Substituent Effect of Photo and Thermal Decomposition Rate of Diazocompounds with Inclusion Compounds

Kieko Harada1, Wumaierjiang Aimaiti1, Masahiro Nakada1, Yukari Morihito2, Tadashi Narita2, Reiko Aoki2, Masahito Kushida1 and Kazuyuki Sugita1

1 Education Center of Chiba Institute of Technology, 2-1-1 Shizhazono, Narashino-shi, Chiba 275-0023 Japan
2 Faculty of Engineering, Saitama Institute of Technology, 1690 Fusaij, Hukaya-shi, Saitama 369-0293, Japan
3 Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522 JAPAN

When 18-crown-6(18C6) was added to p-substituted benzene diazo compounds (SBD) in methanol, λ max of SBD shifted to shorter wavelength, but did not shift in an aqueous solution. Degree of the shift with electron-withdrawing substituent (WSBD) was larger than that with electron-donating substituent (DSBD). WSBD with poor electron density was coordinated by six oxygen atoms of 18C6 more tightly than DSBD. Photo decomposition of SBD with 18C6 in methanol were suppressed through the coordination. Photo decomposition of WSBD were slightly suppressed with polyethylene glycol 300 (PEG), while did not change with β-cyclodextrin (CD). Thermal decomposition of DSBD with 18C6 in methanol and an aqueous solution were suppressed similarly to that of photodecomposition in methanol. Thermal decomposition rate of SBD can be suppressed through the complex formation by adding PEG or CD, and the rate may be accelerated with the coexistence of hydroxy groups. These results indicate that; when DSBD with 18C6 are used for information recording materials, thermal stability will be improved. DSBD with CD will be improved in thermal stability without decreasing sensitivity. When WSBD with CD or PEG were used for acid generators for polymerization, the rate will increase.

Keywords: photosensitive diazo compound, 18-crown-6, polyethylene glycol 300, β-cyclodextrin, acid generator

1. Introduction
The para-substituted benzene diazo compounds (SBD) with electron-donating (DSBD) are used as the photoacid generators for micro resists [1], photosensitive emulsions for the screen printing resist [2], the binders for phosphors powders on the multicolor screens [3] and UV-fixable thermal recording paper [4-5]. SBD with electron withdrawing substituted (WSBD) were used for acid generators for polymerization. 18-Crown-6 (18C6) complexes with benzene diazonium cation improve photo and thermal stability of diazo compounds [6-11]. Thermal decomposition of less expensive β-cyclodextrin (CD) complex with diphenylamine-4-diazonium sulfate/formaldehyde condensate / PVA resist(DSR-PVA) was suppressed[12]. The coloring of the DSR/PVA emulsion films was suppressed by inclusion of 18C6 or PEG[12].

In this report, the control of the photo and thermal decomposition of p-substituted benzene diazocompounds (SBD) by forming a complex with 18C6 which includes the diazo group of the SBD, and CD[13] and PEG[14] which include the benzene ring of SBD was studied by measuring the rate constant and a degradation temperature (d.t). There are solvent effects for the formation of inclusion complex of the diazo compounds[14]. The rates were measured in an aqueous solution for application of diazo / PVA resist and methanol for application of diazo-polyvinyl acetate (diazo / PVA resist).

2. Experimental
2.1 Materials
p-substituted benzene diazonium tetrafluoroborates (SBD) were precipitated by adding hydrogen tetrafluoroborate to an aqueous solution of the cor-
responding benzene diazonium chloride prepared from p-substituted aniline. The solid product was recrystallized from ethanol. The additives used were 18C6, PEG and CD of extra pure grade.

Concentration of SBD for aqueous solution was 5X10^3 mol/l. Inclusion compounds are 5X10^1 - 5X10^3. Solid for thermal analysis was formed in the following. SBD with 18C6 dissolved in methanol, then methanol was removed by volatilization. SBD with PEG dissolved in PEG. SBD with CD mixed with CD powder.

2.2 Measurements

Photo and thermal decompositions of SBD in an aqueous solution and methanol were studied by measuring the absorption intensity at λ max under light-shielded condition. Photo decomposition of SBD in an aqueous solution and methanol were conducted by irradiation with a Toshiba Super High-Pressure Mercury lamp SHL100. The incident energy was 3.1 mW/cm^2. The absorbances at λ max of UV spectra were measured with a Shimazu UV-1600 PC spectrophotometer. Thermal degradation temperature was measured by TDA and TGA in solid by a Shimazu ETG-60.

3 Results and Discussion

3.1 λ max of SBD and SBD with inclusion compounds

When diazo group of the diazo compound is included by the inclusion compound, the λ max of the diazo group shifted to a shorter wavelength.

When 18C6, CD or PEG was added to SBD in an aqueous solution, λ max of SBD or diazo group did not shift. In an aqueous solution, SBD associated with oxygen atoms of water, so a complex with the inclusion compound was not formed. When 18C6, CD and PEG were added to SBD in methanol, λ max of SBD with 18C6 or PEG were shifted to shorter wavelength. SBD with CD which includes the benzene ring did not shift.

