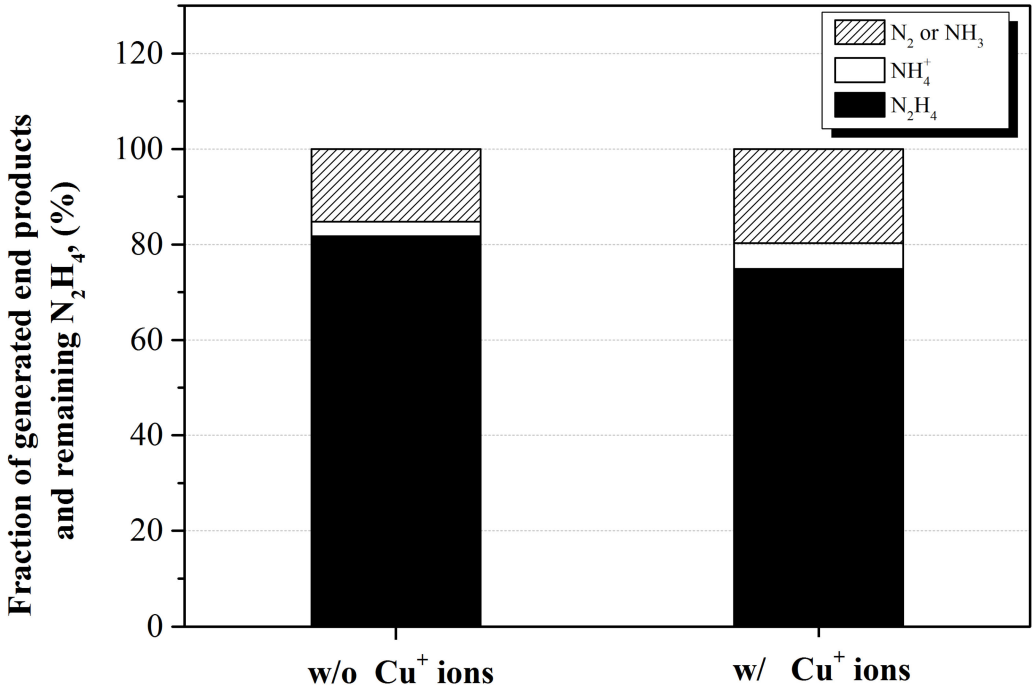

Figure 6. Fraction of radiolysis products and chemical species of N_2H_4 in the solution without and with Cu^+ ions after 20 kGy of γ-ray irradiation.

As shown in Figure 6, N_2H_4 decomposed into N_2, NH_3, and NH_4^+ ion. It is well known that most of NH_3 reacts with H^+ ions in the acidic solution and exists in the form of NH_4^+ [40]. Therefore, it was considered that most of the remaining gas phase end product was composed of N_2 after irradiation in this study. It was judged that the NH_3 was converted into NH_4^+ ion after the irradiation. When the Cu^+ ion is present in the N_2H_4–HNO_3 solution, $N_2H_3^\bullet$ is generated, as indicated in Figure 5 and Equation (41). $N_2H_3^\bullet$ participated in the reaction, generating N_2 or NH_3, as shown in Equations (19) and (20). Therefore, it was confirmed that the fraction of N_2 and NH_4^+, the form of NH_3 in the acidic condition, increased when the Cu^+ ions were present in the N_2H_4–HNO_3 solution, as represented in Figure 6.

To confirm the effect of HNO_3 on the decomposition mechanism of N_2H_4 in the N_2H_4–Cu^+ solution, the fraction of remaining N_2H_4 and end products in each sample after 40 kGy of absorbed dose irradiation at pH 1, 3, and 5 was analyzed. The initial concentrations of N_2H_4 in the solutions were 50×10^{-3} mol dm^{-3}. The result is represented in Figure 7. As mentioned above, NH_3 is converted into NH_4^+ ion in the solution because of the acidic condition. As shown in Figure 7, NH_4^+ ions were not generated after 40 kGy of absorbed dose irradiation at pH 1. Therefore, it was considered that most of N_2H_4 was decomposed into N_2. The obtained result at pH 1 can be explained as follows. At pH 1, N_2H_4 exists in the form of $N_2H_6^{2+}$ as a result of hydrolysis, as shown in Equation (3). The $N_2H_6^{2+}$ ion generated N_2 through the decomposition reaction, as indicated in Equation (5).

