Photochemical Reaction of 1,3,5-Tris(diphenylamino)benzene

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Photochemical reaction of a new aromatic amine with dual reaction sites for the ring closure, 1,3,5-tris(diphenylamino)benzene (TDAB), was investigated to clarify its photochemical reaction course and the effect of oxygen on the photochemical reaction. It was found that TDAB undergoes photocyclization reaction in solution in the absence or presence of oxygen to produce N-phenyl-2,4-bis(diphenylamino)carbazole. The product analysis and the result of laser flash photolysis indicate that the reaction mechanism for the photocyclization of TDAB is different between the deaerated and oxygen-saturated systems. Photocyclization reaction of TDAB in the absence of oxygen takes place via the electronically excited triplet state of TDAB, followed by the formation of the dihydrocarbazole. In the presence of oxygen, the dihydrocarbazole radical cation is suggested to be involved as an intermediate.

Keywords: 1,3,5-tris(diphenylamino)benzene, photocyclization, N-phenyl-2,4-bis(diphenylamino)carbazole

1. Introduction

It is known that aromatic amines, e.g., diphenylamine and N-methyldiphenylamine, undergo intramolecular cyclization by photoirradiation in solution to produce carbazoles [1-9]. It has been shown that the photocyclization reaction of aromatic amines takes place via the electronically excited triplet state of aromatic amines, which undergo ring closure to yield dihydrocarbazoles, leading to the formation of carbazoles. However, the mechanism of the step leading to carbazoles from dihydrocarbazoles and the effect of oxygen on the photochemical cyclization of aromatic amines have not been well clarified.

In the present study, we have investigated the photochemical reaction of a new reaction system with dual sites for intramolecular cyclization, 1,3,5-tris(diphenylamino)benzene (TDAB), in order to clarify its photochemical reaction course and the effect of oxygen on the photochemical reaction.

2. Experimental

TDAB was prepared by the Ullmann reaction of 1,3,5-tris(phenylamino)benzene with iodobenzene in the presence of copper powder and potassium hydroxide in decalin at 170 °C according to our previous paper [10]. It was purified by silica-gel column chromatography, followed by recrystallization from benzene/hexane to give colorless needles, mp. 256-257 °C.

Photochemical reaction was carried out using a merry-go-round apparatus at room temperature. The reaction solution was irradiated with a 500 W high-pressure mercury lamp through a pyrex filter. The quantum yield was measured with a potassium ferrioxalate actinometer by irradiation with 313 nm monochromatic light from a 500 W high-pressure mercury lamp through a Toshiba UV-D33S glass filter and an aqueous potassium chromate solution.
The reaction products were identified by IR, electronic absorption, and $^1$H-NMR spectroscopy, mass spectrometry, and elemental analysis.

N-phenyl-2,4-bis(diphenylamino)carbazole (N-PDACz): mp. 210 - 211 °C, MS m/z(EI) 577 (M$^+$).

Calc. for C$_{42}$H$_{31}$N$_3$: C, 87.35; H, 5.37; N, 7.28%.

Found: C, 87.09; H, 5.33; N, 7.24%.

$^1$H-NMR (600 MHz, acetone-d$_6$) δ (ppm) 6.74(s, 1H), 6.93(s, 1H), 6.96(t, 5H), 7.06(d, 4H), 7.12(d, 4H), 7.23(t, 10H), 7.47(t, 1H), 7.55(d, 2H), 7.60(t, 2H), 7.66 (d,1H).

HPLC was carried out using a WATERS 600E with a photodiode array detector (WATERS 991J). $^1$H-NMR and mass spectra were recorded on a Bruker AM-600 and a JEOL JMS-DX303, respectively. Electronic absorption spectra were measured on a HITACHI U-3200 spectrophotometer. Laser flash photolysis was carried out by irradiation with a third harmonic pulse (355 nm; 4 ns pulse width) from a Nd:YAG laser using a 450 W xenon pulse lamp (Osram OPG-450), a monochromator (Nikon G-250), a photomultiplier tube (R-928), and a programmable digitizer (Tektronix 7912 AD). The system was controlled by a computer.

