SINGLET SENSITIZED REACTIONS

by

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Thesis Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Doctor of Science

The University of Tsukuba

1980

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FORWARD

The author express his deep gratitude to Professor Katsumi Tokumaru for his expert guidance and encouragement throughout the course of this investigation. He wishes to thank to Dr. Hirochika Sakuragi for his constant discussions and suggestions. He is also grateful to Professor Masayuki Yoshida of The University of Tokyo for his helpful guidance and encouragement. Thanks are also due to Mr. Haruki Kawada, Mr. Toshiyuki Urano, Mr. Hiroaki Misawa, Mr. Shigeru Takahara, and other members of Professor Tokumaru's research group for their encouragement and constant interest. And in the experiment of electrochemistry, thanks are due to Mr. Tatsuya Kanno for his appropriate suggestions.
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INTRODUCTION.

Interactions of electronically excited molecules with ground-state molecules are of great interest. Photochemical decomposition of dibenzoyl peroxide has been shown to be sensitized by a number of organic compounds; however, many aspects of reaction mechanisms remain uncertain.

In this work mechanisms for singlet sensitized decomposition of dibenzoyl peroxide was studied in respect with i) product distributions compared with its thermolysis and direct photolysis and ii) quenching of aromatic hydrocarbon fluorescence by dibenzoyl peroxide.

In Chapter 1 attempts were made to elucidate the mechanism for efficient production of a geminate product, and it was found that two-bond cleavage of the O-O and C(α)-C(carbonyl) bonds of dibenzoyl peroxide resulting in the efficient formation of the geminate product.

It was proposed that exciplex formation between aromatic hydrocarbons and dibenzoyl peroxide play a predominant role in the sensitization process (Chapters 2 and 3). In Chapter 2 naphthalene-sensitized decomposition of dibenzoyl peroxide was investigated in detail, and in Chapter 3 fluorescence
quenching rate constants of series of aromatic hydrocarbons and naphthalene derivatives by dibenzoyl peroxide and dimethyl fumarate were measured using single photon counting technique, and their correlation with structural factors of sensitizers was discussed.

As an extending study on exciplexes, photocurrents were successfully observed in several systems when two components of an exciplex were placed separately in different compartments and the light-absorbing component was irradiated (Chapter 4).
CHAPTER 1

PHOTOLYSIS OF DIBENZOYL PEROXIDE UNDER DIRECT AND SINGLET SENSITIZED IRRADIATIONS. MECHANISM FOR THE FORMATION OF THE GEMINATE PRODUCT

SUMMARY

Attempts have been made in order to elucidate the mechanism for the efficient production of phenyl benzoate, the geminate product, from direct and singlet sensitized irradiations of dibenzoyl peroxide in solution. It is concluded that these irradiations produce a reactive state of the peroxide which can undergo two-bond cleavage of the O-O and C(α)-C(carbonyl) bonds to give a phenyl-benzoyloxy radical pair in a solvent cage, followed by the recombination of the component radicals to give the geminate product or by their diffusion out of the solvent cage to give diffusion products.
Introduction

Although direct or aromatic hydrocarbon-sensitized photolysis\textsuperscript{1-8} of dibenzoyl peroxide (BPO) has been shown to proceed through the singlet excited pathway,\textsuperscript{9-15} some aspects of the reaction remain uncertain. Previously we reported\textsuperscript{10} that direct photolysis and singlet sensitized decomposition of BPO give a noticeable amount of phenyl benzoate in contrast with triplet sensitization\textsuperscript{4,8,16} and thermal decomposition\textsuperscript{17,18} which give only a low yield of the ester. It is shown that phenyl benzoate arises from the geminate recombination of benzoyloxy radicals and phenyl radicals on the basis of its noticeable formation from photolysis of BPO in toluene, p-xylene, and chlorobenzene\textsuperscript{5} as well as CIDNP results.\textsuperscript{11-15}

The efficient formation of the geminate product in the photolysis of BPO can not be accounted for by the usual cleavage of the peroxide bond to give a pair of benzoyloxy radicals as results from thermolysis,\textsuperscript{17,18} because benzoyloxy radicals decarboxylate too slowly\textsuperscript{19} to afford a benzoyloxy-phenyl radical pair within the lifetime of the primary solvent-cage. The noticeable formation of the geminate product can be explained by a mechanism in which a significant fraction of excited peroxide molecules decompose by either concerted or unusually rapid stepwise cleavage of the O-O and C(\(\alpha\))-C(carbonyl) bonds to give benzoyloxy-phenyl radical pairs followed by the cage
recombination \((\text{eq.1}).^3,^8,^20\)

\[
\begin{align*}
\text{(PhCO}_2\text{)}_2 & \xrightarrow{h\nu} \text{PhCO}_2^\cdot + \cdot\text{OCOPh} \\
\text{PhCO}_2^\cdot + \text{Ph}^\cdot + \text{CO}_2 & \rightarrow \text{PhCO}_2\text{Ph}
\end{align*}
\]

Lemaire's group\(^8\) investigated direct photolysis of BPO in solution, particularly in view of wavelength dependence of its quantum yield, and postulated that benzoyloxy radicals would be formed in the vibrationally excited state on 313-nm light irradiation and irradiation with shorter wavelength light would directly generate phenyl radicals which, in high concentrations of BPO, might attack the peroxide to give phenyl benzoate and benzoyloxy radicals.

On the other hand, McBride et al.\(^{21}\) by ESR spectroscopic investigation, reported that UV-irradiation of crystalline acetylbenzoyl peroxide at 64 K gave benzoyloxy-methyl radical pairs, and subsequent irradiation with visible light led to the decarboxylation of the benzoyloxy radicals to give phenyl-methyl radical pairs, with the highest efficiency on irradiation with 750-nm light. The photo-induced decarboxylation of benzoyloxy radicals could explain the noticeable formation of phenyl benzoate in the photolysis of BPO.

In the present paper we report some features of the
photolysis of BPO and attempts to elucidate the mechanisms for the formation of the geminate product. The present results described below will show that the simultaneous two-bond cleavage play an important role in the noticeable formation of the geminate product and concurrent irradiation of visible light does not remarkably contribute to the formation of the geminate product.
Results

Thermal and Photochemical Decomposition of Substituted Dibenzoyl Peroxides. Dibenzoyl, bis(4-methoxybenzoyl), bis-(4-methylbenzoyl), and bis(4-chlorobenzoyl) peroxides (ArCO$_2$OCOAr, 0.03 M) were thermally decomposed at 80, 90, and 100$^\circ$C and photolyzed at room temperature without any sensitizer in benzene and with chrysene (0.002 M) as a singlet sensitizer in benzene until the peroxides were completely decomposed. The resulting geminate products, ArCO$_2$Ar, were determined by GLPC analysis. The results are summarized in Table 1.\textsuperscript{22}

CIDNP in Photolysis of BPO. In order to clearly observe a CIDNP spectrum due to the geminate product, deuteriated BPO was employed to eliminate nuclear spin-spin couplings between aromatic ring protons and lengthen spin-lattice relaxation times of the products. When BPO-2,2',4,4',6,6'-d$_6$ was photolyzed in benzene-d$_6$ at room temperature with a 1 kW high pressure mercury lamp in the probe of an NMR spectrometer, a very clear polarized spectrum was observed as shown in Figure 1. The enhanced absorption represents the meta protons on the phenoxy1 segment of the geminate product, phenyl-2,4,6-d$_3$ benzoate-2,4,6-d$_3$, and the emission is assigned to biphenyl-2,2',3,4,4',5,6,6'-d$_8$. Irradiation of a solution of BPO-d$_6$ in the presence of naphthalene or chrysene in benzene-d$_6$
gave the same polarized NMR spectrum as the direct irradiation.

**Sensitized Decomposition of BPO in the Presence of a Radical Scavenger.** BPO (0.02 M) was irradiated with 366-nm light at room temperature in a mixed solvent consisting of varying fractions of styrene and benzene in the presence of chrysene (0.002 M) as a singlet sensitizer until the peroxide was completely decomposed (3.75 h). The yields of phenyl benzoate were determined by GLPC analysis to be 0.10, 0.10, 0.07, and 0.09 mole per mole of the peroxide at the concentrations of styrene in 0, 1.74, 4.35, and 6.09 M, respectively.

**Trapping of Carbon Dioxide in Thermal and Photochemical Decompositions of BPO in the Presence of a Radical Scavenger.** In a mixture of varying fractions of benzene and styrene, BPO (0.02 M) was thermally decomposed at 80°C and photolyzed at room temperature with a 400 W high pressure mercury lamp through a Pyrex wall. The resulting carbon dioxide was absorbed with an Ascarite tube and determined by gravimetry. The results are depicted in Figure 2. The yields of carbon dioxide were suppressed to approach limiting values as the fraction of styrene increased in both photolysis and thermalysis. The limiting yields, however, are different between the photolysis (ca. 0.7 mole per mole of the peroxide) and
the thermolysis (ca. 0.3 mole).

Spin Trapping in Decomposition of BPO. When a solution of BPO (0.01 M) in benzene containing N-benzylidene-t-butylamine oxide (0.1 M) was irradiated in the cavity of an ESR spectrometer at room temperature with 400 W high pressure mercury lamp for several minutes, signals due to both of the benzoyloxy spin adduct, N-t-butyl-α-benzoyloxybenzylaminyloxyl (PhCO₂-SA, a₆ = 14.0 G),²³ and the phenyl spin adduct, N-t-butyldiphenylmethanaminyloxyl (Ph-SA, a₆ = 15.5 G),²³ were observed in the ESR spectrum. The ratio of these spin adducts, PhCO₂-SA/Ph-SA, was determined to be ca. 5.6. This value was not varied with irradiation time (5-10 min). On the other hand, heating of a benzene solution of the same composition as above at 40°C for 8 minutes gave only the signals due to the benzoyloxy spin adduct.

Effects of Singlet Excitation Energy of Sensitizers on the Geminate Product Yield. BPO (0.03 M) was irradiated in benzene at room temperature in the presence of aromatic hydrocarbons (1.3 x 10⁻⁴ - 1.8 x 10⁻² M) as sensitizers with a 1 kW high pressure mercury lamp through a Pyrex wall. The concentrations of the sensitizers were chosen so that the sensitizers absorbed more than 95% of incident light at 313 nm.
Table 2 summarizes the yields of the products determined by GLPC analysis. The yield of phenyl benzoate tends to increase with increasing singlet excitation energy of the sensitizers.

**Effects of Longer Wavelength Light on the Product Yields.**

In order to explore the contribution of the light-induced decarboxylation of benzoyloxy radicals to the formation of the geminate and diffusion products, in the course of the thermal decomposition, UV-irradiation, and nitrogen laser irradiation of BPO (0.03 M) in benzene, the solutions were concurrently irradiated with light of wavelengths longer than 400 nm. In this wavelength region neither BPO nor chrysene has any absorption band. Table 3 summarizes the yields of the products determined by GLPC analysis. The yield of biphenyl seems to be increased by irradiation of the longer wavelength light; however, no remarkable effects on the yield of phenyl benzoate are observed.

**Effects of Light Intensity on the Product Yields.** BPO (0.03 M) in benzene was irradiated with 313-nm light of varying intensity. The yields of the products determined by GLPC analysis are summarized in Table 4, which shows that the increase of light intensity in nearly five times does not remarkably affect the distribution of the products, although
the yields of phenyl benzoate and benzoic acid tend to be slightly reduced with increasing light intensity.