In addition, the amount of end products of N_2H_4 decomposition were decreased with increasing pH. This was the case because the large amount of $H^\bullet$ produced by the reaction between H^+ ions and e_{aq}^- affected the N_2H_4 decomposition, as shown in Figure 5. For this reason, the decrease in the concentration of end products of N_2H_4 decomposition following an increase in the pH was caused by a decrease in the N_2H_4 decomposition reaction.

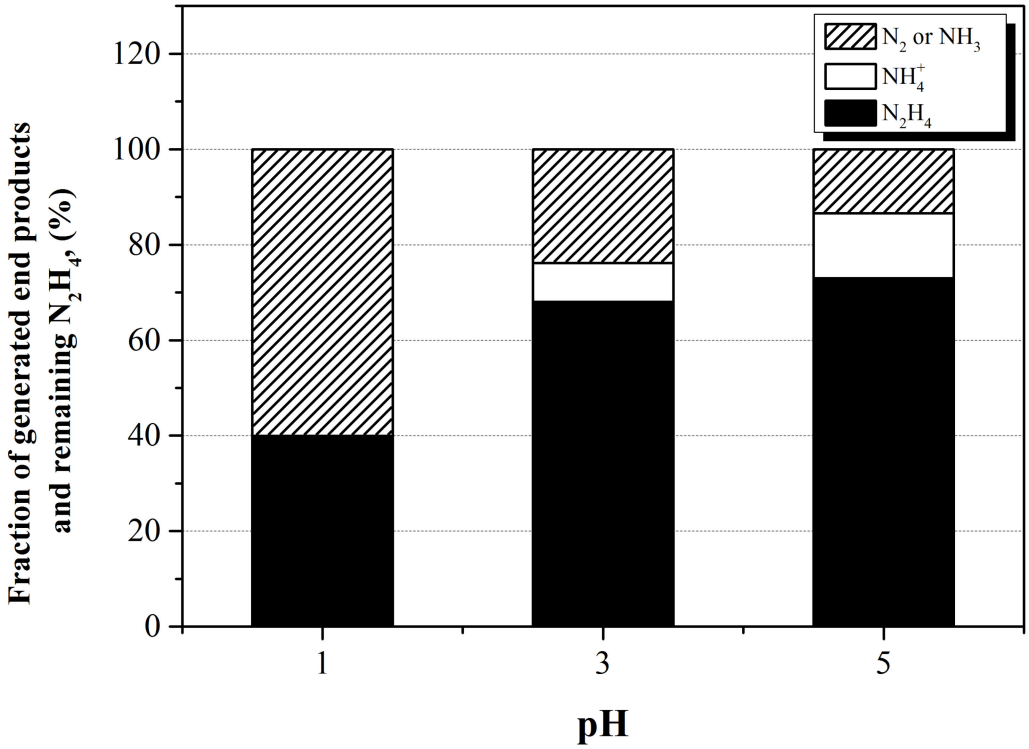

Figure 7. Fraction of radiolysis products and chemical species of N_2H_4 at different pH after 40 kGy of γ-ray irradiation.

However, the concentration of NH_4^+ ions generated after irradiation increased with increasing pH. This was the case because the N_2H_4 exists as a form of the $N_2H_5^+$ ion rather than the $N_2H_6^{2+}$ ion as the pH increases. As indicated in Equations (6)–(23), the end products of the reactions with a high reaction rate, among the consecutive reactions of $N_2H_5^+$ ion decomposition in which $H^\bullet$ participated, were mainly N_2 and NH_3. The NH_3 reacted with the H^+ ion in an acidic condition and existed in the form of NH_4^+ ions, as mentioned above. NO_3^- ions were also related to the generation of N_2 and NH_3. The reaction between the $N_2H_5^+$ ion and $NO_3^\bullet$ shown in Equation (43) might affect the generation of $N_2H_4^{\bullet+}$, NO_3^- ion and H^+ ion. As shown in Equations (15) and (16), the end products generated by the reactions of $N_2H_4^{\bullet+}$ were mostly N_2 and NH_3. Otherwise, the N_2H_2 is produced when the $N_2H_4^{\bullet+}$ reacts with NO_3^- ions, as shown in Equation (42). N_2H_2 is the intermediate of N_2H_4 decomposition and it generates $^\bullet N_2H_3$ after the reaction with $H^\bullet$, as represented in Equation (23). The end reaction products involving $^\bullet N_2H_3$ are also N_2 and NH_3, as represented in Equations (17)–(22). The NH_3 generated by the reaction between $N_2H_5^+$ and $NO_3^\bullet$ also existed in the form of NH_4^+ ion in the acidic condition. Therefore, it is concluded that HNO_3 can affect the decomposition of N_2H_4 through the mechanisms listed in Equations (5)–(23) and Equations (42) and (43) by investigating the end product of the expected decomposition paths.

