Photolysis of Quaternary Ammonium Dithiocarbamates and Their Use as Photobase Generators

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1. INTRODUCTION

In previous papers [1-4], we have already reported photochemical behavior of compounds bearing acyloxyimino or carbamoyloxyimino groups as photobase generators, which generate primary amines. Although photobase generators which generate tertiary amines are very interesting from the viewpoint of practical use, papers on them are very few. Neckers et al. reported that a quaternary ammonium borate acts as a photobase generator to generate tertiary amines.[5,6] Although we have also reported that quaternary ammonium salts having a dithiocarbamate anion act as photobase generators [7], details of their photolysis were not clarified. In this paper, we report the mechanism of photolysis of quaternary ammonium dithiocarbamates and their use as photobase generators.

2. EXPERIMENTAL

Preparation of QA salts

Quaternary ammonium bromide (QA salt I-Br) and quaternary ammonium N,N-dimethyldithiocarbamate (QA salt I-S) were prepared by the method in a previous paper.[7] QA salt having tetraphenylborate anion (QA salt I-B) and naphthoylmethyl moiety (QA salt II-S) were similarly prepared. Table 1 shows structure of QA salts.

Analysis of photo-products of QA salt I-S

Photo-products were analyzed by the use of an acid-base indicator (Phenol Red) and ¹H-NMR (Joel GX-270, 270MHz). A chloroform solution of QA salt I-S was irradiated at 366 nm. After the irradiation, the chloroform was evaporated and an aqueous solution of Phenol Red was added to the residue. Then, UV spectrum of the solution was measured. A CDCl₃ solution of QA salt I-S and a very small amount of toluene as an internal standard in a

<table>
<thead>
<tr>
<th>QA salt</th>
<th>mp (°C)</th>
<th>Td (°C)</th>
<th>ε max (MeOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA salt I-Br</td>
<td>238.0-239.0</td>
<td>232.0</td>
<td>ε₁₉₆ = 26000, ε₂₅₂ = 17000</td>
</tr>
<tr>
<td>QA salt I-S</td>
<td>138.0-140.0</td>
<td>115.0</td>
<td>ε₂₀₅ = 22000, ε₂₅₀ = 19000, ε₂₈₀ = 10000</td>
</tr>
<tr>
<td>QA salt I-B</td>
<td>211.1-212.0</td>
<td>213.5</td>
<td>ε₂₃₆ = 17200, ε₂₇₄ = 3000</td>
</tr>
<tr>
<td>QA salt II-S</td>
<td>110.0-112.0</td>
<td>125.0</td>
<td>ε₂₀₅ = 20100, ε₂₅₂ = 25600, ε₂₉₀ = 9000, ε₃₄₅ = 2200</td>
</tr>
</tbody>
</table>

Table 1 Characterization of QA salts.
quartz cell attached to a tube was irradiated at 366 nm with a medium-pressure mercury lamp (Ushio UM-102, 100W) and a UV cut filter (Toshiba Glass UV-D36B) in air or under N2. After the irradiation, their $^1$H-NMR spectra were measured.

Conversion in the photolysis of QA salt II was determined by the peak area at 4.21 ppm (a) due to methylene protons of the salt shown in Scheme 1. Amounts of resulting TEDA and naphthoylmethyl N,N-dimethyldithiocarbamate were estimated by the use of the area of peaks at 2.81 ppm (b) due to TEDA and at 5.02 ppm (c) due to methylene protons of naphthoylmethyl N,N-dimethyldithiocarbamate, respectively. NMR peaks were normalized by the use of a standard peak at 2.50 ppm due to methyl protons of toluene.

**Photo- and thermal insolubilization of poly(glycidyl methacrylate) (PGMA) films with QA salt**

PGMA thin films containing 5 mol% of a QA salt (ca. 0.3 μm thick) were prepared from their methylene chloride solution on a glass plate. The films were irradiated at 254 nm with a low-pressure mercury lamp (Ushio ULO-6DQ, 6W) at room temperature in air and followed by baking on a hot plate. The insoluble fraction of the films was determined by the ratio of the film thickness before and after soaking in tetrahydrofuran (THF) for 10 min at room temperature. Film thickness was determined by the use of two-beam interferometry with an interference microscope (Nikon OPTIPHOT).

**3. RESULTS AND DISCUSSION**

QA salt I-Br was prepared by the reaction with phenacyl bromide and triethylene diamine (TEDA), and anion exchange of QA salt I-Br was carried out by the use of sodium N,N-dimethyldithiocarbamate or sodium tetrakis(diphenylphosphinyl)borate.