In order to investigate the effect of strong laser pulses on the geminate product formation, an equimolar mixture of BPO (0.015 M) and deuteriated BPO, \((\text{C}_6\text{D}_5\text{CO}_2)_2\), (0.015 M) was irradiated in toluene with chrysene with a nitrogen laser at room temperature. Mass spectrometric examination of the resulting ester showed that only the undeuteriated ester, \(\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_5\), and the ester deuteriated on both of the aromatic rings, \(\text{C}_6\text{D}_5\text{CO}_2\text{C}_6\text{D}_5\), were produced but even a trace amount of the ester with one deuteriated aromatic ring, \(\text{C}_6\text{D}_5\text{CO}_2\text{C}_6\text{H}_5\) or \(\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{D}_5\), was not produced.
Discussion

Production of phenyl benzoate from decomposition of dibenzoyl peroxide (BPO) in solutions under nitrogen remains in a low yield from thermolysis\textsuperscript{17,18} but is noticeable from direct and singlet sensitized photolyses.\textsuperscript{2,5,7,10} As Table 1 indicates, substituted dibenzoyl peroxides behave like unsubstituted BPO. These findings suggest that the direct and singlet sensitized photolyses effectively produce benzoyloxy-phenyl radical pairs to give phenyl benzoate.

Formation of phenyl benzoate as the geminate product is further confirmed by the effect of styrene and CIDNP. As described above, increasing fractions of styrene added in the photolyzing system did not show any significant effect on the yield of phenyl benzoate. In addition, in CIDNP (Fig. 1), the sharp enhanced absorption due to the meta protons on the phenoxy segment of the resulting phenyl benzoate-\textsubscript{d\textsubscript{6}} indicates that the polarization must be due to phenyl-\textsubscript{d\textsubscript{3}} radicals which have escaped the initial polarizing cage and retained some polarization through their recombination with benzoyloxy radicals.\textsuperscript{13} This observation accords well with the prediction by Kaptein's\textsuperscript{24} and Closs's\textsuperscript{25} rules applied to the polarizing pair of benzoyloxy and phenyl radicals.

The effect of styrene and a spin trap revealed the effective decarboxylation taking place during the photolysis.
Figure 2 indicates that as the fraction of styrene increases, the production of carbon dioxide is rapidly suppressed to approach limiting yields in both photolysis and thermolysis. The limiting yield is much higher from the photolysis (ca. 0.7 mole per mole of peroxide) than the thermolysis (ca. 0.3 mole).

On decomposition of BPO in the presence of the spin trap, N-benzylidene-t-butyamine oxide, both of the phenyl-spin adduct and the benzoyloxy spin adduct were obtained in the photolysis in a ratio of 1 : 5.6, whereas only the benzoyloxy spin adduct was obtained in the thermolysis. The extent of the decarboxylation under spin trapping conditions is estimated to be $1/(1 + 5.6) = 15\%$ and this figure is lower than that estimated from scavenging by styrene to measure carbon dioxide, $0.71/2 = 35\%$. This difference probably reflects the different ability between styrene and the nitrone to trap benzoyloxy radicals.

From the results mentioned above, it is obvious that the photolysis of BPO produces certain amounts of phenyl radicals and carbon dioxide without the intervention of benzoyloxy radicals of usual lifetimes which would be effectively scavenged by styrene or the spin trap. For the efficient formation of the benzoyloxy-phenyl radical pairs the following three possibilities can be envisaged.

The first possibility is a simultaneous two-bond cleavage of the peroxide in which the singlet excitation energy will be
converted to vibrational energy enough to break both oxygen-oxygen and carbon(α)-carbon(carbonyl) bonds giving simultaneously a benzoyloxy radical, a phenyl radical, and a carbon dioxide molecule (one-photon simultaneous process, eq. 2). Direct excitation and excited singlet sensitizers seem to provide sufficient energies for the peroxide bond cleavage and the decarboxylation of benzoyloxy radicals in the thermal processes, ca. 31.26 and 13.19 kcal mol⁻¹, respectively.

The second possibility is a rapid successive two-bond cleavage in which the photolysis gives vibrationally or electronically excited benzoyloxy radicals followed by their rapid decarboxylation within the lifetime of the solvent cage (one-photon successive process, eq. 3).

A two-photon process is the third possibility where benzoyloxy radicals once formed are excited by continuing irradiation and decarboxylate within the lifetime of the solvent cage (two-photon successive process, eq. 4).

\[ \text{PhCO}_2\text{OCOPh} \xrightarrow{h\nu} \text{PhCO}_2^- + \text{CO}_2 + \text{Ph} \]  
\[ \text{PhCO}_2\text{OCOPh} \xrightarrow{h\nu} (\text{PhCO}_2^-)^* + \text{PhCO}_2 \]  
\[ \text{Ph}^- + \text{CO}_2 + \text{PhCO}_2^- \]  

(2)  
(3)
In the singlet sensitization, the singlet excited hydrocarbon molecule will interact with the peroxide molecule to give a reactive exciplex. In this exciplex the singlet excitation energy of the hydrocarbon moiety would be converted to the vibrational energies of the complex to cause the cleavage of the peroxide moiety into free radicals. Table 2 shows that the yield of phenyl benzoate tends to increase with increasing singlet excitation energy of the sensitizers. This result suggests that, on formation of the reactive exciplex, the higher the singlet excitation energy of the sensitizer, the more efficient the cleavage of both of the oxygen-oxygen and carbon-carbon bonds of BPO to give the geminate product.

Table 3 indicates that the concurrent irradiation with a bromine lamp gives no pronounced effect on the product distribution, although it seemingly enhances the formation of biphenyl in both the photolysis and thermolysis. Consequently, under the present experimental conditions, the visible light illumination does not significantly accelerate the decomposition of benzoyloxy radicals in contrast with the reported results.
for crystalline acetyl benzoyl peroxide. 21)  

Concurrent illumination of a bromine lamp on the samples irradiated by a nitrogen laser was undertaken for the following intention. Thus, under laser irradiation, the excited peroxide molecules undergo decomposition almost during the nanosecond duration of the pulse, and the resulting benzoyloxy radicals would decarboxylate during the "dark period" of nearly 10 ms before the next pulse irradiation. Accordingly, the concurrent irradiation with a bromine lamp could act during the "dark period" on the free radicals. However, as Table 3 indicates, the bromine lamp was not effective to induce the decarboxylation of benzoyloxy radicals.

Furthermore, Table 4 shows that on irradiation at 313 nm the increase of light intensity in nearly five times does not remarkably affect the distribution of the products, although the yields of phenyl benzoate and benzoic acid tend to be slightly reduced with increasing light intensity. This finding suggests that 313-nm light also does not significantly induce the decarboxylation of benzoyloxy radicals.

On laser irradiation, it would be expected that the laser pulses of strong intensity would transiently generate high concentrations of free radicals, and hence benzoyloxy and phenyl radicals diffused from the different initial solvent cages would combine to give phenyl benzoate as a diffusion
product in addition to the geminate product. However, chrysene-sensitized laser irradiation of an equimolar mixture of BPO and BPO-d_{10} in toluene gave no diffusion products, C_{6}H_{5}CO_{2}C_{6}D_{5} and C_{6}D_{5}CO_{2}C_{6}H_{5}, but gave only a mixture of the geminate products, C_{6}H_{5}CO_{2}C_{6}H_{5} and C_{6}D_{5}CO_{2}C_{6}D_{5}. This result shows that even on irradiation with strong intensity light, benzoyloxy-phenyl radical pairs effectively result in the geminate product and the radicals escaped from the solvent cage undergo decomposition or reactions with the solvent before they would randomly combine to give phenyl benzoate.

Therefore it is reasonable to conclude that in the decomposition of BPO from its excited singlet state, the one-photon simultaneous or successive two-bond cleavage mainly contributes to the efficient formation of the benzoyloxy-phenyl radical pairs leading to the noticeable formation of the geminate product and the contribution of the two-photon process involving the light-induced decarboxylation of benzoyloxy radicals would be negligible.

Finally, it should be mentioned that both the direct irradiation and singlet sensitized irradiation of BPO give nearly the same distribution of the products, suggesting that both photolytic reactions will proceed through the same reactive state of the peroxide. On direct photolysis, the initially produced (Franck-Condon-state), electronically excited peroxide
molecule would relax into a reactive state which can dissociate at both of the O-O and C-C bonds. In the singlet sensitization, however, the singlet excited sensitizers do not have sufficient energies to be transferred to give electronically excited peroxide molecule as produced on direct photolysis. Consequently, the excited sensitizer molecules would complex with ground-state peroxide molecules to give reactive exciplexes, in which the electronic excitation energy would be relaxed through vibrational energy probably leading the peroxide moiety to the same reactive state as produced on direct photolysis.
Experimental

Materials. Dibenzoyl peroxide-2,2',4,4',6,6'-d₆, dibenzoyl peroxide-2,2',3,3',4,4',5,5',6,6'-d₁₀, bis(4-chlorobenzoyl), bis(4-methylbenzoyl), and bis(4-methoxybenzoyl) peroxide were prepared from the corresponding acyl chlorides and sodium peroxide, and recrystallized from dichloromethane-methanol. Dibenzoyl peroxide commercially obtained was purified similarly. Benzoyl-2,4,6-d₃ chloride was prepared in the following manner. Anilinium chloride was refluxed in deuterated water. This process was repeated three times. Anilinium-2,4,6-d₃ chloride obtained was converted to benzonitrile-2,4,6-d₃ by the Sandmeyer reaction, and its hydrolysis and chlorination gave benzoyl-2,4,6-d₃ chloride. Other substituted benzoyl chlorides were prepared from the corresponding, commercially purchased acids in a usual manner. Aromatic hydrocarbons used as singlet sensitizers were purified by column chromatography and crystallization. Benzene and styrene were purified by distillation. Phenyl-2,4,6-d₃ benzoate-2,4,6-d₃ was prepared by irradiation of BPO-d₆ in carbon tetrachloride in the presence of naphthalene.

Photolysis. A solution of a peroxide (0.03 M) in benzene (3 ml) in a Pyrex tube was degassed by the usual freeze-thaw cycles or deaerated by bubbling of nitrogen, and irradiated by a 400 W or a 1 kW high pressure mercury lamp immersed in a Pyrex cooling well or furthermore surrounded by Toshiba UV-D36B glass
filters when chrysene (0.002 M) was used as a sensitizer using a merry-go-round type Riko Rotary Photochemical Reactor, Model RH400-10W. Irradiation was continued for five times half-life periods of the peroxide determined by iodometric analysis under the same conditions.

**Thermolysis.** A solution of a peroxide (0.03 M) in benzene (3 ml) in a Pyrex tube was degassed by the usual freeze-thaw cycles and heated in an air bath constantly maintained at 80°, 90°, and 100°C for five times half-life periods. The reaction times were decided according to the reported decomposition rate constants of peroxides.27

**Product analyses.** Phenyl benzoate, substituted phenyl benzoates, biphenyl, and benzoic acid were determined by GLPC analysis on a Shimadzu 4CM gas chromatograph equipped with a flame ionization detector. The following columns were used for quantitative analyses: Diethylene glycol succinate (5%) with H₃PO₄ (2%), Polyethylene glycol 20M (5%), and Silicone GE SE-30 (2%). Carbon dioxide was determined gravimetrically using an Ascarite tube.

**Irradiation by a bromine lamp during thermolysis and photolysis.** A solution of BPO (0.03 M) in benzene (10 ml) was irradiated under nitrogen atmosphere at room temperature for 3 h by two lamps at the same time, a 1 kW high pressure mercury lamp immersed in a Pyrex cooling well and a 650 W bromine lamp (Ushio,
Type JCD) through a Toshiba Y-43 glass filter which transmits light longer than 400 nm.

