Structural Analysis of Ionic Photobase Generators and Lithographic Patterning of Polysilane Films Containing the Photobase Generators

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Photobase generator is recently attracting more attention because it is freed from oxygen inhibition and metal corrosion, compared to photoacid generator and photo radical generator. 2-(9-Oxoxanthen-2-yl)propionic acid (OXTA) has an absorption in the range of i-line wavelength and it can form a salt with phosphazene base (P2tBu). It is photobase generator (PBG) to generate an organic superbase efficiently by UV irradiation. In this study, we synthesized a series of salts of OXTA and P2tBu (OXTA-P2tBu) at several anion-cation ratio. Then, we analyzed the PBG with each ratio by pH, UV absorption and ESR, and calculated OXTA-P2tBu complex by (TD)B3LYP/6-31+G(d,p) level. The crystal of OXTA-P2tBu synthesized at optimum ratio was analyzed by single crystal X-ray diffraction and we described the crystal structure. Furthermore, we obtained nega-type pattern with polysilane solution containing OXTA-P2tBu in the optimum ratio.

Keywords: Photobase generator, Phosphazene, Ionic complex, Crystal structure, superbase

1. Introduction

Photobase generator (PBG) has an advantage from the view point of inhibition by oxygen and metal corrosion. So, it is expected that PBG is useful for a wide range of photosensitive fields such as reaction initiator of epoxide’s polymerization and dehydration condensation of polyimide at low temperature. However, there are few reports about PBG to generate superbase efficiently [1]. Recently, Arimitsu focused on decarboxylation reactions of ketoprofen under UV irradiation (L. L. Costanzo’s paper) [2] and synthesized PBG to generate base high efficiently by forming a salt with the base [3]. On the basis of the study, they chose 2-(9-Oxoxanthen-2-yl)propionic acid (OXTA) that had an absorption in the i-line and cleavage efficiency comparable to ketoprofen, and synthesized PBG with it [4].

On the other hand, phosphazene base is recently attracting more attention because of its high basicity [5]. Phosphazene easily abstracts proton from alcohol and generates conjugate base which behaves as a reaction initiator [6]. To focus on these properties, we synthesized photobase generator OXTA-P2tBu to generate superbase under UV irradiation by forming a salt with OXTA and 1-tert-butyl-2,2,4,4,4-pentaxyth(dimethylamino)-2,5-catenadi(phosphazene) (P2tBu). In another study, we studied the pattern forming with polysilane solution containing this PBG without functional groups such as acrylate and epoxide [7]. However, it has not become clear yet the behavior of pH and salt forming of OXTA-P2tBu at each ratio when it was synthesized and under UV irradiation.

In this paper, we synthesized OXTA-P2tBu with the change of ratio between P2tBu and OXTA and observed pH of that before and after UV irradiation. To presume the behavior of the salt-forming at each ratio, energy levels and edge absorption wavelength \( \lambda_{\text{edge}} \) of them were calculated. By comparison of the

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measured and calculated UV absorption spectra, we observed the behavior of salt-forming at the ratio. From above results, we observed generated radical of them under UV irradiation by ESR and evaluated the salt stability at the synthesis. We analyzed the crystal of OXTA-P2tBu at optimum ratio by single crystal X-ray diffraction and determined the crystal structure. We efficiently formed pattern with polysilane solution containing OXTA-P2tBu at optimum ratio.

2. Experimental
2.1. Materials
2.1.1. Synthesis of OXTA-P2tBu
Into a 50 mL vial were added 30 mL THF, 2-(9-oxoxanthen-2-yl)propionic acid (Purity>98.0%, made by Tokyo Kasei) and P2tBu (~2 M in THF, made by Aldrich) as shown in Table 1 and the mixture was stirred to react for a day (sample a-1 ~ a-4). Obtained solution was evaporated and THF was removed, then highly viscous objective substance was obtained.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a-1</th>
<th>a-2</th>
<th>a-3</th>
<th>a-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXTA (g)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>P2tBu (mL)</td>
<td>0.24</td>
<td>0.30</td>
<td>0.36</td>
<td>0.42</td>
</tr>
<tr>
<td>THF (mL)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Molecular ratio of OXTA anion and P2tBu cation</td>
<td>2.3:1</td>
<td>1.8:1</td>
<td>1.4:1</td>
<td>0.9:1</td>
</tr>
</tbody>
</table>

2.1.2. Synthesis of Polymethylphenylsilane (PMPS)
Polymerization reaction of polymethylphenylsilane (PMPS) was carried out as described in the literature [8]. We obtained PMPS of $\text{M}_\text{w}$: 4400 and $\text{M}_\text{w}/\text{M}_\text{n}$: 3.46.

