Photochemical Interaction of Diimide Compounds with Fullerene C₆₀

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1. Introduction

The photochemical properties of fullerene derivatives, particularly in regards to photosensitizing and electron acceptor capabilities, have been intensively studied in recent years [1]. Fullerene C₆₀ is known to be an efficient photosensitizer for the production of singlet oxygen [2]. Previously, we found that UV-vis irradiation of a furan-substituted polymer with C₆₀ in air led to the formation of a polymer network via a photo-oxidation-induced polycondensation (POP) mechanism [3]. We also demonstrated that the POP mechanism involves the dehydration process of a furan endoperoxide, which is formed by oxidation of a furan ring with singlet oxygen.

Recently, we have been focusing on the development of a new heat-resistant photosensitive polyimide resin based on the POP mechanism and we have shown that this resin's physical properties are so excellent that it can be used as a packaging material for sealing high-density semiconductor chips [4]. During the course of our development of the POP polyimide, we have found that the triplet state of fullerene C₆₀ ($^{3}$C₆₀) is quenched by POP polyimides in γ-butyrolactone solution [4]. This fact suggests the possibility that $^{3}$C₆₀, having high electron affinity, may be quenched by electron transfer from the imide group to $^{3}$C₆₀. To confirm this possibility, we have studied the photochemical interaction of $^{3}$C₆₀ with model diimides prepared from phthalic anhydride and the diamines employed for the preparation of POP polyimide. In the present paper, we report detailed results of $^{3}$C₆₀ quenching behavior of the model diimides using both the decay kinetics of transient $^{3}$C₆₀ T-T absorption by a laser flash photolysis and the calculation of free energy change for electron transfer by the Rehm-Weller equation. We also describe the relationship between the quenching rate constants and free energy changes for electron transfer from the model diimides to $^{3}$C₆₀.

2. Experimental

2.1. Materials

Fullerene C₆₀ (Term. Co., >99.98%), phthalic anhydride (Tokyo Kasei Co.), γ-butyrolactone (Tokyo Kasei Co.), and dehydrated acetonitrile (Wako Pure Chemical Industries Ltd.) were commercially available. 1,3-Bis(4-aminophenoxy) benzene (p-APB) and 1,3-bis(3-aminophenoxy) benzene (m-APB) were obtained from Wakayama Seika Kogyo Co. Ltd. and Mitsui Chemicals Inc., respectively. The furan-substituted diamines DBF, p-BABF, p-DABF, and DFDA, shown in Fig. 1, were prepared according to the method described in the previous report [4].

2.2. Measurements

Melting points were measured with a Stuart Scientific melting point apparatus SMP 3 and were not corrected. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. $^{1}$H and $^{13}$C NMR spectra were measured using a JEOL JNM- EX270
or a JEOL GSX-500 spectrometer in CDCl₃ or dimethyl sulfoxide-d₆ with TMS as an internal standard. Elemental analyses were performed using a Perkin-Elmer 240 elemental analyzer.

2.3. Preparation of model diimides

The typical procedure for preparation of the model diimide is as follows: To a γ -butyrolactone solution of phthalic anhydride (403 mg, 2.73 mmol) was added 3,5-bis(4-aminophenoxy) benzyl 2-furoate (p-BABF, 564 mg, 1.36 mmol) for 5 min. The mixture was stirred at room temperature for 2.5 h by which time the diamine p-BABF had been totally consumed as judged by a TLC analysis. To the reaction solution were added acetic anhydride (2.08 g, 20.4 mmol) and sodium acetate (178 mg, 2.18 mmol). The mixture was then heated at 80°C for 1.5 h. The reaction mixture was added dropwise into 150 ml of methanol, and the crude diimide (IIIb) precipitated was filtered off and dried in vacuo at 40°C (640mg, 70%). The recrystallization of the crude product from ethyl acetate gave the pure diimide (IIIb) as slightly orange prisms, m.p. 191.0-192.5°C. Following a similar procedure, the model diimides (IIIa), (IIIc), (III), (IIIe), and (III) were obtained from the diamine DBF, p-DABF, DFDA, p-APB, and m-APB, respectively. All the model diimides thus obtained were fully characterized based on spectroscopic data (FT-IR, ¹H and ¹³C NMR) and gave satisfactory elemental analyses.

2.4. Laser flash photolysis studies

Laser flash photolysis studies of C₆₀ were performed using an Nd-YAG laser (HY 500 from JK Laser Ltd.) equipped with the second harmonic generation (532 nm). To monitor the decay of the transient ³C₆₀* T-T absorption at 740 nm, analyzing beams from a pulsed Xe lamp were passed through the γ -butyrolactone solution of C₆₀ (10⁻⁴ M) and a model diimide in a quartz cell, which was deaerated by bubbling Ar for 15 min. Output signals from the photomultiplier (R758 from Hamamatsu Photonics) were fed to a digital oscilloscope (Model Gould 630 from Gould Instrument System Ltd.) and analyzed by a personal computer.

2.5. Electrochemical measurements

All of the measurements of oxidation potentials for the model diimides were performed using a Potentiostat HA-301 (Hokuto Denko) at room temperature in acetonitrile solutions, containing tetra-n-butylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte, with a Pt disc electrode as the working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The scan range was 0 to 2 V at a scan rate of 10 to 100 mVs⁻¹.