Thermolysis under illumination of visible light was performed in a water bath kept at 80°C for 23.75 h, during which the reacting solution was irradiated by the 650 W bromine lamp through a water layer and a Toshiba Y-43 glass filter.

Irradiation of 313-nm light of varying intensity. A solution of BPO (0.03 M) in benzene (10 ml) was irradiated under nitrogen atmosphere at room temperature for 11.5 - 51 h through a filter solution (NiSO₄·7H₂O, 0.5 g/ml; transmittance, ca. 70% at 313 nm) and a Pyrex wall using a 1 kW high pressure mercury lamp. Light intensity was reduced by inserting piled silk cloth between a sample tube and the filter solution. Relative light intensity was calculated from half-life periods determined by iodometry.

CIDNP measurements and ESR spectra. CIDNP measurements were performed on a JEOL JNM-PX-100 NMR spectrometer and ESR spectra were recorded on a JEOL JES-ME-1X ESR spectrometer. A 1 kW and a 400 W high pressure mercury lamp were used as light sources in the CIDNP and ESR measurements, respectively.

Laser photolysis. Nitrogen laser pulses were supplied from a 1 MW (3.5 mJ) Lambda Physik laser pulse generator. A solution of BPO (0.03 M) in benzene (2 ml) containing chrysene (0.006 M) was irradiated by the laser (100 pulses per second).
Irradiation was continued for five times the half-life period determined by iodometry in advance.

**Mass Spectrometry.** A solution of BPO and BPO-d₁₀ (0.015 M, respectively) in toluene (2 ml) containing chrysene (0.006 M) was irradiated by the nitrogen laser. The photolyzed sample was examined by gas chromatography/mass spectrometry (Hitachi RMU-6M GC/MS). The relative intensities of the parent peaks of phenyl benzoate and phenyl benzoate-d₁₀ were found to be different between the ascending part and descending part of the gas chromatographic peak (e.g., 0.7 and 1.6, respectively), but in neither case a peak was detected at m/e 203 attributable to phenyl benzoate-d₅, C₆H₅CO₂C₆D₅ or C₆D₅CO₂C₆H₅.
References and Notes

22) Bradley and Roth⁷ reported that direct photolysis of bis-(4-chlorobenzoyl) and bis(4-methylbenzoyl) peroxide gave the corresponding geminate products in the yields of 0.04 and 0.16 moles per mole peroxide, respectively.
Table 1. Yield of Substituted Phenyl Benzoates in Thermal and Photochemical Decompositions of Bis(4-substituted benzoyl) Peroxides

<table>
<thead>
<tr>
<th>Ar in ArCO₂Ar</th>
<th>Mode of decomposition</th>
<th>MeOC₆H₄</th>
<th>MeC₆H₄</th>
<th>C₆H₅</th>
<th>ClC₆H₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct photolysis</td>
<td>0.047</td>
<td>0.072</td>
<td>0.13</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>Chrysene sensitized photolysis</td>
<td>0.037</td>
<td>0.056</td>
<td>0.12</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>Thermolysis at 80°C</td>
<td>0.011</td>
<td>0.006</td>
<td>0.022</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>Thermolysis at 90°C</td>
<td>0.011</td>
<td>0.006</td>
<td>0.023</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Thermolysis at 100°C</td>
<td>0.010</td>
<td>0.007</td>
<td>0.025</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Table 2. Yields of Products in Hydrocarbon-Sensitized Photolysis of BPO (0.03 M) in Benzene

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Singlet Excitation Energy of Sensitizer</th>
<th>Concentration (M) of Sensitizer</th>
<th>Yield (mole/mole peroxide)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_g$ (kcal/mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>91</td>
<td>$1.8 \times 10^{-2}$</td>
<td>0.16 0.35 0.22</td>
</tr>
<tr>
<td>Triphenylene</td>
<td>83</td>
<td>$6.7 \times 10^{-3}$</td>
<td>0.15 0.33 0.22</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>80</td>
<td>$5.0 \times 10^{-4}$</td>
<td>0.10 0.31 0.22</td>
</tr>
<tr>
<td>Pyrene</td>
<td>77</td>
<td>$1.3 \times 10^{-4}$</td>
<td>0.10 0.44 -0.29</td>
</tr>
<tr>
<td>Anthracene</td>
<td>75</td>
<td>$1.7 \times 10^{-3}$</td>
<td>0.091 0.46 0.27</td>
</tr>
<tr>
<td>9,10-Diphenylanthracene</td>
<td>70</td>
<td>$1.2 \times 10^{-3}$</td>
<td>0.096 0.41 0.24</td>
</tr>
<tr>
<td>Perylene</td>
<td>65</td>
<td>$3.2 \times 10^{-3}$</td>
<td>0.063 1.5 0.16</td>
</tr>
</tbody>
</table>

Table 3. Yields of Products in Thermal and Photochemical Decomposition of BPO (0.03 M) in Benzene with Concurrent Irradiation of a Bromine Lamp

<table>
<thead>
<tr>
<th>Light source</th>
<th>Yield (moles/mole peroxide)</th>
<th>PhCO₂Ph</th>
<th>PhCO₂H</th>
<th>Ph-Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPML&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>0.13</td>
<td>0.45</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>HPML&lt;sup&gt;a)&lt;/sup&gt; + BL&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>0.11</td>
<td>0.44</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Thermal (80°C)</td>
<td>0.02</td>
<td>0.31</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>Thermal (80°C) + BL&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>0.02</td>
<td>0.22</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>N₂ Laser&lt;sup&gt;c)&lt;/sup&gt;</td>
<td>0.16</td>
<td>0.45</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>N₂ Laser&lt;sup&gt;c)&lt;/sup&gt; + BL&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>0.16</td>
<td>0.45</td>
<td>0.35</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a)</sup> HPML stands for a high pressure mercury lamp.
<sup>b)</sup> BL stands for a bromine lamp.
<sup>c)</sup> Sensitized with chrysene (6 x 10⁻³ M)
Table 4. Yields of Products in Photolysis of BPO with 313-nm Light of Varying Intensity

<table>
<thead>
<tr>
<th>Relative Light Intensity</th>
<th>Yield (moles/mole peroxide)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PhCO₂Ph</td>
</tr>
<tr>
<td>0.23</td>
<td>0.21</td>
</tr>
<tr>
<td>0.37</td>
<td>0.17</td>
</tr>
<tr>
<td>0.58</td>
<td>0.17</td>
</tr>
<tr>
<td>0.61</td>
<td>0.08</td>
</tr>
<tr>
<td>0.68</td>
<td>0.17</td>
</tr>
<tr>
<td>1</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Figure 1. CIDNP Spectrum of BPO-\(d_6\) in Benzene-\(d_6\) before Irradiation (a) and during Irradiation (b)
Figure 2. Change of Carbon Dioxide Yield in Thermolysis and Photolysis of BPO with Concentration of Styrene in Benzene
APPENDIX.

ELECTRON SPIN RESONANCE AND CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION SPECTRA.
Figure 1. ESR signal on thermolysis (40°C) of dibenzoyl peroxide (0.01 M) in the presence of N-benzylidene-t-butylamine oxide (0.1 M) in benzene.
Figure 2. ESR signal on photolysis of dibenzoyl peroxide (0.01 M) in the presence of N-benzyldene-t-butylamine oxide (0.1 M) in benzene.
Figure 3. Photo-CIDNP spectrum of BPO-d₆ in the presence of naphthalene in CCl₄ before irradiation (a) and during irradiation (b).
Figure 4. Photo-CIDNP spectrum of BPO-d₆ in the presence of chrysene in benzene-d₆ before (a) and during (b) irradiation.
CHAPTER 2

CHEMICAL EVIDENCE FOR EXCIPEX FORMATION IN THE PHOTOSENSITIZATION PROCESS BETWEEN AROMATIC HYDROCARBON AND DIBENZOYL PEROXIDE

SUMMARY

Naphthyl benzoates and phenylnaphthalenes were produced in naphthalene sensitized photolysis of dibenzoyl peroxide in different distribution of their isomers from thermolysis of dibenzoyl peroxide in the presence of naphthalene, suggesting that naphthalene as a sensitizer interacts with dibenzoyl peroxide in a specific orientation in the sensitization process.
Introduction

Aromatic hydrocarbon-sensitized photolysis of dibenzoyl peroxide (BPO) has been shown to proceed through a singlet excited pathway via an exciplex, although no exciplex emission was observed.\(^1,2\)

In the sensitization process, the excited hydrocarbon sensitizer molecule will take a favourable orientation with respect to the peroxide molecule to form efficiently the exciplex. The resulting exciplex will undergo cleavage of the peroxide moiety into free radicals. It could be expected that immediately after the cleavage the resulting free radicals would react with the hydrocarbon molecule which still exists in a close proximity with a specific orientation to give specific or characteristic reaction products.

This chapter describes the role of the exciplex as an intermediate in the sensitized decomposition of dibenzoyl peroxide on the basis of the observation that benzoyloxy radicals and phenyl radicals reacted with naphthalene as a singlet sensitizer to afford products of different isomer distributions from those of the thermolysis of dibenzoyl peroxide in the presence of naphthalene.
Results and Discussion

Solutions of dibenzoyl peroxide (0.03 M) and naphthalene (0.05 M) in benzene were irradiated under nitrogen atmosphere at room temperature with a 400 W high pressure mercury lamp through a Pyrex wall. For comparison, dibenzoyl peroxide (0.03 M) was allowed to decompose thermally in the presence of naphthalene (0.05 M) in benzene at 80°C. The products were quantitatively analyzed by GLPC. The results are summarized in Table 1.

Production of biphenyl, phenyl benzoate, and benzoic acid was referred to in the previous chapter. More remarkable are the formation of naphthyl benzoates and phenylnaphthalenes and the difference in the yield of these compounds between the decomposition modes. Based on reactivity of benzoyloxy radicals, it is reasonable to assume that naphthyl benzoates were formed through addition of benzoyloxy radicals to naphthalene followed by loss of a hydrogen atom from the resulting cyclohexadienyl radicals (eq. 1).³ Phenylnaphthalenes

\[
\text{PhCO}_2^- + \text{Naphthalene} \rightarrow \text{PhCO}_2\text{Ph} + \text{Cyclohexadienyl radicals}
\]

(1)
are similarly formed through addition of phenyl radicals to naphthalene (eq. 2).

\[
\text{Ph}^- + \text{Naphthalene} \xrightarrow{\text{Ox.}} \text{Ph}
\]

Table 1 shows that the total yield of 1- and 2-phenyl-naphthalenes in the naphthalene-sensitized photolysis of dibenzoyl peroxide is about five times higher than that in its thermolysis in the presence of naphthalene. This fact indicates that in the sensitized photolysis phenyl radicals react more efficiently with naphthalene than in the thermolysis and this is interpreted, as discussed in Chapter 1, in terms of the photodecomposition mechanism of dibenzoyl peroxide involving two-bond cleavage of the O-O and C(\(\alpha\))-C(carbonyl) bonds to give a phenyl-benzoyloxy radical pair in a solvent cage (eq. 3) and the proximity of a naphthalene molecule.

\[
\text{PhCO}_2\text{OCOPh} \overset{\text{heat}}{\longrightarrow} \text{PhCO}_2^- + \cdot \text{OCOPh}
\]

\[
\text{PhCO}_2^- + \cdot \text{OCOPh} \overset{\text{hv}}{\longrightarrow} \text{PhCO}_2^- + \text{CO}_2 + \text{Ph}^-
\]
and a peroxide molecule in the sensitization process, which enables phenyl radicals to attack the naphthalene molecule before they diffuse. The great difference between the decomposition modes in isomer ratios of naphthyl benzoates formed also indicates that the circumstances around benzoyloxy radicals are much different between the sensitized photolysis and the thermolysis. Thus, the yields of 1- and 2-naphthyl benzoates are very similar in the thermolysis, whereas 1-naphthyl benzoate was yielded in a higher yield than 2-naphthyl benzoate in the sensitized photolysis. These results show that in the sensitization process dibenzoyl peroxide would interact with the excited naphthalene in a specific orientation. The exciplex thus formed is estimated, from molecular models, as having a structure where a naphthalene molecule overlaps a phenyl moiety of a dibenzoyl peroxide molecule (Figure 1). When the 0-0 bond cleavage occurs, the distance from the radical center of a benzoyloxy radical to the carbon atoms at the 1 and 8 positions of a naphthalene molecule would be closer than that to the carbon atoms at the 2 and 7 positions. In the case of the interaction of the phenyl radicals and naphthalene molecules the same situate could be thought.