2.2. Evaluation of photobase generator
2.2.1. Determination of ratio of OXTA-P2tBu (1H-NMR)
We analyzed OXTA-P2tBu synthesized at each ratio by NMR ADVANCE III (600 MHz, made by Bruker). CDCl$_3$ was used as a deuterated solvent. Compared to 8.2 ppm peak area derived from OXTA and 1.2 ppm peak area derived from P2tBu, the anion-cation ratio of OXTA-P2tBu was calculated.

2.2.2. Determination of pH
The solutions were prepared by dissolving OXTA-P2tBu synthesized at each ratio 1.0 g in THF 9 mL. They were dropped to pH test paper and pH of them was determined by color change.

2.3. Quantum chemical calculation
2.3.1. Energy level calculation of OXTA and OXTA anion
Each energy level of OXTA and OXTA anion under UV irradiation was calculated by gaussian09. B3LYP 6-31+G(d,p) was used at calculation in ground state and B3LYP TD-DFT was used at excited state to determine the electron state.

2.3.2. Calculation of stabilization energy of complex
Predicted interaction energy $\Delta E$, HOMO, LUMO, H-L gap, edge absorption wavelength $\lambda_{\text{edge}}$ and oscillation strength $f$ of OXTA-P2tBu 2:1 complex and 1:1 complex were calculated by gaussian09 [9] to evaluate the stabilization energy. Their complexes were calculated by (TD)B3LYP/6-31+G(d,p) level. The complex calculations include empirical dispersion parameters (GD3).

2.4. UV absorption spectrum
The solutions were prepared by dissolving OXTA-P2tBu 0.064 g in THF 10 mL. They were measured by UV-3100PC (UV-VIS-NIRSCANNING SPECTROPHOTOMETER, made by SHIMADZU) at measurement wavelength in a region from 200 to 500 nm.

2.5. Observation of radical behavior of OXTA-P2tBu by ESR
Generated radical of OXTA-P2tBu under UV irradiation was observed by Electron Spin Resonance apparatus JES-RE3X (made by JEOL) as follows. Resonance frequency: X-band (~9 GHz), magnetic field variation width: 0.5 mT, magnetic field variation frequency: 100 kHz, time constant: 0.03 sec, sweep time: 30 sec, integration time: 1, marker: Mn$^{2+}$/MgO.

2.6. Analysis of crystal structure
2.6.1. Preparation of OXTA-P2tBu single crystal
Highly viscous objective (a-2) synthesized in section 2.1.1. was stored at 5 °C for 2 weeks. After the storage, the crystal was grown in vial. The crystal was washed with hexane to remove the impurities. Then, we obtained the objective crystal.

2.6.2. Determination of crystal structure by single crystal X-ray diffraction
We fixed the obtained crystal in section 2.6.1. to glass capillary by an adhesive, and analyzed by Single Crystal X-Ray Diffractometer R-AIXS-IV (made by Rigaku) as follows. X-ray Source: Mo, 50
kV, 100 mA (5 kW), Collimator: $\phi = 1.0$ mm, Detector: MERCURY MLD, Measurement temperature: 298 K, Space Group: P-1 (#2).

Crystal Clear was used as a measurement software and Crystal Structure (the Oxford CRYSTALS package) was used as an analysis software.

2.7. Lithographic evaluation

2.7.1. Preparation of solution

Into 50 mL vial were added OXTA-P$_{2tBu}$ (sample a-1~a-4) 0.72 g, cyclohexyl acetate (CHXA) 21 mL and PMPS 9.0 g and the mixture was stirred to dissolve for 1h (Sol. A-1~A-4).

2.7.2. Pattern forming

The thin films were formed on Si wafer by spin-coating of the solution at 400 rpm and then baked at 80 °C for 2 minutes under air. UV irradiation was carried out by using an ORC HDW-532D. The thin films were irradiated through a 20 $\mu$m L/S mask with UV which illuminance was 20 mW/cm$^2$ and exposure amount was 500 mJ/cm$^2$. The films were baked at 160 °C for 2 minutes under air and developed with CHXA for 20 sec., the patterns were obtained. After patterning, the substrate with pattern was baked at 230 °C for 20 minutes under air. The pattern shape was observed with FE-SEM (HITACHI S-4300).

