Synthesis and Radiation Sensitivity of Tris(4-*N,N*-dimethylaminophenyl)methanethiol

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A leuco crystal violet analog, tris(4-*N,N*-dimethylaminophenyl)methanethiol (**1**) was synthesized and utilized to the γ rays detection system. Acetonitrile solution of leuco dye **1** showed significant absorbance change after γ irradiation of 1 Gy, and the change was more significant than those of tris(4-*N,N*-dimethylaminophenyl)methanol (**2**) and leuco crystal violet (**3**).

Keywords: functional dye, leuco crystal violet, triarylmethanethiol, γ rays dosimeter

1. Introduction

The research in color changing materials by the change of light or thermal conditions has been very noteworthy to develop novel optical devices.[1] Radiation has been widely utilized in fields such as radiometric analysis, food hygiene and medical treatment. The development of highly sensitive radiation monitoring labels is of overriding importance to radiation institutions. Leuco crystal violet (LCV, **3**) has been utilized to the γ rays detection system with halocarbons.[2] We developed the LCV and halocarbon system and reported that 2-propanol solution of LCV (1×10^{-3} M) showed blue color change after γ irradiation of 5 Gy in the presence of an equal molar amount of halocarbon (CCl_4 or CBr_4).[3]

The C-S cleavage by γ irradiation would occur more easily than those of C-H and C-O bonds, as shown in the sulfur containing polymers[4] or sulfides.[5] For example, poly(butane-1-sulphone) is 50 times more sensitive to electron beam or deep UV radiation than poly(methyl metacrylate), PMMA.[4] Tris(4-*N,N*-dimethylaminophenyl)methanethiol (**1**) will be a better color former for γ rays detection system than tris(4-*N,N*-dimethylaminophenyl)methanol (**2**) or LCV (**3**). In this paper, we report synthesis of **1** and the absorbance

change of its solution by γ irradiation, and comparison of radiation sensitivity of **1** with those of **2** and **3**.

2. Synthesis

Several methods to prepare compound **1** using H_2S , NH_4SH , or Na_2S_2 have been reported.[6] However, reaction time, amount of reagents, purification method, and yield were not described in the reference. We have synthesized compound **1** by the similar method to prepare compound **2**. [7] Thus, compound **1** was synthesized from crystal violet (CV, **4**•Cl⁻) and sodium hydrosulfide (NaSH). As expected, CV reacted with sodium hydrosulfide more easily than sodium hydroxide because the nucleophilicity of hydrosulfide is larger than that of hydroxide. The yields in our preparations were

22 % and 11 % for compounds **1** and **2**, respectively. The melting points of these products could not be determined because of the decomposition, however, ^1H NMR, IR, UV/VIS and MS analyses supported their expected structures.

3. Experimental

3.1 Materials

Commercially available tris(4-*N,N*-dimethylaminophenyl)methane **3** was recrystallized from ethanol before use for γ irradiation. Crystal violet **4**•Cl⁻ (Wako Pure Chemical Industries, Ltd.) was used without further purification. Toluene and acetonitrile were distilled before use.

Synthesis of tris(4-*N,N*-dimethylaminophenyl)methanethiol (**1**)

Crystal violet (**4**•Cl⁻) (370 mg, 1.0 mmol) was dissolved in *N,N*-dimethylformamide (3.5 ml) by heating at 40 °C; 30% sodium hydrosulfide (NaSH) solution (0.50 ml, 2.5 mmol) was added dropwise to the mixture; the solution was stirred at 40 °C for 2 h. The mixture was poured into 12.5 ml of ice water. Addition of sodium chloride (625 mg) gave the precipitates of the product. The precipitates were collected by suction filtration and successively washed with 2% solution of sodium hydrosulfide and cold water. The collected products were dried and recrystallized from methanol to give **1**: yield 154 mg (22 %) pale purple powder: ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.41 (AA'BB', 6H, H_a) 6.49 (AA'BB', 6H, H_b) 3.08 (s, 1H, SH) 2.55 (s, 18H, CH_3), IR (KBr, cm^{-1}) 1609, 1519, 1354, 816; UV/VIS (acetonitrile) λ_{max} 269.5 nm ($\epsilon = 27,000$), MS (DI, m/z) 347 (M^+).