From these considerations as well as the quenching experiments described in the accompanying chapter it is concluded that exciplexes between aromatic hydrocarbon and
dibenzoyl peroxide play an important role in the sensitized decomposition of dibenzoyl peroxide.

As Table 1 shows, three isomeric binaphthyls were produced in different distributions between the sensitized photolysis and the thermolysis. It was reported that 1,1'-, 1,2'-, and 2,2'-binaphthyl are produced in a ratio of 16:12:1 in thermal decomposition of dibenzoyl peroxide in naphthalene.\textsuperscript{3,4} These are considered to be formed through the dimerized intermediate, 2, of the cyclohexadienyl radicals (eq. 4) by analogy with the behavior of benzoyloxy radicals in anisole.

Thus, photo-decomposition of dibenzoyl peroxide in anisole produced 3,3'-dimethoxybiphenyl in the highest yield among the six possible dimethoxybiphenyls. Formation of 3,3'-dimethoxybiphenyl is accounted for by dimerization of methoxybenzoyloxy-cyclohexadienyl radicals which were formed by addition of benzoyloxy radicals to anisole at the ortho and para positions (eq. 5).\textsuperscript{5} The higher yields of binaphthyls
in the sensitized photolysis than in the thermolysis could be attributed to a high concentration of the intermediate which result more facilely from the photolysis than the thermolysis. Furthermore, the lower temperature in the photolysis would partly contribute to the increase of the concentration of the intermediate because the benzoyloxy-cyclohexadienyl radical formation is reversible (eq. 6) and the equilibrium shifts to the right side at lower temperature.6

\[
\text{PhCO}_2^\cdot + \text{PhH} \rightleftharpoons \text{PhCO}_2\text{O}
\]
Experimental

Materials. Dibenzoyl peroxide (WAKO Chemical Co.) was purified by recrystallization from dichloromethane-methanol. Naphthalene was recrystallized three times from ethanol. Special grade benzene (WAKO Chemical Co.) was distilled before use. 1,2'-Binaphthyl and 2,2'-binaphthyl were prepared according to literature.\(^4\) Naphthyl benzoates were prepared from naphthoyl chlorides and phenol in the presence of pyridine. 2,3'-Dimethoxy- and 2,4'-dimethoxybiphenyl were prepared from diazotization of meta- and para-anisidine, respectively, followed by decomposition of the resulting diazotates in anisole. 3,3'-Dimethoxy- and 4,4'-dimethoxybiphenyl were prepared by heating of meta- and para-iodoanisole with copper powder, respectively. 3,4'-Dimethoxybiphenyl were prepared by heating of a mixture of meta- and para-iodoanisole with copper powder. Other reagents were purchased from Tokyo Kasei Co.

Photolysis and thermolysis of dibenzoyl peroxide with naphthalene in benzene. A solution of dibenzoyl peroxide (3.00 g, 0.03 M) and naphthalene (2.00 g, 0.05 M) in benzene (400 ml) was irradiated under nitrogen atmosphere for 2.33 h. (five times half-life periods determined by iodometry) by a 400 W high pressure mercury arc lamp immersed in a Pyrex cooling well. Thermolysis was carried out at a half scale
of photolysis at 80°C in an oil bath for 21.67 h. (five times half-life periods determined by iodometry) under nitrogen gas bubbling.

Photolysis of dibenzoyl peroxide in anisole. A solution of dibenzoyl peroxide (0.03 M) in anisole (3 ml) in a Pyrex tube was deaerated by bubbling of nitrogen, and irradiated by a 1 kW high pressure mercury lamp immersed in a Pyrex cooling well using a merry-go-round type Riko Rotary Photo-chemical Reactor, Model RH400-10W. Irradiation was continued for five times half-life periods of the peroxide determined by iodometric analysis under the same conditions.

Product analyses. In the case of the reactions in benzene, after the reaction was completed the solution was concentrated to one-tenth of its original volume. Naphthalene, biphenyl, phenyl-naphthalenes, naphthyl benzoates, and binaphthyls were determined by VPC analysis on a Hitachi K53 gas chromatograph equipped with a flame ionization detector. A Silicone GE SE-30 (5%) column was used for quantitative analysis. Benzoic acid was isolated by extraction with aqueous sodium bicarbonate solutions and determined gravimetrically. In the experiments in anisole, dimethoxybiphenyls were determined by VPC analysis on a Shimadzu GC-4CM gas chromatograph equipped with a flame ionization detector. A Thermon 1000 (5%) column was used for analysis.
References


Table 1. Yield of products in photolysis and thermolysis of dibenzoyl peroxide in the presence of naphthalene in benzene.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>Yield&lt;sup&gt;b)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>photolysis</td>
<td>thermolysis</td>
</tr>
<tr>
<td></td>
<td>photolysis</td>
<td>thermolysis</td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td>0.77</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>0.28</td>
<td>0.40</td>
</tr>
<tr>
<td>Phenyl benzoate</td>
<td>0.23</td>
<td>0.029</td>
</tr>
<tr>
<td>1-Phenynaphthalene</td>
<td>0.036</td>
<td>0.047</td>
</tr>
<tr>
<td>2-Phenynaphthalene</td>
<td>0.011</td>
<td>0.004</td>
</tr>
<tr>
<td>1-Naphthyl benzoate</td>
<td>0.036</td>
<td>0.043</td>
</tr>
<tr>
<td>2-Naphthyl benzoate</td>
<td>0.007</td>
<td>0.013</td>
</tr>
<tr>
<td>1,1'-Binaphthyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2'-Binaphthyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2'-Binaphthyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.15&lt;sup&gt;c)&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

a) Yields in moles/mole peroxide.

Average values of data obtained by duplicate runs.

b) Yields in moles/mole naphthalene.

c) Determined by isolation.
Figure 1. Formation of oriented complex between dibenzoyl peroxide and naphthalene.
CHAPTER 3

STRUCTURE-REACTIVITY RELATIONSHIPS IN QUENCHING OF FLUORESCENCE FROM AROMATIC COMPOUNDS BY DIBENZOYL PEROXIDE AND DIMETHYL FUMARATE

SUMMARY

Fluorescence from aromatic hydrocarbons and substituted naphthalenes was quenched by dibenzoyl peroxide with variable efficiency in benzene solutions. The quenching rate constants are linearly correlated with ionization potentials of the excited singlet states of the fluorescent compounds ($I_p - E_g$), suggesting that exciplex formation by charge transfer from the sensitizers in their excited singlet states to the peroxide in the ground state plays a predominant role in the enhancement of the quenching rate constants. The intermediacy of the exciplex in the quenching by dibenzoyl peroxide was supported by the same trends found in the fluorescence quenching by dimethyl fumarate, which formed fluorescent exciplexes with the sensitizers.
Introduction

The singlet sensitized photolysis of dibenzoyl peroxide gives the same products as its direct photolysis as described in Chapters 1 and 2. For example, dibenzoyl peroxide undergoes decomposition sensitized by singlet excited chrysene. The singlet excitation energy of chrysene is 79 kcal/mol.\(^1\) On the other hand, the singlet excitation energy of dibenzoyl peroxide is estimated to be about 100 kcal/mol. from its absorption spectrum. Therefore, singlet energy transfer from chrysene to dibenzoyl peroxide by the resonance mechanism cannot be considered; however, the quenching rate constant of excited singlet chrysene by dibenzoyl peroxide is \(6.2 \times 10^9\) \(1/\text{mol} \cdot \text{sec}\),\(^2\) nearly diffusion-controlled. This fact together with the results described in the previous chapter suggests that the quenching takes place through formation of an exciplex between dibenzoyl peroxide and an excited sensitizer.

The mechanism for the singlet sensitized decomposition of dibenzoyl peroxide (BPO) can be described as follows,

Scheme

\[\begin{align*}
\text{ArH} & \xrightarrow{h\nu} ^1\text{ArH}^* \\
^1\text{ArH}^* + \text{BPO} & \xrightarrow{k_q} ^1(\text{ArH} \cdot \text{BPO})^* \\
^1(\text{ArH} \cdot \text{BPO})^* & \xrightarrow{k_r} \text{Radicals}
\end{align*}\]
In the above scheme, a molecule of an aromatic hydrocarbon is excited by absorption of a photon to its singlet excited state (1), which subsequently collides with a BPO molecule in the ground state to form a complex (2), then this complex either gives free radicals and the ground-state sensitizer or decays to BPO and the sensitizer.

In the present system, the singlet excited aromatic compounds ($D^*$) are considered to serve as the donor to the electronegative carboxyl quencher ($A$). In nonpolar solvents the free-energy change, $\Delta G_c$, for charge transfer (eq. 5) may be represented by eq. 6, where the four terms on the right are, respectively, the singlet excitation energy of $D$, the ionization potential of $D$, the electron affinity of $A$, and the coulombic energy gained by bringing $A^-$ and $D^+$ from infinity to the encounter distance. Therefore,
for a series of donors, a constant acceptor, and the same solvent, the free-energy change may be expected to be represented by eq. 7, if the encounter distance is constant.

$$\Delta G_c \approx IP(D) - E_S(D) + \text{Const.}$$  \hspace{1cm} (7)

The general mechanism would give the experimental rate constant, $k_q$, the significance shown in eq. 8. If $k_2$ is much larger than $k_1$, $k_q \approx k_1$ and it could be logically assumed that the potential barrier of the irreversible step is proportional to the potential energy of formation of a radical ion pair by charge transfer, then

$$\log k_q \approx \alpha[IP(D) - E_S(D) + C]$$  \hspace{1cm} (9)

On the basis of these considerations an attempt has been done to investigate the sensitization mechanism of aromatic hydrocarbons by measuring quenching rate constants of hydrocarbon fluorescence by BPO and determine whether correlation between the quenching rate constants and free-energy changes
hold or other structural factors such as the singlet excitation energy control the quenching rate.
Results and Discussion

Fluorescence of a series of aromatic hydrocarbons and a series of substituted naphthalenes (cf. Table 1) was quenched by addition of dibenzoyl peroxide ($0 - 10^{-2}$ M) in benzene solutions at room temperature. In all cases unquenched portion of the fluorescence had the same spectral distribution as that observed in the absence of the quencher, no new emission being detected. Quenching via formation of a ground-state complex can be ruled out because UV/Visible spectra of the sensitizer-quencher mixtures revealed no new absorption bands.