3. Results and discussion

3.1. Determination of ratio of OXTA-P$_{2tBu}$ ($^1$H-NMR)

It is shown that anion-cation ratio calculated by $^1$H-NMR peak areas of synthesized OXTA-P$_{2tBu}$ at each ratio in Table 1. It was confirmed an increase of OXTA-anion ratio when OXTA input was increased.

3.2. Observation of pH change before and after UV irradiation

We observed pH change of OXTA-P$_{2tBu}$ synthesized in section 2.1.1. before and after UV irradiation. The result was shown in Table 2.

Table 2. pH of OXTA-P$_{2tBu}$ synthesized at each ratio before and after UV irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a-1</th>
<th>a-2</th>
<th>a-3</th>
<th>a-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before UV irradiation</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>After UV irradiation</td>
<td>10</td>
<td>12</td>
<td>12</td>
<td>13</td>
</tr>
</tbody>
</table>

Generally, it is appropriate for PBG property that pH of PBG is near 7 before UV irradiation and higher value after UV irradiation. Therefore, it was considered the pH change before and after UV irradiation was best at a ratio near 1.8:1 (a-2).

3.3. Quantum chemical calculation

3.3.1. Evaluation of stabilization energy of complex by calculation

Predicted interaction energy $\Delta E$ of 1:1 and 2:1 OXTA-P$_{2tBu}$ complex were calculated by gaussian09 (Table 3). In contrast that the stabilization energy of 1:1 complex was -38.2 kcal/mol, that of 2:1 complex was -69.2 kcal/mol. Therefore, it was suggested that OXTA-P$_{2tBu}$ is more stable as 2:1 complex than as 1:1 complex which is general ratio of ionic salt.

Table 3. Predicted interaction energy $\Delta E$, HOMO, LUMO, H-L gap, edge absorption wavelength $\lambda_{edge}$ and oscillation strength $f$ of OXTA, P$_{2tBu}$ and their complexes calculated by (TD)B3LYP/6-31+G(d,p) level. The complex calculations include empirical dispersion parameters (GD3).

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$ (kcal/mol)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Gap (eV)</th>
<th>$\lambda_{edge}$ (nm)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXTA</td>
<td>-6.58</td>
<td>-2.25</td>
<td>4.33</td>
<td>324</td>
<td>0.059</td>
<td></td>
</tr>
<tr>
<td>P$_{2tBu}$</td>
<td>-5.09</td>
<td>-0.41</td>
<td>4.68</td>
<td>277</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>1:1 complex</td>
<td>38.2</td>
<td>-5.42</td>
<td>-2.10</td>
<td>3.32</td>
<td>401</td>
<td>0.014</td>
</tr>
<tr>
<td>2:1 complex</td>
<td>69.2</td>
<td>-5.99</td>
<td>-2.02</td>
<td>3.97</td>
<td>358</td>
<td>0.022</td>
</tr>
</tbody>
</table>

3.3.2. Energy at each state by calculation

Energy at each state of OXTA and OXTA anion were calculated by (TD)B3LYP/6-31+G(d,p) level (Fig. 1).

Energy at vertical excited singlet of OXTA was higher than that at ground singlet by 3.05 eV. Energy at relax excited triplet was higher by 2.99 eV. Then, the difference between them was 0.06 eV.

On the other hand, energy at vertical excited
singlet of OXTA anion was higher than that at ground singlet by 1.86 eV. Energy at relax excited triplet was higher by 1.6 eV. Then, the difference between them was 0.26 eV. Therefore, OXTA anion could efficiently carry out intersystem crossing from excited singlet to excited triplet under UV irradiation rather than OXTA. It was suggested that stable radicals after relax excited triplet of OXTA anion was observed in ESR described below.

3.4. Analysis of complex forming at each ratio of OXTA-P2tBu by UV absorption spectra

Measured UV spectra of OXTA-P2tBu synthesized at each ratio were shown in Fig. 2.