Synthesis of tris(4-*N,N*-dimethylaminophenyl)methanol (**2**)

Crystal violet (**4**•Cl⁻) (370 mg, 1.0 mmol) was dissolved in *N,N*-dimethylformamide (3.5 ml) by heating at 40 °C; 30% sodium hydroxide solution (0.30 ml, 2.5 mmol) was added dropwise to the mixture; the solution was stirred at 40 °C for 2 h. The mixture was poured into 12.5 ml of ice water. Addition of sodium chloride (625 mg) gave the precipitates of the product. The precipitates were collected by suction filtration and washed successively with 2% solution of sodium hydroxide and ice water. The collected products were dried and recrystallized from toluene to give **2**: yield 154 mg (11 %) brown needles: ^1H NMR (200 MHz, toluene- d_8) δ (ppm) 7.51 (AA'BB', 6H, H_a) 6.58 (AA'BB', 6H, H_b) 2.56 (s, 18H, CH_3); IR (KBr, cm^{-1}) 3436, 2885, 1611, 1519, 1349, 1062, 816; UV/VIS (acetonitrile) λ_{max} 265.5 nm ($\epsilon = 31,000$), MS(DI, m/z) 389 (M^+).

3.2 Methods

γ rays were irradiated to the solution of dyes with a dose rate of 600 Gy / h using ^{60}Co source. UV/VIS spectra were recorded on UV-2500 or UV-3100 spectrometer (Shimadzu). ^1H NMR, IR, and Mass spectra were recorded on Gemini 2000 spectrometer (Varian), 1600 series FT-IR spectrometer (Perkin Elmer), and JMS-DX303HF mass spectrometer (JEOL), respectively.

4. γ Irradiation

Dry acetonitrile solutions of compounds **1** - **3** (2.0×10^{-5} M) were prepared and irradiated with γ rays. The absorbance changes were recorded by UV/VIS spectrometer. The first absorption wavelengths of leuco dyes **1**, **2**, and **3** (2.0×10^{-5} M) were 269.5 nm ($\epsilon = 2,700$), 265.5 nm ($\epsilon = 3,100$) and 269.5 nm ($\epsilon = 3,200$) in acetonitrile, respectively. The first absorption wavelength of Crystal violet (CV, **4**•Cl⁻) (2.0×10^{-5} M) was 587.5 nm ($\epsilon = 120,000$) in acetonitrile. The absorbance changes at 587.5 nm observed for the acetonitrile solutions of **1** - **3** after γ irradiation are shown in Figure 1.

Figure 1 Absorbance changes of **1** (◆), **2** (□) or **3** (▲) to give colored form **4** (587.5 nm) in acetonitrile by γ irradiation, $[1]_0 = [2]_0 = [3]_0 = 2.0 \times 10^{-5}$ M.

For compound **2** or **3**, the absorbance at 587.5 nm increased gradually until the irradiation dose came to 100 Gy, and an absorbance increase was about 0.004 absorbance units per 10 Gy. The conversion ratio from **2** or **3** to **4** by γ irradiation was about 1.7 % at 100 Gy. On the other hand, for compound **1**, the absorbance at 587.5 nm showed the maximum at the dose of 40 Gy and an absorbance increase at the dose of first 10 Gy became 0.44 absorbance units. The conversion ratio from **1** to **4** by γ irradiation at 10 Gy was 18 % in acetonitrile. The absorbance increase at 587.5 nm for **1** to give **4** was about 100 times larger than those for **2** and **3** to give **4** at irradiation of 10 Gy. The cleavage of the C-S bond was obviously easier than those of the C-O and C-H

Figure 2 Absorbance change of **1** (269.5 nm; ○) to give colored form **4** (587.5 nm; ◆) in acetonitrile after γ irradiation, $[1]_0 = 2.0 \times 10^{-5}$ M.

bonds. These results coincide with the fact that leuco phenothiazine dye could not produce the corresponding colored form by γ irradiation.[8] The coloration of the acetonitrile solution of **1** can be recognized by the naked eye after irradiation of 10 Gy. Significant absorbance change of 0.044 at 587.5 nm due to **4** was observed for the leuco dye **1** after γ irradiation of 1 Gy