The fluorescence lifetimes of the polycyclic aromatic hydrocarbons ($10^{-3} - 10^{-5}$ M) and substituted naphthalenes ($10^{-3}$ M) were directly measured in benzene under argon atmosphere at room temperature in the presence of varying concentrations of BPO ($0 - 10^{-2}$ M) using the single photon counting technique. Excellent to good linear Stern-Volmer relationships hold for all the sensitizers employed. Typical examples are shown in Figure 1. The quenching rate constants, $k_q$, determined are summarized in Table 1.

In Table 2 are given the singlet excitation energies and ionization potentials of the sensitizers. The singlet excitation energies, $E_S$, were determined from the fluorescence spectra in benzene. The ionization potentials were determined
as adiabatic values from the onset of the reported and observed photoelectron spectra. The values, $I_p - E_S$, refer to the ionization potentials of the singlet excited sensitizers.

Plots of $\log k_q$ against $IP(D) - E_S(D)$ give a linear correlation in both series of hydrocarbons and naphthalene derivatives as shown in Figures 2 and 3. The numbers in the figures refer to the entries in Table 1 and 2. Plots of the quenching data against the singlet excitation energies showed no correlation because of the relatively random distribution of the data points (Figure 4).

The correlation between the quenching rate constants and the free-energy changes suggests that the exciplexes, though non-emissive, having a charge-transfer nature are involved in the sensitization processes.

In order to extend this finding, similar measurements were carried out for the aromatic sensitizer-dimethyl fumarate systems, because dimethyl fumarate has been reported to quench fluorescence from aromatic hydrocarbons, phenanthrene, pyrene, and chrysene, forming fluorescent exciplexes with these hydrocarbons, and assumed to behave as a charge acceptor like BPO. The fluorescence of the two series of the sensitizers ($10^{-3}$ - $10^{-5}$ M) was found to be quenched by dimethyl fumarate ($0$ - $10^{-2}$ M) and weak red-shifted emissions
were observed when naphthalene, triphenylene (Figure 5), and benz[a]anthracene as well as phenanthrene, pyrene and chrysene were used as sensitizers; however, fluorene, anthracene, 9,10-diphenylanthracene, perylene, and tetracene gave no emission with dimethyl fumarate. Quenching rate constants by dimethyl fumarate (DF) were determined by the similar way to the case of dibenzoyl peroxide and summarized in Table 1 and Figures 6 and 7. Figures 6 and 7 show that the quenching rate constants by dimethyl fumarate are linearly correlated with the values of $I_p - E_S$ of sensitizers as expected. From these results it can be concluded that exciplex formation by charge transfer from the singlet excited sensitizers to dibenzoyl peroxide plays a predominant role in the sensitization process through which dibenzoyl peroxide is decomposed. The only processes that should be examined thereafter are those which the exciplexes undergo, i.e., their decay giving the ground-state sensitizer and BPO ($k_d$ in the Scheme) and chemical reactions affording free radicals ($k_r$).

Finally it should be mentioned that while structure-reactivity relationships in the quenching of fluorescence seem to be generally governed by the composite of many structural factors,$^8$-$^{12}$ the above result presents remarkable cases in which $\log k_q$ values linearly correlate with one of the structural factors.

- 56 -
Experimental

Materials. All chemicals were purified before use. Zone-refined phenanthrene was purchased from Tokyo Kasei Co. and recrystallized three times from hexane. Triphenylene and anthracene were synthesized according to published procedures.\textsuperscript{13,14} Analyzed grade 9,10-diphenylanthracene and perylene were obtained from Aldrich Chemical Co., and other polycyclic hydrocarbons were purchased from Wako Chemical Co. After being recrystallized twice from hexane, the aromatic hydrocarbons were passed through columns of silica gel with petroleum ether as eluent. In the case of tetracene benzene was used as eluent. Then the reagents obtained were recrystallized several times from hexane and ethanol. 1-Methoxy- and 1-methylnaphthalene were distilled twice under vacuum, with middle fractions being collected each time. 2-Methoxy-, 2-methyl-, 2-chloro-, 1-cyano-, and 2-cyanonaphthalene were recrystallized several times from hexane and ethanol. Purity of the aromatic hydrocarbons and naphthalene derivatives was checked by comparing their fluorescence lifetimes measured by the single-photon counting method with reported values.\textsuperscript{1} Dibenzoyl peroxide was purified by recrystallization from dichloromethane-methanol. Dimethyl fumarate was recrystallized twice from hexane. Benzene (Dotite, Luminasol) was used as received.
Spectral measurements. Fluorescence lifetimes were measured on a single photon counting apparatus, Applied Photo-Physics Model SP-3X, at room temperature, after 30 minute argon bubbling. In this system, a gated lamp of which a full width of half maximum pulse intensity is 3 ns and a frequency is 7 - 12 kHz was used. Fluorescence photons were detected on a photomultiplier, RCA Model 8850. A time-to-pulse height converter, ORTEC Model 467, provided a voltage pulse, and this voltage subsequently fed to a ORTEC Model 6240 multichannel analyzer. Obtained data were recorded by a Hewlett Packard X-Y Recorder 7004B and a Point plotter 17012B.

Photoelectron spectra were recorded on the instrument reported previously by T. Kobayashi et al.\textsuperscript{15} using the He I resonance line (21.22 eV) as the excitation source, and were calibrated using Xe as an internal standard. The sample inlet and target chamber system was heated up to ca. 110 - 140°C to obtain sufficient vapor pressure.
References


Table 1. Quenching Rate Constants, $k_q$, of Dibenzoyl Peroxide (BPO) and Dimethyl Fumarate (DF).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_q/10^9$ l·mol⁻¹·s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Fluorene $(1.9 \times 10^{-3})$</td>
<td>17</td>
</tr>
<tr>
<td>2) Naphthalene $(3.3 \times 10^{-3})$</td>
<td>9.2</td>
</tr>
<tr>
<td>3) Triphenylene $(1.9 \times 10^{-4})$</td>
<td>4.8</td>
</tr>
<tr>
<td>4) Phenanthrene $(4.7 \times 10^{-4})$</td>
<td>5.8</td>
</tr>
<tr>
<td>5) Chrysene $(1.8 \times 10^{-4})$</td>
<td>6.1</td>
</tr>
<tr>
<td>6) Pyrene $(4.4 \times 10^{-4})$</td>
<td>8.0</td>
</tr>
<tr>
<td>7) Anthracene $(4.7 \times 10^{-4})$</td>
<td>11</td>
</tr>
<tr>
<td>8) Benz[a]anthracene $(2.6 \times 10^{-4})$</td>
<td>5.4</td>
</tr>
<tr>
<td>9) 9,10-Diphenylanthracene $(9.9 \times 10^{-5})$</td>
<td>5.7</td>
</tr>
<tr>
<td>10) Perylene $(7.6 \times 10^{-5})$</td>
<td>8.3</td>
</tr>
<tr>
<td>11) Tetracene $(1.6 \times 10^{-5})$</td>
<td>4.2</td>
</tr>
<tr>
<td>12) 1-Methoxynaphthalene $(3.6 \times 10^{-3})$</td>
<td>17</td>
</tr>
<tr>
<td>13) 2-Methoxynaphthalene $(5.1 \times 10^{-3})$</td>
<td>9.6</td>
</tr>
<tr>
<td>14) 1-Methylnaphthalene $(4.2 \times 10^{-3})$</td>
<td>14</td>
</tr>
<tr>
<td>15) 2-Methylnaphthalene $(5.2 \times 10^{-3})$</td>
<td>8.9</td>
</tr>
<tr>
<td>16) 2-Chloronaphthalene $(4.1 \times 10^{-3})$</td>
<td>6.2</td>
</tr>
<tr>
<td>17) 1-Cyanonaphthalene $(2.7 \times 10^{-3})$</td>
<td>5.0</td>
</tr>
<tr>
<td>18) 2-Cyanonaphthalene $(2.8 \times 10^{-3})$</td>
<td>3.4</td>
</tr>
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</table>
Table 2. Structural Factors of Sensitizers

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$E_S$ /kcal mol$^{-1}$</th>
<th>IP /eV</th>
<th>(IP-$E_S$) /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Fluorene</td>
<td>95</td>
<td>$7.8^b$</td>
<td>3.7</td>
</tr>
<tr>
<td>2) Naphthalene</td>
<td>91</td>
<td>$7.9^{c,d}$</td>
<td>3.9</td>
</tr>
<tr>
<td>3) Triphenylene</td>
<td>83</td>
<td>$7.8^d$</td>
<td>4.2</td>
</tr>
<tr>
<td>4) Phenanthrene</td>
<td>82</td>
<td>$7.7^{d,e}$</td>
<td>4.1</td>
</tr>
<tr>
<td>5) Chrysene</td>
<td>79</td>
<td>$7.5^{d,e}$</td>
<td>4.1</td>
</tr>
<tr>
<td>6) Pyrene</td>
<td>77</td>
<td>$7.4^f$</td>
<td>4.1</td>
</tr>
<tr>
<td>7) Anthracene</td>
<td>75</td>
<td>$7.4^{d,e}$</td>
<td>4.1</td>
</tr>
<tr>
<td>8) Benz[a]anthracene</td>
<td>74</td>
<td>$7.4^e$</td>
<td>4.2</td>
</tr>
<tr>
<td>9) 9,10-Diphenylnanthracene</td>
<td>70</td>
<td>$7.1^d$</td>
<td>4.1</td>
</tr>
<tr>
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<td>65</td>
<td>$6.9^e$</td>
<td>4.1</td>
</tr>
<tr>
<td>11) Tetracene</td>
<td>60</td>
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<td>4.3</td>
</tr>
<tr>
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<td>88</td>
<td>$7.6^c$</td>
<td>3.8</td>
</tr>
<tr>
<td>13) 2-Methoxynaphthalene</td>
<td>86</td>
<td>$7.7^c$</td>
<td>4.0</td>
</tr>
<tr>
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<td>90</td>
<td>$7.8^h$</td>
<td>3.9</td>
</tr>
<tr>
<td>15) 2-Methylnaphthalene</td>
<td>89</td>
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</tr>
<tr>
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<td>89</td>
<td>$8.1^h$</td>
<td>4.4</td>
</tr>
<tr>
<td>17) 1-Cyanonaphthalene</td>
<td>88</td>
<td>$8.6^i$</td>
<td>4.8</td>
</tr>
<tr>
<td>18) 2-Cyanonaphthalene</td>
<td>86</td>
<td>$8.6^i$</td>
<td>4.9</td>
</tr>
</tbody>
</table>
a) Values of $7.5 \times 10^9$ and $8.5 \times 10^9$ L mol$^{-1}$ s$^{-1}$ were reported by Caldwell$^5$ and Farid$^6$, respectively.


Figure 1. Stern-Volmer plots for quenching of triphenylene fluorescence by dibenzoyl peroxide in deaerated benzene.
Figure 2. Correlation of $\log k_q$ of dibenzoyl peroxide with $I_p - E_S$ of aromatic hydrocarbon.
Figure 3. Correlation of log $k_q$ of dibenzoyl peroxide with $I_p - E_S$ of naphthalene derivative.
Figure 4. Correlation of log $k_q$ of dibenzoyl peroxide with $E_S$ of aromatic hydrocarbon.
Figure 5. Fluorescence of triphenylene (1.9 x 10^{-4} M) in deaerated benzene in the presence of dibenzoyl peroxide. Concentration of quencher (M): a, nil; b, 4.5x10^{-3}; c, 1.4x10^{-2}; d, 2.3x10^{-2}; e, 3.2x10^{-2}. 