4. Materials and Methods

4.1. Chemicals and Sample Preparation

Hydrazine monohydrate (Junsei, Tokyo, Japan, 98.0%), nitric acid (EMSure, Darmstadt, Germany, 65.0%) and copper (I) chloride (SIGMA-ALDRICH, St. Louis, MO, USA, 97.0%) were used to prepare N_2H_4–Cu^+–HNO_3 solution in this study. The conditions of each sample is listed in Table 4. All the solutions contain 50.0 mM of N_2H_4. In order to investigate the effects of Cu^+ ions on N_2H_4 decomposition, the solutions were prepared according to the presence of 0.5 mM of copper ions. Each sample was adjusted to pH 3 by adding nitric acid. To analyze the effects of HNO_3 on N_2H_4 decomposition, each solution was adjusted to pH 1, 3, and 5 by adding 144.7 mM, 50.8 mM, and 49.9 mM of nitric acid, respectively.

All the sample solutions included 0.5 mM of copper ions. The 30 mL of sample solutions were stored in the 50 mL vials. After storing the solution in the vial, the nitrogen purging was conducted for 10 min. during the γ-ray irradiation.

Table 4. Sample preparation.

Sample Solution	Concentration (mM)		
	N_2H_4	Cu^+ Ions	HNO_3
pH 1	50	0.5	144.7
pH 3 (without Cu^+ ion)	50	-	50.8
pH 3 (with Cu^+ ion)	50	0.5	50.8
pH 5	50	0.5	49.9

4.2. γ-rradiation

A high-dose γ-ray irradiator (Co-60 source) at the Korea Atomic Energy Research Institute was used for irradiation on the solutions. Quantities of 0, 5, 10, 20, and 40 kGy of absorbed doses were given to each sample to compare the dose effects on the decomposition of N_2H_4. All irradiation experiments were carried out with a dose rate of 10 kGy/hr at room temperature.

4.3. Analysis

The concentration of chemical species of N_2H_4 in the solutions was measured using a UV Spectrometer (DR 5000, Hach Co., Ames, IA, USA). The p-dimethylaminobenzaldehyde method was applied to detect the chemical species of N_2H_4.

5. Conclusions

The radiolysis of N_2H_4 in the N_2H_4–Cu^+–HNO_3 solution during γ-ray irradiation was verified through the irradiation experiment and the analysis of a chemical species of N_2H_4 concentration. When copper ions were present in the N_2H_4–HNO_3 solution, the N_2H_4 decomposition, via the decomposition of the $Cu^+N_2H_4$, complex was promoted by the catalytic reaction of Cu^+ ions. HNO_3 also accelerated the N_2H_4 decomposition in the N_2H_4–Cu^+–HNO_3 system through the influence of the H^+ ion and NO_3^- ion. This is because $H^\bullet$ produced by the reaction between H^+ ion and e_{aq}^- participated in the N_2H_4 decomposition reaction. Owing to the H^+ ion effect, the N_2H_4 decomposition during irradiation was raised when the pH was decreased. NO_3^- ion and $NO_3^\bullet$ led to an increase in the N_2H_4 decomposition through the reaction with $N_2H_4^{\bullet+}$ or the reaction with $N_2H_5^+$. These additional paths, due to the existence of the Cu^+ and NO_3^- ions, improved the N_2H_4 decomposition under irradiation condition. These findings can be applied, in accordance with the characteristics of radiolysis, to define the conditions of N_2H_4 concentration during chemical decontamination processes.

Author Contributions: Conceptualization, N.C., H.W. and Y.K.; methodology, N.C., H.W. and H.E.; formal analysis, N.C.; investigation, N.C., H.W. and S.P.; resources, S.K. and B.S.; writing—original draft preparation, N.C.; writing—review and editing, N.C. and H.W.; project administration, S.K. and B.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was carried out under the Nuclear R&D program (NRF-2017M2A8A5015144) funded by the Ministry of Science, ICT and Future Planning (MSIP) of Korea.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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