The absorbance at 587.5 nm for compound **1** showed the maximum at the dose of 40 Gy and gradually decreased. The absorbance of **1** at 269.5 nm decreased rapidly until the irradiation dose came to 10 Gy and became almost constant at the irradiation dose more than 10 Gy (Figure 2). The reaction of **1** seems to be complete at the dose of 10 Gy. The absorbance decrease at 587.5 nm shown at the dose more than 40 Gy was caused by the decomposition of **4**. When the acetonitrile solution of CV (**4**·Cl⁻) (2.0×10^{-5} M) was irradiated with γ rays, the absorbance at 587.5 nm showed a gradual decrease. For compound **4** formed from **1**, the absorbance at 587.5 nm showed a decrease of 0.074 absorbance units per 100 Gy in the range from 100 Gy to 300 Gy. This value was almost the same with that of CV. For CV, the absorbance at 587.5 nm showed a decrease of 0.088 absorbance units per 100 Gy in the range from 100 Gy to 700 Gy.

As shown in Figures 1 and 2, the absorbance at 587.5 nm for the acetonitrile solution of **1** was 0.43 absorbance units before irradiation. The coloration was observed at room temperature though it was not so fast as to affect the UV/VIS measurements of the irradiated samples. Thermal- and photo-

Figure 3 Absorbance changes of **1** to give colored form **4** in 19/1 (v/v) toluene/acetonitrile (597.0 nm; ■) or 9/1 (v/v) toluene/acetonitrile (594.0 nm; △) after γ irradiation, $[1]_0 = 2.0 \times 10^{-5}$ M.

stability is important for indicators. Solvent polarity would affect the stability of **1**. Thus, γ irradiation to **1** in non-polar solvents, such as toluene, was attempted. Compound **1** easily dissolves in toluene but the colored form **4** has not any tendency to dissolve in toluene. Therefore, toluene/acetonitrile mixture (19/1 or 9/1, v/v) was used. The absorbance changes at 587.5 nm after γ irradiation to the toluene/acetonitrile solutions of **1** are shown in Figure 3. The absorbance at 587.5 nm before γ irradiation was suppressed to 0.015 absorbance units for 19/1 toluene/acetonitrile solution and 0.030 absorbance units for 9/1 toluene/acetonitrile solution, respectively. The absorbance at 587.5 nm after γ irradiation increased linearly in the range from 0 to 100 Gy. The absorbance increment at 587.5 nm by γ irradiation of 40 Gy was 0.024 absorbance units for 9/1 toluene/acetonitrile solution and 0.006 absorbance units for 19/1 toluene/acetonitrile solution, respectively. The increment was 1/19 or 1/73 of that for pure acetonitrile solution, respectively. The reason of these absorbance decreases is explained by the decrease of the molar absorption coefficient of CV in toluene/acetonitrile mixture. UV/VIS spectra of CV have been known to show the solvent effects.[9, 10] The molar absorption coefficient of CV in 9/1 toluene/acetonitrile solution was 16,000 ($\lambda_{\max}$ = 594 nm) which is 1/7.5 of that in acetonitrile. The conversion ratio from **1** to **4** in 9/1 toluene/acetonitrile solution was 10.6 % at the irradiation of 40 Gy. This is about half of that in acetonitrile. Solvent effect for γ irradiation was also observed in the systems such as fluoran and acid generators.[11] The suitable solvent choice will enable to suppress the undesirable decomposition of the leuco dye.

5. Conclusions

Tris(4-*N,N*-dimethylaminophenyl)methanethiol (**1**) could produce the colored form **4** by the C-S bond cleavage initiated by γ rays. Compound **1** was prepared by a novel method using sodium hydrosulfide. Acetonitrile solution of **1** showed significant absorbance change after γ irradiation of

1 Gy. The conversion ratio from **1** to **4** by γ irradiation of 10 Gy was 18 % in acetonitrile, which was about 100 times larger than that of **2** or **3**. Acetonitrile solution of **1** gave gradual color change at room temperature. The undesirable coloration was suppressed by the use of 9/1 or 19/1 (v/v) toluene/acetonitrile mixture. The cleavage of C-S bond will become a key concept for the detection system of γ rays.

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