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Figure 6. Correlation of log $k_q$ of dimethyl fumarate with $I_p - E_S$ of aromatic hydrocarbon.
Figure 7. Correlation of $\log k_q$ of dimethyl fumarate with $I_p - E_S$ of naphthalene derivative.
SUMMARY

Photocurrent was observed when the light-absorbing component of an exciplex in acetonitrile was irradiated in a platinum electrode or a tin oxide electrode compartment connected through a glass frit with another platinum electrode compartment containing an acetonitrile solution of the other component of the exciplex. The systems examined were chrysene-dimethyl fumarate, perylene-triethylamine, etc. Observation of photocurrent indicates that electrons transfer, through the circuit, from electron donor molecules to electron acceptor molecules in the exciplex formation system.
Introduction

In Chapters 1-3 the mechanism of singlet sensitized decomposition of dibenzoyl peroxide has been described. It is confirmed that singlet sensitized decomposition of dibenzoyl peroxide proceeds via a non-emissive exciplex having a charge transfer nature.

Interaction of an excited molecule and a ground-state molecule is revealed from fluorescence quenching of an excited molecule by a ground-state molecule; new emissions are observed in some cases, and these phenomena refer to a presence of an exciplex having a charge transfer nature.

In exciplex formation, there are two kinds of interactions; one is charge transfer from an electron donor molecule in the ground state to an electron acceptor molecule in the excited state (eq. 1), and the other is that from an electron donor in the excited state to an electron acceptor in the ground state (eq. 2). Systems of excited aromatic hydrocarbons and amines correspond to the former, and those of excited aromatic hydrocarbons and dimethyl fumarate, terephthalonitrile, or dibenzoyl peroxide correspond to the latter (cf. Chapter 3).

\[ A^* + D \rightarrow (A \cdot D)^* \leftrightarrow (A^* \cdot D^+) \quad (1) \]

\[ D^* + A \rightarrow (D \cdot A)^* \leftrightarrow (D^* \cdot A^-) \quad (2) \]
This chapter describes some attempts to observe electron transfer as photocurrents between an electron donor side and an electron acceptor side which form an exciplex. In these experiments two components of an exciplex were placed separately in different compartments joined by a fritted glass and a circuit which joined two electrodes.

In the interactions between irradiated aromatic hydrocarbon solution and electron acceptor solution, photocurrents are observed and are interpreted by electron transfer from excited aromatic hydrocarbons to a Fermi level of platinum which is an anode, followed by electron transfer to the lowest unoccupied molecular orbital of an electron acceptor molecule through a circuit and a Fermi level of cathode platinum. In the interactions between excited aromatic hydrocarbons and an electron donor molecule, the photocurrents to reversed direction were observed.
Results and Discussion

A reaction device was illustrated in Figure 1. Two reaction cells were connected by a glass frit G-4. A platinum anode and a Ag/AgNO₃ (0.1 M) reference electrode were set in cell I. In cell II a platinum cathode was placed. In cell I an aromatic hydrocarbon (0.001 M), chrysene, pyrene, perylene, or 9,10-diphenylanthracene, was dissolved in acetonitrile containing tetraethylammonium perchlorate (TEAP, 0.1 M), as a supporting electrolyte. An electron acceptor (0.01 M), dimethyl fumarate, terephthalonitrile, or dibenzoyl peroxide, and TEAP (0.1 M) were dissolved in acetonitrile in cell II. After 30-min bubbling of purified N₂ gas, cell I was irradiated with a 1 kW super-high pressure mercury arc lamp through a L-35 filter, which passes longer wavelength light than 330 nm.

At first, control experiments in the absence of one or both of the components were carried out. In the presence of one component, a small dark current was observed, but a negligible current was observed on irradiation. In the absence of both components induced currents were negligible both in the dark and under illumination.

Current-potential properties for a platinum electrode have been measured with a standard three-electrode cell and a potentiostat. For all experiments given here the platinum
electrode potential was changed in the bias range used. Current-potential curves for a system of perylene and dimethyl fumarate and a system of chrysene and dimethyl fumarate are given in Figures 2 and 3. Anodic dark currents were observed and increased at potentials more positive than 0.5 V and 0.8 V in cases of perylene and chrysene, respectively. Photocurrents, which were the difference between the currents during irradiation and in the dark at positive potentials up to +1.0 V, were observed when the scan in potentials was begun at 0 V. In both cases no photocurrents were observed at 0 V anodic bias. The photocurrents are larger in the case of perylene than in the case of chrysene, and in both cases, tend to increase with increasing anodic potentials employed.

In the system of perylene and dimethyl fumarate effects of light intensity on the photocurrent were examined using a 500 W xenon lamp and light reducing-filters. The potential of the Ag/Ag\(^+\) electrode bias was controlled at 0.4 V. The photocurrent was decreased with decreasing transmittance of the filters, as shown in Figure 4. This fact shows that the photocurrent was influenced by the concentration of an excited aromatic hydrocarbon.

In the system of chrysene and dimethyl fumarate, when chrysene (0.001 M) was irradiated with a 1 kW super-high
pressure mercury lamp, the relative photocurrent was increased with increasing concentrations of dimethyl fumarate. This effect indicates that the presence of acceptor molecules is responsible for the induction of the photocurrents (cf. Figure 5).

From these results, in the system of perylene and dimethyl fumarate or chrysene and dimethyl fumarate, it is revealed that electrons are transferred from excited aromatic hydrocarbon molecules to acceptor molecules through platinum electrodes and wire (Scheme 1 and Figure 6). But it is uncertain whether electrons are liberated from an excited sensitizer or from a reactive intermediate formed from an excited aromatic hydrocarbon.

Scheme 1

\[
\begin{align*}
\text{ArH} + h\nu & \xrightarrow{} \text{ArH}^* \\
\text{ArH}^* & \xrightarrow{} \text{ArH}^+ + e^- \quad \text{(anode)} \\
e^- + \text{DF} & \xrightarrow{} \text{DF}^- \quad \text{(cathode)} \\
\text{DF}^- & \xrightarrow{} \text{DF} + e^- \\
\text{ArH}^+ + e^- & \xrightarrow{} \text{ArH}
\end{align*}
\]
In the system of pyrene and dimethyl fumarate photocurrents were observed, too. But in this case under the condition of zero voltage bias the apparent photocurrent was larger than the dark current; the dark current was $-0.5 \mu A/cm^2$, but the current of $-1.25 \mu A/cm^2$ was observed on irradiation. The reason is uncertain for this phenomenon.

In the system of 9,10-diphenylanthracene and dimethyl fumarate no photocurrent was observed (Figure 7). The reason is not confirmed, but one important factor is the conformation of the sensitizer molecule. It is assumed that the molecule of 9,10-diphenylanthracene is not coplanar but the phenyl groups are twisted at right angles to the anthracene moiety. Therefore, electron transfer to platinum electrode could not occur because the excited molecule can not approach the surface of the electrode.

In these experiments threshold bias voltages of dark currents are different in each case and those are parallel to ionization potentials of aromatic hydrocarbons. This indicates the participation of the aromatic hydrocarbons in the phenomenon.

Furthermore, results of chrysene and terephthalonitrile or dibenzoyl peroxide are interesting. It is obvious that from observation of the exciplex emission excited singlet chrysene forms an exciplex with terephthalonitrile. But
chrysene gave no new emission with dibenzoyl peroxide and the presence of an exciplex is not certain. As shown in Figure 8 large photocurrent was observed in the system of chrysene and terephthalonitrile, and in the system of chrysene and dibenzoyl peroxide photocurrents are obviously observed. This result means that electron transfer takes place from chrysene to dibenzoyl peroxide through the circuit.

Interaction of an excited aromatic hydrocarbon and triethylamine is explained by charge transfer from the electron donor molecule in the ground state to the electron acceptor molecule in the excited state. At first in the reaction cell in Figure 1, interactions of perylene and chrysene with triethylamine were examined, and in both cases large photocurrents were observed under zero voltage bias condition. Current-time properties are shown in Figure 9. And the photocurrents were observed for a long time; in the case of chrysene photocurrents of $6 \mu A/cm^2$ were observed for two hours and in the case of perylene for half an hour. But the polarity of currents was contrary to the expectation.

Photoelectrochemistry, especially using a semiconductor electrode, titanium dioxide, tin oxide, etc., is interested in the viewpoint of solar energy conversion, and many studies have been reported. However, in non-aqueous solutions only a few experiments have been presented. A merit of use of
a semiconductor is stability of the semiconductor electrode for light of smaller energy than the band gap energy. From these aspects tin oxide was employed in the system of aromatic hydrocarbons and electron donors. These experiments using photogalvanic cells are particularly interesting. When tin oxide which was coated on the surface of Pyrex was used as a working electrode (Figure 10), and the electrode potential was changed in the bias range (-0.2 to +0.3 V vs Ag/Ag⁺), dark current was negligibly small, but photocurrent was large. More negative bias potential induced larger photocurrents (Figure 11). This result suggests that an excited aromatic hydrocarbon molecule accepts an electron from triethylamine; irradiation of an aromatic hydrocarbon induces electron transfer from the amine to a Fermi level of platinum, followed by electron transfer to the lower singly unoccupied molecular orbital of excited aromatic hydrocarbon molecule through a circuit and a Fermi level of tin oxide (Figure 12).

These experiments indicate that in the systems capable of forming exciplex electron transfer from an electron donor molecule to an electron acceptor molecule through circuit is induced by irradiation.
Experimental

Materials. Dibenzoyl peroxide was purified by recrystallization by three times from ethanol. Dimethyl fumarate and terephthalonitrile were recrystallized twice from hexane. Triethylamine was purified by distillation. Analyzed grade 9,10-diphenylanthracene and perylene were obtained from Aldrich Chemical Co. Chrysene and pyrene were purchased from Wako Chemical Co. After prepurification by recrystallization twice from hexane, aromatic hydrocarbons were passed through columns of silica gel by petroleum ether as solvent. Then the reagents obtained were recrystallized several times from hexane and ethanol. Polarographic grade tetraethylammonium perchlorate (TEAP) was purchased from Kanto Kagaku Co., and fresh high pressure liquid chromatographic grade acetonitrile was used.

Electrochemical Instrumentation and Procedures. The cell was a conventional three-compartment design. The counter electrode and reference electrode compartments were separated from the main working compartment by fritted-glass G-4 disks to prevent mixing of solutions. The reference compartment was a removable glass tube slanted toward the working electrode to minimize any uncompensated potential drop across the working and reference electrodes. Platinum plates (6 cm²) or tin oxide coated on a Pyrex glass (Nesa glass, 12.6 cm²)
was used as a working electrode, which had been dipped into a potassium hydroxide solution and electrolyzed at 1.5 V for 20 min. before each experiment. And in the case of tin oxide a copper wire was connected to the ohmic contacts with conducting silver base epoxy cement. The counter electrode was a platinum plate. A large area Pt plate was used for capacitance measurements. And a Ag wire, which immersed in 0.1 M AgNO₃ in acetonitrile, served as a reference electrode. Nitrogen gas was bubbled through the acetonitrile solutions for at least 30 min. before the measurements. All measurements of photocurrents were performed under potentiostatic conditions. A potentiostat, Hokuto Denko Ltd. Model Potentiostat/Galvanostat HA-201, which was connected with a voltage recorder, Rikadenki Electronic Recorder R-21, was used. A 1 kW super-high pressure mercury arc lamp, ORC Co., equipped with a L35 or a L39 glass filter which passes >330 nm and >370 nm light, respectively, was used as a light source. Photocurrent observation was performed in the stationary condition in current under illumination. Stationary currents were obtained after irradiation for a few minutes under various potentiostatic conditions.
References


Aromatic hydrocarbon $10^{-3}$ M
Dimethyl fumarate $10^{-2}$ M

(in CH$_3$CN, Et$_4$N$^+$ClO$_4^-$)

Cell 1  Cell 2

Figure 1. Reaction device.
Figure 2. Current-potential property in a system of perylene and dimethyl fumarate.