3. Results and Discussion

Photochemical reaction of TDAB was carried out in solution in the absence or presence of oxygen. Fig. 1 shows the electronic absorption spectral changes of TDAB by photoradiation. Upon irradiation of an oxygen-saturated or deaerated cyclohexane solution of TDAB ([TDAB] = 3.0 x 10$^{-5}$ mol dm$^{-3}$), the absorption band with $\lambda_{\text{max}}$ at 300 nm gradually decreased and a new absorption band with $\lambda_{\text{max}}$ at ca. 360 nm increased with isosbestic points at 285 and 322 nm. The results show that the photochemical reaction of TDAB takes place both in the absence and in the presence of oxygen.

Irradiation of an oxygen-saturated benzene solution of TDAB ([TDAB] = 1.8 x 10$^{-3}$ mol dm$^{-3}$) with light (313 and 334 nm) from a 500 W high-pressure mercury lamp for 5 hr produced a single product, N-phenyl-2,4-bis(diphenylamino)carbazole (N-PDACz), in a 70% yield (quantum yield : 0.07) together with hydrogen peroxide. The formation of hydrogen peroxide was confirmed by iodometry.

Irradiation of a deaerated benzene solution of TDAB ([TDAB] = 1.8 x 10$^{-3}$ mol dm$^{-3}$) also produced N-PDACz together with two other products, as indicated by HPLC (Fig. 2). The electronic absorption spectra and mass spectra (M$^+$ = 581) of the other products strongly suggest that they are 2,4-bis(diphenylamino)tetrahydrocarbazoles.

TDAB has dual reaction sites for intramolecular...
cyclization, sites A and B, with a statistical probability of 2:1. However, the photochemical cyclization of TDAB in solution was found to be regioselective, taking place at site B.

In order to gain insight into the primary process of the photocyclization reaction of TDAB, laser flash photolysis of a TDAB solution was carried out in the absence and presence of oxygen.

Fig. 3 shows the transient absorption spectra of a benzene solution of TDAB obtained by laser flash photolysis in the absence and presence of oxygen. In the deaerated system, an absorption band with a λ<sub>max</sub> at 500 nm was observed at 160 ns after laser pulse. This band decayed with a lifetime of ca. 580 ns, accompanied by an increasing absorption band with λ<sub>max</sub> at 700 nm, which had a lifetime of 47 µs. The former and the latter absorption bands are assigned to the TDAB triplet state and the dihydrocarbazole, a precursor of the final product N-PDACz, respectively. These assignments are supported by the result of pulse radiolysis of a deaerated benzene solution of TDAB. Transient absorption spectra similar to Fig. 3 were obtained by pulse radiolysis, in which the electronically excited triplet state of TDAB was produced via energy transfer from the triplet state of benzene.

In the air-saturated system, however, the transient absorption bands assignable to the triplet state TDAB and the dihydrocarbazole disappeared. Instead, broad absorption bands in the wavelength range from 500 to 800 nm appeared.

The present study shows that a new aromatic amine with dual sites for intramolecular cyclization, TDAB, undergoes photocyclization in solution in the absence and presence of oxygen and that the photocyclization is regioselective, taking place at site B to give a single product N-PDACz. In addition, it is suggested that the mechanism of the photocyclization of TDAB in solution is different between the deaerated and oxygen-saturated systems (Scheme 2). That is, the photochemical reaction of TDAB in the absence of oxygen takes place via the electronically exited triplet state of TDAB, which undergoes ring closure to give the dihydrocarbazole. The resulting dihydrocarbazole undergoes disproportionation to give N-PDACz and tetrahydrocarbazole [5]. On the other hand, oxygen participates in the photochemical reaction of the oxygen-saturated solution of TDAB, forming hydrogen peroxide [9]. The mechanism involving the intermediacy of the dihydrocarbazole radical

![Figure 3 Transient absorption spectra of a benzene solution of TDAB ([TDAB] = 0.15×10⁻³ mol dm⁻³) obtained by irradiation with 355 nm pulsed light. a) deaerated at 10⁻³ torr and b) saturated with air.](image)

Scheme 2 Proposed mechanisms of the photocyclization reaction of TDAB in the absence and presence of oxygen
cation generated by electron transfer from the electronically excited state of TDAB \( (E_{\text{ox}} = 0.58 \text{ V vs Ag/Ag}^+ 0.01 \text{ mol dm}^{-3}) \) to the ground state oxygen is suggested to be operative in the photocyclization of TDAB in the oxygen-saturated system.

References