As the ratio of OXTA to P2tBu decreased from 2.3 to 0.9, the absorption of region near $\lambda$=370 nm increased. On the other hand, $\lambda_{\text{edge}}$ of each OXTA-P2tBu complex calculated in section 3.3.1. were shown in Table 3. In contrast $\lambda_{\text{edge}}$ of 2:1 complex was 336 nm and 358 nm, 1:1 complex was 401 nm and 442 nm. Therefore, it was presumed that $\lambda_{\text{edge}}$ of 1:1 complex was absorption would be red-shifted as the ratio of OXTA decreased from 2 to 1. From the measured and calculated results, OXTA-P2tBu synthesized contained many 2:1 complex at optimum ratio (a-2, 1.8:1) and 1:1 complex at the lower ratio (a-4, 0.9:1)

3.5. Evaluation of radical behavior of PBG by ESR

Generated radicals from OXTA-P2tBu synthesized at each ratio under UV irradiation were observed by ESR (Fig. 3).

On the other hand, at higher OXTA ratio ((a-1) 2.3:1) than optimum ratio, pH was changed between before and after UV irradiation was low. Peaks derived from OXTA were observed at this ratio.

At the optimum ratio ((a-2) 1.8:1), irreversible peak under UV irradiation was observed in ESR spectrum and peaks derived from OXTA were observed after long UV irradiation without peaks derived from P2tBu. Therefore, OXTA-P2tBu ionic compound was synthesized at this ratio without isolation of OXTA and P2tBu.

3.6. Evaluation of crystal structure

Crystal of OXTA-P2tBu at optimum ratio (a-2) as a PBG was analyzed by single crystal X-ray diffraction. Image of crystal structure obtained from analysis of observed lattice images by Crystal Structure is shown in Fig. 4.

From the results, the crystal was 2:1 OXTA-P2tBu complex as presumed by calculation and UV absorption spectrum. From the packing structure, we can confirm the length between xanthone plane structures were close partially (3.84 Å), and $\pi$-$\pi$ stacking structure might exist. Also, -NH$^+$ - directly bonded with t-Bu in P2tBu were far from -COO$^-$ in OXTA. It presumed that bulky structure of P2tBu inhibited ionic bond between OXTA and P2tBu. Therefore, OXTA-P2tBu synthesized at optimum ratio had the structure that P2tBu was included by 2 OXTA units.
Fig. 4. Crystal structure of OXTA-P$_2$tBu (a-2) derived from single crystal X-ray diffraction. 
((a): 1 lattice, (b): packing structure) ($a = 11.0390(3)$ Å, $b = 12.4045(3)$ Å, $c = 17.5975(6)$ Å, $\alpha = 87.518(2)^\circ$, $\beta = 86.474(3)^\circ$, $\gamma = 87.816(2)^\circ$, $V = 2401.35(12)$ Å$^3$, $T = 298$ K, $Z = 2$, $R_1 = 0.0823$, $wR_2 = 0.2524$).

OXTA anion decomposes with decarboxylation reaction under UV irradiation [1]. From the analysis of crystal structure, it was suggested that pH of OXTA-P$_2$tBu change with the decomposition process under UV irradiation holding 2:1 complex as shown in Scheme 1.

3.7. Pattern forming

Remaining thickness of patterns formed with Sol. A-1~A-4 were shown in Table 4. Sol. A-2 containing the optimum ratio OXTA-P$_2$tBu was efficiently remained after development because of pH change under UV irradiation.

SEM image of pattern formed with Sol. A-2 was shown in Fig. 5. Irradiated part through 20 µm L/S mask was remained and line width of pattern was 25.2 µm. The nega-type pattern was formed by polymerization of polysilane with generated superbase in Scheme 1.

Table 4. Remaining thickness of patterns formed with Sol. A-1~A-4 after development (Thickness after coating was 2.0 µm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>A-1</th>
<th>A-2</th>
<th>A-3</th>
<th>A-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remaining Thickness (µm)</td>
<td>1.1</td>
<td>1.3</td>
<td>0.5</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 5. SEM image of formed pattern with Sol. A-2.

4. Conclusion

We synthesized OXTA-P$_2$tBu changing the ratio of OXTA and P$_2$tBu. We determined optimum ratio of OXTA-P$_2$tBu (1.8:1) as a PBG by observation of pH change and ESR spectra under UV irradiation. It was presumed that OXTA-P$_2$tBu at optimum ratio behaved as a 2:1 complex by UV absorption spectra and quantum chemical calculation. Crystal of OXTA-P$_2$tBu at optimum ratio was 2:1 OXTA-P$_2$tBu complex including $\pi$-$\pi$ stacking partially by single crystal X-ray diffraction. Polysilane solution
containing OXTA-P$_2$tBu synthesized at optimum ratio provided nega-type patterns efficiently rather than the other ratio.

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References
7. To be submitted to Org. Lett.