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Figure 3. Current-potential property in a system of chrysene and dimethyl fumarate.

- 86 -
Figure 4. Effect of light intensity on photocurrent in a system of perylene and dimethyl fumarate.
Figure 5. Effect of acceptor concentration on photocurrent intensity in a system of chrysene and dimethyl fumarate.
Figure 6. Electron transfer path.
Figure 7. Current-potential properties in systems of pyrene and dimethyl fumarate (left) and of 9,10-diphenylanthracene and dimethyl fumarate (right).
Figure 8. Current-potential properties in systems of chrysene and terephthalonitrile (left) and of chrysene and dibenzoyl peroxide (right).
Figure 9. Change of current intensity with time in systems of aromatic hydrocarbons and triethylamine.
Figure 10. Reaction device using a tin oxide electrode.

Aromatic hydrocarbon \(10^{-3} \text{ M}\) Triethylamine \(10^{-2} \text{ M}\)

(in CH\(_3\)CN, \(\text{Et}_4\text{N}^+\text{ClO}_4^-\))
Figure 11. Current-potential property in a system of perylene and triethylamine.
Figure 12. Electron transfer path.
APPENDIX 1.

INTERACTION OF DIBENZOYL PEROXIDE WITH TRIPLET BENZOPHENONE.
Introduction

Photodecomposition of dibenzoyl peroxide sensitized with aromatic carbonyl compounds has been studied. Benzophenone ($E_T = 68.5$ kcal·mol$^{-1}$), acetophenone ($E_T = 73.6$ kcal·mol$^{-1}$), and 2-acetonaphthone ($E_T = 59.3$ kcal·mol$^{-1}$) induce photodecomposition of dibenzoyl peroxide in benzene and cyclohexane. However, 2,3-pentadienone ($E_T = 54.3$ kcal·mol$^{-1}$), benzil ($E_T = 53.7$ kcal·mol$^{-1}$), and fluorenone ($E_T = 53.3$ kcal·mol$^{-1}$) are not effective. A photo-CIDNP spectrum due to chlorobenzene (emission at 7.25 p.p.m.) in the acetophenone-sensitized photolysis of dibenzoyl peroxide has been interpreted as the triplet mode of decomposition. Benzophenone gave a similar, but weak, CIDNP spectrum. This phenomenon could be ascribed to a lower triplet energy of benzophenone compared with acetophenone, if the reaction proceeds through energy transfer from triplet benzophenone to dibenzoyl peroxide. The yield of benzoic acid resulting from the benzophenone sensitized decomposition of the peroxide in benzene increased with decreasing initial peroxide concentration. This result was interpreted to mean that triplet benzophenone abstracted hydrogen atoms from solvent benzene at low peroxide concentrations, and that the resulting ketyl radicals induced decomposition of the peroxide (Scheme 1).
Results and Discussion

Phosphorescence intensity of benzophenone was found not to change on addition of dibenzoyl peroxide (0.04 M) in CC\textsubscript{14}, and in the presence of dibenzoyl peroxide (0.04 M) the phosphorescence lifetime (\(\tau_T\): 23 \(\mu\)s) was the same as that in the absence of dibenzoyl peroxide, as measured by single photon counting technique. Furthermore, irradiation (366-nm) of a CC\textsubscript{14} solution of dibenzoyl peroxide (0.03 M) containing benzophenone (0.002 M) caused no decomposition of dibenzoyl peroxide.

These results indicate that decomposition of dibenzoyl peroxide in the presence of benzophenone in benzene does not proceed through the triplet sensitized process, but proceed through the induced decomposition with benzophenone ketyl radicals and/or cyclohexadienyl radicals resulting from addition of triplet benzophenone to benzene (Scheme 2).
Scheme 1.

\[(\text{PhCOO})_2 + \text{Ph}_2\text{COH} \rightarrow \text{PhCOO}^\cdot + \text{PhC-O-C-Ph} \]

\[\text{PhC-O-C-Ph} \rightarrow \text{PhCOH} + \text{Ph}_2\text{C}=\text{O} \]

Scheme 2.

\[\text{Ph}_2\text{C}=\text{O}^* + \text{PhH} \rightarrow \text{Ph}^\cdot \text{C}=\text{O} \]

\[\text{Ph}^\cdot \text{C}=\text{O} \rightarrow 2\text{Ph}_2\text{COH} + \text{Ph-Ph} \]

\[\text{PhCOH} + (\text{PhCOO})_2 \rightarrow \text{PhCO}_2^\cdot + \text{PhC-O-C-Ph} \]

- 100 -
**Experimental**

**Materials.** Commercial dibenzoyl peroxide was purified by precipitation from dichloromethane-methanol. Benzophenone (Wako Chemical Co.) was recrystallized three times from ethanol. Carbon tetrachloride was purified by distillation before use. Carbon tetrachloride (Dotite, Luminasol) was used for spectral measurements.

**Photolysis.** A solution of dibenzoyl peroxide (0.03 M) and benzophenone (0.002 M) in CC\(_4\) (3 ml) in a Pyrex tube was degassed by bubbling of nitrogen, and irradiated by a 1 kW high pressure mercury lamp immersed in a Pyrex cooling well and furthermore surrounded by Toshiba UV-D36B glass filters. Decomposition of the peroxide was monitored by iodometric analysis.

**Spectra Measurements.** Phosphorescence lifetimes were measured on a single photon counting apparatus, Applied Photo- physic Model SP-3X, at room temperature, after 30 minute argon bubbling. Emission spectra were recorded on a Hitachi MPF-2A fluorescence fluorimeter.
References

Di-1-naphthoyl and di-2-naphthoyl peroxides (0.03 M, respectively) were decomposed by irradiation with a 1 kW high pressure mercury lamp and by heating at 80°C in benzene, and obtained products, naphthyl naphthoates and phenyl-naphthalenes were quantitatively analyzed by VPC. Results are shown in Table.
Table. Photolysis and Thermolysis of Di-1- and Di-2-naphthoyl Peroxide.

<table>
<thead>
<tr>
<th></th>
<th>Yield (moles/mole)</th>
<th>NpCO₂Np</th>
<th>Np-Ph</th>
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</thead>
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<td><strong>Di-1-naphthoyl Peroxide</strong></td>
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<tr>
<td>Photolysis</td>
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<tr>
<td>Thermolysis</td>
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<tr>
<td><strong>Di-2-naphthoyl Peroxide</strong></td>
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<td></td>
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<tr>
<td>Photolysis</td>
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</tr>
<tr>
<td>Thermolysis</td>
<td>0.016</td>
<td>0.28</td>
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PHOTOLYSIS OF DIBENZOYL PEROXIDE CRYSTAL.

A single crystal and powder of dibenzoyl peroxide were decomposed by irradiation with a 1 kW super-high pressure mercury lamp. Conversions were determined by iodometry and obtained products were analyzed by VPC. Experimental conditions and results are shown in Table.
Table. Photolysis of dibenzoyl peroxide

<table>
<thead>
<tr>
<th>Irradiation time (hr)</th>
<th>Conversion (%)</th>
<th>Yields (moles/mole)</th>
<th>PhCO₂Ph</th>
<th>Ph-Ph</th>
<th>PhCO₂H</th>
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</thead>
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<tr>
<td>Crystal</td>
<td>1) 10</td>
<td>51</td>
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<td>tr.</td>
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</tr>
<tr>
<td></td>
<td>2) 5</td>
<td>52</td>
<td>0.10</td>
<td>tr.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3) 3</td>
<td>46</td>
<td>0.16</td>
<td>tr.</td>
<td></td>
</tr>
<tr>
<td>Powder in H₂O</td>
<td>1) 0.8</td>
<td>10</td>
<td>tr.</td>
<td>tr.</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>2) 1</td>
<td>9</td>
<td>0.30</td>
<td>tr.</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>3) 3</td>
<td>80</td>
<td>0.06</td>
<td>0.09</td>
<td>0.62</td>
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</table>
APPENDIX 4.

QUENCHING RATE CONSTANTS FOR FLUORESCENCE OF AROMATIC HYDROCARBONS BY TEREPTHALONITRILE.

Fluorescence of aromatic hydrocarbons were quenched by terephthalonitrile in benzene, and exciplex emissions were observed in all cases. Quenching rate constants were measured by single photon counting technique, and results are summarized in Table.
Table. Quenching Rate Constants, $k_q$, of Terephthonitrile.

$$k_q \text{ (l.mol}^{-1}\text{.sec}^{-1})$$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Triphenylene</td>
<td>$1.1 \times 10^8$</td>
</tr>
<tr>
<td>2) Phenanthrene</td>
<td>$2.3 \times 10^8$</td>
</tr>
<tr>
<td>3) Chrysene</td>
<td>$7.5 \times 10^7$</td>
</tr>
<tr>
<td>4) Pyrene</td>
<td>$2.6 \times 10^9$</td>
</tr>
<tr>
<td>5) Anthracene</td>
<td>$2.6 \times 10^9$</td>
</tr>
<tr>
<td>6) Benz[a]anthracene</td>
<td>$1.2 \times 10^8$</td>
</tr>
</tbody>
</table>
APPENDIX 5.

PRINCIPLE AND INSTRUCTIONS FOR SINGLE PHOTON COUNTING APPARATUS.

Principle

The basis of the method is the timing of the arrival of the first fluorescence photon at the photodetector relative to an arbitrary time zero, which is fixed as the time of firing of the excitation lamp, a gated lamp. This time difference is caused in part by the time taken for the molecule to reemit an absorbed photon. The time before reemission defines their decay function. A time-to-pulse height converter provides a voltage pulse that is proportional to the time difference. This voltage subsequently fed to a multichannel analyzer. Repetitive lamp pulsing and photon collection eventually in a histogram of voltages being obtained in the memory of the multichannel analyzer which is a direct analog of the fluorescence decay function.
Operating Instructions for Single Photon Counting Apparatus.

The positions of the various optical components are shown in Figure 1. The monochromator is normally placed before the sample and after the gated lamp. The lamp should first be filled with nitrogen or air at a pressure of 0.5 atmosphere with an electrode gap of approximately 2-3 mm.

Connections should be made between the lamp and gated lamp control unit (3 connecting leads) and the lamp operated at 4.2 kV at repetition rate of 12 kHz (pulse width is 3-5 ns). Connection should be made between the START photomultiplier and low output of the power supply. Turn on the power supply for the START photomultiplier and operate it at 1250 V. The output of the START photomultiplier may be observed on an oscilloscope (50 ohm termination, oscilloscope setting 10-20 ns/div, 0.1 to 0.5 v//div). The high voltage lead from the gated lamp control unit should be well separated from both the leads from the START and STOP photomultipliers.