3. Results and Discussion

3.1. Preparation of model diimides

The POP polyimides described in the previous paper [4] have a diimide (III) moiety in the polymer backbone. Therefore, we chose the diimide (III) as a model compound for POP polyimide, and carried out ³C₆₀* quenching experiments employing them as quenchers. The model diimides (III) were prepared by the ring-opening addition reaction of the diamine (I) shown in Fig. 1 with phthalic anhydride in γ -butyrolactone, followed by chemical imidation with acetic
anhydride and sodium acetate (Scheme 1). The results are summarized in Table 1. The model diimides (III) were obtained in 70-80% yield except for the diimide (IIIc). The TLC analysis of the chemical imidation of the amic acid (IIe) revealed that prolonged imidation more than 2 h accompanied increase in the formation of by-products. This fact demonstrates that the diimide (IIIc) once formed is easily subject to further reaction under the imidation conditions, thus causing decrease in the yield of the diimide (IIIc).

Table 1. Preparation of Model Diimides (III)

<table>
<thead>
<tr>
<th>Model Diimide</th>
<th>Diamine</th>
<th>Yield, %</th>
<th>m.p., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIIa</td>
<td>DBF</td>
<td>79</td>
<td>260.3-261.8</td>
</tr>
<tr>
<td>IIIb</td>
<td>p-BABF</td>
<td>70</td>
<td>191.0-192.5</td>
</tr>
<tr>
<td>IIIc</td>
<td>p-DABF</td>
<td>77</td>
<td>191.5-193.5</td>
</tr>
<tr>
<td>IIId</td>
<td>DFDA</td>
<td>79</td>
<td>125.5-148.0</td>
</tr>
<tr>
<td>IIId</td>
<td>p-APB</td>
<td>43</td>
<td>207.0-209.0</td>
</tr>
<tr>
<td>IIIf</td>
<td>m-APB</td>
<td>68</td>
<td>175.0-179.0</td>
</tr>
</tbody>
</table>

3.2. Photochemical studies

The previous studies on POP polyimides revealed that they quenched $^3$C$_{60}$* in γ-butyrolactone solution, and the quenching rate constant was determined to be on the order of $10^5$ M$^{-1}$s$^{-1}$ [5]. We assumed that the quenching would occur by electron transfer from an imide group of the POP polyimide to $^3$C$_{60}$*, which has a high electron affinity. In order to clarify the photochemical interaction between an imide group and $^3$C$_{60}$* in more detail, precise $^3$C$_{60}$* quenching experiments by using the model diimides (III) as a quencher were performed by the laser flash photolysis method. The $^3$C$_{60}$* quenching rate constants ($k_q$) of the diimides (III) in γ-butyrolactone were determined from the decay kinetics of transient $^3$C$_{60}$* T-T absorption at 740 nm following excitation at 532 nm. In each case, the quenching followed equation (1):

$$K_{obsd} = k_d + k_q [Q]$$  (1)

where $K_{obsd}$ is the observed first-order decay rate of the triplet, $k_d$ is the rate constant without quencher, $k_q$ is its bimolecular quenching rate constant.

Stern-Volmer plots of $K_{obsd}$ vs [Q] (four concentrations from 0.05 M to 0.2 M) gave straight lines. The quenching rate constants ($k_q$) are listed in Table 2 together with the oxidation potentials [E(D/D$^+$)] of the diimides (III) measured in acetonitrile solution. The free energy change for electron transfer ($\Delta G_{et}$) from a model diimide (III) to $^3$C$_{60}$* shown in Table 2 is calculated from Rehm-Weller equation (2) [6]:

$$\Delta G_{et} \text{ (in kJ mol}^{-1}\text{)} = 96.48[E(D/D^+)] - E(A/A^-) - \Delta E_{0,0} - e_0^2/a \varepsilon$$  (2)

where $E(D/D^+)$ is the oxidation potential of the donor (diimide), $E(A/A^-)$ is the reduction potential of the acceptor (C$_{60}$), $\Delta E_{0,0}$ is the triplet energy of C$_{60}$, and $e_0^2/a \varepsilon$ is the energy gained in bringing the two radical ions to the encounter distance $a$ in a solvent of dielectric constant $\varepsilon$, where $e_0$ is the electronic charge. The observed quenching rate constants ($k_q$) are correlated with the free energy changes for electron transfer ($\Delta G_{et}$), and are in fair agreement with the calculated rate constants for electron transfer ($k_q$) using the semi-empirical Rehm-Weller equation [6]. These results suggest that quenching occurs by electron transfer from the diimide to $^3$C$_{60}$*. The electron transfer process from the diimide (IIIa), having large $\Delta G_{et}$ (62.34 kJ mol$^{-1}$), becomes too endothermic to occur and indeed quenching by (IIIa) was not observed at all. On the other hand, the electron transfer from the amic acid (IIb), the precursor of the diimide (IIIb), is slightly exothermic as judged by the negative value of $\Delta G_{et}$ (-3.26 kJ mol$^{-1}$), in agreement with a quenching rate constant that was 100 times larger than the constants for the diimides. This result predicts that even small amounts of contamination of unchanged poly(amic acid) in a POP polyimide will considerably lower the POP polyimide's photosensitivity. Therefore, the complete imidation of poly(amic acid) for a POP polyimide preparation is required in order to obtain highly photosensitive POP polyimide. The observed quenching rate
constant of the diimide (III) is abnormally large in spite of its high oxidation potential, and is more than 10 times larger than the calculated $k_q$ value. A quenching process other than electron transfer is considered to occur in this system. But so far we cannot make any reasonable explanation for this abnormality in quenching behavior.

4. Conclusion

We performed $^3C_{60}^*$ quenching experiments using the model diimides prepared from the furan-substituted diamines employed for POP polyimides and phthalic anhydride. The results in the quenching experiments revealed that the $^3C_{60}^*$ quenching rate constants of the model diimides are correlated with the free energy changes for electron transfer from the model diimides to $^3C_{60}^*$. We have concluded that the quenching involves electron transfer from an imide group to $^3C_{60}^*$ which is known as a powerful electron acceptor. This conclusion would give us an important clue for the development of a highly photosensitive POP polyimide system.

References