We have already reported that TEDA, phenacyl N,N-dimethyldithiocarbamate and acetophenone were detected in the photolysis of QA salt I-S in methanol.[7] In this paper, we report quantitative results on TEDA by the use of an acid-base indicator and NMR analysis.

Fig.1 shows UV spectral changes of QA salt I-S in methanol on irradiation at 254 nm under N₂. Absorption bands around 250 nm due to π-π* and 290 nm due to dithiocarbamate anion decreased rapidly on irradiation. The decomposition rate on irradiation in air was lower than that under N₂. The decreasing rate of UV spectra of QA salt I-Br was

![Fig.1 UV spectral changes of QA salt I-S on irradiation at 254 nm.](image1)

![Fig.2 UV spectral changes of Phenol Red solution by the addition of irradiated QA salt.](image2)
lower than that of QA salt I-S, which shows that the photolysis rate of the salts depends on the anionic groups.

Fig. 2 shows UV spectral changes of an aqueous solution of Phenol Red by the addition of irradiated QA salt I-S. The addition of unirradiated QA salt I-S did not affect the absorption band at 430 nm due to Phenol Red. The addition of irradiated QA salt I-S induced the shift of the absorption band at 430 nm to 560 nm. This shift corresponds to the structural change from the phenol type to the quinoid type of Phenol Red by an organic base (Scheme 2). Fig. 3 shows relationship between the conversion of QA salt I-S and the yield of TEDA. The resulting amount of TEDA paralleled the conversion of QA salt I-S. This fact shows TEDA was produced by the photolysis of QA salt.

\[ \text{Scheme 2} \]

Fig. 4 shows \(^{1}\)H-NMR spectral changes of QA salt II-S on irradiation at 366 nm under N\(_2\). QA salt II-S which has absorption band around 366 nm was used to avoid the effect of halogen radicals from CDCl\(_3\) at 254 nm irradiation. With irradiation, a decrease of NMR peak at 4.21 ppm (Scheme 1 (a)) was observed. The decrease of this peak means the photo-decomposition of QA salt II. At the same time, the peaks at 2.81 ppm (Scheme 1 (b)) and 5.02 ppm (Scheme 1 (c)) increased. As shown in Fig. 5, the amounts of the resulting TEDA and naphthoylmethyl N,N-dimethylthiocarbamate corresponded with that of the decreased QA salt II-S. These facts show that the photolysis of QA salt II-S under N\(_2\) resulted in the quantitative formation of TEDA and naphthoylmethyl N,N-dimethylthiocarbamate.

\[ \text{Fig.3 Relationship between decomposed fraction of QA salt I-S and yield of amine on irradiation.} \]
\[ *1: \text{calculated from UV spectral changes at 286 nm.} \]
\[ *2: \text{determined by UV spectra of Phenol Red at 560 nm.} \]

\[ \text{Fig.4 \(^{1}\)H-NMR spectral changes of QA salt I-S in CDCl}_3\text{ on irradiation.} \]
\[ \text{(A) before irradiation,} \]
\[ \text{(B) after irradiation at 366 nm with 300 mJ/cm}^2\text{,} \]
\[ \text{(C) after irradiation at 366 nm with 1800 mJ/cm}^2\text{.} \]

\[ \text{Fig.5 Relationship between decomposition of QA salt II-S and yields of products.} \]
\[ \text{[ ] QA salt II-S, [ ) TEDA,} \]
\[ \text{(O) dithiocarbamate derivative.} \]
carbamate. However, photolysis rate of QA salt II-S in air was lowered to 1/5 of that under N₂, and other peaks due to by-products were observed. This fact suggests that oxygen in air inhibited the photolysis of QA salt II-S and induced the formation of oxidative products. When QA salt I-S was irradiated at 254 nm under N₂, TEDA and phenacyl N,N-dimethyldithiocarbamate were also detected.

Fig.6 shows photo-induced thermal crosslinking of PGMA films with 5 mol% of QA salts. (▲, △) QA salt I-Br, (■, □) QA salt I-S, (●, ○) QA salt I-B. Open symbols: only irradiation, Closed symbols: post-baking at 80 °C for 5 min.

tetraphenylborate anion was not effective for the photo-insolubilization of PGMA films.

4. CONCLUSION
We have investigated the photolysis of QA salts and their use as photobase generators. QA salts having dithiocarbamate anion were found to generate TEDA by their photolysis. The photolysis of QA salt II-S under N₂ resulted in the quantitative formation of TEDA and a dithiocarbamate derivative. QA salts having dithiocarbamate anion were found to be most effective photo- and thermal crosslinker of PGMA films in comparison with QA salts having bromide and tetraphenylborate.

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