λ max of SBD and SBD with 18C6 (SBD/18C6) were plotted to substituent constant σ in methanol, as shown in Fig.1. A reaction constant ρ of SBD showed different between σ > 0 and σ < 0. It is reported [15] that the electron transfer (by calculation) of SBD from the diazo group to the benzene ring of SBD with electron withdrawing group (WSBD) are easier than that of SBD with electron drawing group (DSBD). The constitution of WSBD is assigned to Scheme 1-(2) and DSBD is assigned to Scheme 1-(3-1), respectively.

![Fig.1 Hammett plots of λ max of p-substituted Diazocompounds with or without 18C6 in methanol](image)

Scheme 1. Resonance structures of benzenediazonium ion
Scheme 2  Tight and less tight inclusion complex

The degree of shift of $\lambda$ max of WSBD was larger than that of DSBD. Inside of 18C6, it is electron-rich, then WSBD in which the electron density of the diazo group is poor by electron withdrawing group, was used for tight inclusion complex as shown in Scheme 2-(1) DSBD showed less tight inclusion as shown in Scheme 2-(2).

3.2 Photo decomposition of SBD

The residual SBD and SBD with 18C6 or PEG in methanol after UV irradiation were measured by UV spectrophotometry and the rate constants were calculated. Hammett plots of photo decomposition rate of SBD and SBD with or without inclusion compounds are shown in Fig.2. The reaction constants $\rho$ of SBD and SBD with inclusion compounds were similar to that of $\lambda$ max of SBD and SBD with 18C6. The rates of SBD with 18C6 and PEG were suppressed. The rate of SBD with CD did not changed. SBD were photo decomposed by absorbing the photon of each wavelength of SBD at $\lambda$ max. $\lambda$ Max of SBD with CD which include benzene ring of SBD was same as that of SBD.

3.3 Thermal decomposition of SBD and SBD with inclusion compounds

In order to estimate storage stability, thermal decomposition rates of SBD and SBD with inclusion compounds in various solvents were studied by measuring the spectral change in the dark.

3.3.1 In aqueous solution

Hammett plots of thermal decomposition rates of SBD and SBD with inclusion compounds in an aqueous solution are shown in Fig.3. Thermal decompositions of SBD in an aqueous solution are ionic reaction [16]. WSBD with CD [13] and PEG [14] were accelerated and the rates were, in decreasing order, CD>PEG> 18CD > no additives. Reaction mechanism is shown in Scheme 3.

When CD or PEG is added to WSBD, a cationic
diazo group of WSBD bonds with the hydroxy group of CD or PEG. The WSBD included with CD or PEG generates nitrogen gas and an alkoxy and a phenyl radicals via homolysis by heating. The homolysis is accelerated by formation of a complex with CD or PEG as shown in Scheme 3-(1) and 3-(2).

![Chemical structures](image)

Scheme 3 Interaction of hydroxy group and diazo group

DSBD with 18C6, PEG and CD were suppressed. The thermal decomposition rate of DSBD with inclusion compounds were, in decreasing order, 18C6, PEG > CD > no additives.

An anion of diazo group of DSBD does not bond with a hydroxy group of CD or PEG. The DSBD included CD or PEG generates nitrogen gas and a phenyl cation via heterolysis as shown in Scheme 3-(3) and 3-(4).

3.3.2 In methanol
Hammett plots of thermal decomposition rates of SBD and SBD with inclusion compounds in methanol as shown in Fig. 4.

SBD with 18C6 were suppressed. The degree of the suppress was according to the degree of the shift of λ max. The rates of SBD with inclusion compounds were in decreasing order, 18C6 > PEG = CD = no additives.

![Graph](image)

Fig. 4 Hammett plots of thermal decomposition rates of p-substituted diazo compounds with or without inclusion compounds in methanol at 40°C

![Graph](image)

Fig. 5 Hammett plots of degradation temperature of p-substituted diazo compounds with or without inclusion compounds in solid state
3.3.3 Degradation temperature of in solid state

Hammett plots of degradation temperature (d.t.) in solid state were shown in Fig.5. The d.t. of SBD with 18C6 were higher than that without 18C6. Diazoo group was perfectly included by 18C6 in solid state. The d.t. of SBD with PEG were lower than that without PEG. PEG has a hygroscopic property. The d.t. of DSBD with CD were higher and WSBD with CD were lower than that without CD, respectively. The result of SBD with CD were same as that of thermal decomposition in an aqueous solution.

4. Conclusion

Photo and thermal decomposition rate was found to be suppressed through the complex formation by adding 18C6, PEG or CD, or to be accelerated with the coexistence of hydroxy groups.

The thermal decomposition of SBD in methanol and storage instability of the diazo/PVA resist, are suppressed by addition of 18C6. Thermal decomposition in an aqueous solution, and instability of the diazo/PVA are suppressed with 18C6, PEG or CD. When DSBD with 18C6 are used for information recording materials, thermal stability will be improved. DSBD with CD will be improved thermal stability without decreasing sensitivity. When WSBD with CD or PEG were used for the acid generator for polymerization, the rate will be promoted.

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