The lamp box should be separated from the base plate and the position of the lamp adjusted with the micrometers so that the arc is exactly aligned to the center of the lens. The gated lamp box should be replaced on the base plate. The monochromator should be set to 337 nm with slits and a 20 nm band-pass (i.e. maximum) and a suitable strongly fluorescent sample placed in the sample holder. By observing the position of the exciting
light, adjustments can be made of the position of the cell holder and the lamp so that the excitation beam passes symmetrically through the center of the cell. The cell holder must be aligned with the slot in front of the port to the STOP photomultiplier. Exciting light may be focused into the sample by adjusting the lenses of the gated lamp and flanges of the monochromator. When the lens is used before the STOP photomultiplier, the fluorescence must fall on the central portion of the photocathode of the STOP photomultiplier.

Connection should be made between the STOP photomultiplier and HV output of the photomultiplier power supply (for the 8850 photomultiplier, an operating voltage of 2.5 kV, the scale of 860, is recommended). The output of the STOP photomultiplier should be observed on an oscilloscope. The output from the START photomultiplier is connected to the negative input of a 100 MHz discriminator and the fast output of this discriminator connected to the oscilloscope with a 50 ohm termination. With the discriminator level at minimum, all pulses attributable to the lamp plus associated noise should be observed. The discriminator level should be increased until a single pulse due to the lamp alone is observed (the level where the scale is 100 on the discriminator is best). The high voltage for the START photomultiplier should be switched OFF. No pulses should now be observed. Under these conditions, if this is not the
case, the discriminator level should be increased until the pulse disappears.

The fast negative output of the 100 MHz discriminator should now be connected to the start input of the time-to-amplitude converter (TAC). The output of the STOP photomultiplier should be connected to the negative input of the constant fraction (snap-off) discriminator. The fast negative output of the constant fraction discriminator, through the nanosecond delay, should be connected to the stop input of the TAC. The output of the TAC should be connected to the oscilloscope (50 ohm termination) and the output observed. The output from the TAC is subsequently connected to the ADC input of the multichannel analyser (MCA).

Incorporation of a ratio counter—the slow positive output of the fast discriminator should be connected to the input of the counter and the slow positive output of the constant fraction discriminator connected to the clock input of the counter. The ratio of the counts in the START and STOP channels can now be read directly off the counter (it is recommended that this ratio should be of the order of 100 : 1).

A scattering sample should now be placed in the sample holder in order to observe the build-up of the lamp profile observed at 337 nm or 384 nm on the MCA operated in the pulse height analysis mode. The level on the constant fraction
discriminator should be set at maximum and slowly decreased until counts are observed on the MCA. The discriminator level for the optimum signal-to-noise ratio should be adjusted by subsequent runs while keeping the ratio of the counts in the START and STOP channels to about 100 : 1. The STOP photomultiplier may be tuned at this stage to give the best pulse shape and reproducibility. But practically the level on the constant fraction discriminator should be set at 10, which is the scale, and signal-to-noise ratio should be adjusted with the slit of monochromator which is placed before the STOP photomultiplier and after the sample.

The example of decay curves obtained are shown in Figures 2-4, and measurable decay time is from ca. 3 ns to 100 μs in this apparatus.
Figure 1. Single Photon Counting Apparatus.
Figure 2. Fluorescence decay curve of 9,10-diphenylanthracene ($9.9 \times 10^{-5}$ M) in deaerated benzene ($\tau_S = 7.5$ ns).
Figure 3. Fluorescence decay curve of triphenylene ($1.9 \times 10^{-4}$)
in deaerated benzene ($\tau_g = 35$ ns).
Figure 4. Fluorescence decay curve of pyrene (4.4 \times 10^{-4} \text{ M}) in deaerated benzene (\tau_S = 185 \text{ ns}).
"Singlet Sensitized Reactions" 概要

光励起状態分子と基底状態分子との相互作用は非常に興味が持たれている。本論文においては、過酸化ベンゾイル(BPO)の光一重項増感分解の機構を次の2点すなわち、1) 熱分解と光分解における生成物の分布の比較2) 迴酸化ベンゾイルによる芳香族多環炭化水素のケイ光の消光、の観点から行った研究について述べる。

第一章では、過酸化ベンゾイルは熱分解においては一結合開裂で分解するのに対して、光分解においては二結合開裂で分解する事実をかご内生成物の収量から明らかにした。

第二章においては、過酸化ベンゾイルの光一重項増感分解はその増感過程において励起鍵体を形成して反応していることをナフタレン増感分解を例として、反応生成物の分布から明らかにした。
土にカーティンでは、その動起電体の電子移動型の動起電体であることを種々の芳香族多環炭化水素を用いて、そのケイ光の消光速度定数を求めることにより明らかにした。また次に章においては、動起電荷移動電体の研究の拡張として、電荷移動電体を形成する2つの物質を別々の反応槽に入れ、一方にだけ光を照射することにより、互いの反応槽の間で電流が流れることを明らかにした。

2章。過酸化ベンゾイルの光分解細胞生成物の生成機構。

過酸化ベンゾイル（BPO）はホモリシスによりラジカルに分解するが、その分解の様式が光分解と熱分解とは異なることをこの章において述べる。BPOの熱分解は酸素-酸素結合が開裂して2個のベンゾイルオキシラジカルを生ずる一結合開裂により進行すると考えられる。しかしながらBPOの光分解は、ラジカルから反応生成物である安息香酸フェニル
が熱分解と比較して極めて多く生成することから、酸素-酸素結合の開裂と同時に、あるいはそれらに引きつづいて速かに炭素-炭素結合開裂が起こる二結合開裂で進行すると考えられることが以下の実験により明らかにした。

\[
\text{PhCOO} + \text{Ph} \xrightarrow{\Delta} \text{PhCO}_2^+ + \cdot \text{CO}_2 \text{Ph} \\
\text{PhCOO} + \text{Ph} \xrightarrow{\text{hv}} \text{PhCO}_2^+ + \text{Ph} + \text{CO}_2
\]

まず光分解で得られる安息香酸フェニルがかけこ生成物であること、また光分解においては最初からかけこ生成物においてフェニルラジカルと二酸化炭素が存在していることを示す。

BPOの光分解反応の反応系内にラジカル捕捉剤としてステレンを加え、その濃度を変化し、得られる安息香酸フェニルの収量を調べたがほとんど変化はなかった。この事実は得られた安息香酸フェニルがかけこ生成物であることを示しており、さらにBPO-d₆の光CIDNPの結果もこのことを支持する。またかけこ内に
二酸化炭素が存在することは、反応系内に各種濃度のスチレンを存在させ二酸化炭素の発生量を調べたところ、高い濃度のスチレン存在下においても光分解の場合は熱分解の場合よりはるかに多くの二酸化炭素が発生することから明らかとなった。これらはかご内にフェニルラジカルが存在することも、スピントラップ法により明らかにした。すなわち、フェニル-N-テトラチルニトロンを反応系内に存在させ、熱分解および光分解を行ったところ、熱分解においてはベンゾイルオキシラジカルとニトロンの付加体に由来するESRシグナルが観測されただけであるのに対して、光分解においてはフェニルラジカルとニトロンの付加体に由来するシグナルも観測された。
以上の実験結果から、光分解は二結合開裂で進行することは明らかであるが、土らにその二結合開裂の様式として次の2通りが考えられる。1) 同時にベンゾイルオキシラジカル、フェニルラジカル、および二酸化炭素が発生
する協奏的開裂（43）。2）結合開裂して発生したベンゾイルオキシラジカルがさらに光を吸収してフェニルラジカルと二酸化炭素を発生する段階的開裂（44）。

\[
\text{PhCOOCCPh} \xrightarrow{\text{hv}} \text{PhCO}_2^\cdot + \text{Ph}^\cdot + \text{CO}_2 \quad (3)
\]

\[
\text{PhCOOCCPh} \xrightarrow{\text{hv}} \text{PhCO}_2^\cdot + \text{PhCO}_2^\cdot \quad \text{hv}' \quad (4)
\]

いずれの機構で分解が進行しているかを調べるために以下の実験を行った。

まず段階的開裂の寄与を調べるためにハロゲンランプを照射しながらのBPOの熱分解および光分解および単位時間当りの光量を変化させたBPOの光分解を行ったが、生成物の収量に大きな変化は見られなかった。他方、協奏的開裂の寄与を調べるために励起エネルギーの異なる種々の増感剤を用いてBPOの光増感分解を行ったところ、増感剤のエネルギーが高いほど安息香酸フェニルの収量が多く
なる傾向を見い出した。
以上の実験結果から、BPOの光分解は二重結合開裂で進行し、さらにその開裂様式は協奏的であることが明らかになった。

次に、過酸化ベンゾイルの芳香族多環化水素による光感応過程における励起錯体形成の化学的根拠。

過酸化ベンゾイルを一重項感剤であるナフタレン存在下、ベンゼン懸媒中、光照射し得られたフェニルナフタレン類およびフェニルナフタレン類の収量を熱分解の場合と比較検討して、BPOのナフタレンによる光感応過程において励起錯体が形成することを明らかにした。すなわち、熱分解では1-フェニルナフタレンと2-フェニルナフタレンの収量はほぼ等しく、また無酸化酸1-ナフチルと無酸化酸2-ナフチルの収量もほぼ等しいが、一方光分解においては、いずれの場合も2-置換体の方が2-置換体よりも多く得られる。この結果は
感度過程において、一重項増感剤であるナフタレンが過酸化ベンゾイルに対して特定の配向をとり、そのためにBPOが分解して発生するラジカルが増感剤であるナフタレンと特定の配向を持って反応することを示すと考えられる。

オニ章。過酸化ベンゾイルおよびフマル酸ジメチルによる芳香族多環炭化水素のケイ光消光における増感剤の構造因子と反応性との相関。過酸化ベンゾイルは芳香族多環炭化水素などの一重項増感剤により増感分解する。その機構は一重項に励起した増感剤がBPO分子(A)と非発光性の励起錯体を形成し、その励起錯体から速離基を発生すると考えられる。

\[
D + h\nu \rightarrow \overset{1}{D^*} \\
\overset{1}{D^*} + A \rightarrow (\overset{1}{D^*}, A) \\
(\overset{1}{D^*}, A) \rightarrow D + A
\]
(1d*-A) \[ \rightarrow \text{Radical} \]

本章においては、BPOの光一重項増感分解における増感剤の構造因子と増感作用の反応性との相関を調べることにより、その増感過程において形成する励起鍵体が電子移動型の鍵体であることを明らかにした。

まず増感作用の反応性として、種々の芳香族多環炭化水素およびナフタレン誘導体のケイ光をBPOによって消光し、その消光速度定数（k_t）をシングルフォトンカウンティング法により求めた。またこれらの炭化水素との間で励起電荷移動鍵体の発光が観測されるフマル酸ジメチルによる消光速度定数も求めた。

一方、増感剤の構造因子としては、励起一重項エネルギー（Es）およびイオン化ポテンシャルと励起一重項エネルギーの差（Ip-Es）を用いた。

求めたk_t値と構造因子との相関を調べたところ、log k_t値はEsよりもIp-Esとよい相関があることがBPOとフマル酸ジメチルの両方
の場合とも認められた。この結果から、BPOの芳香族多環炭化水素による光—電気増感分解では、その増感過程において電子移動型の励起錯体を形成することが明らかになった。

第四章。芳香族炭化水素と過酸化物などとの気の光電気化学。

励起電荷移動錯体を形成する気において、電子供与体と電子受容体を別々の反応槽に入れ、励起体をもつ気体だけ光を照射することにより、励起体側と基底状態側との間に電流が流れることを見出した。

すなわち、2つの反応槽をグラスフレットで連結し、光照射側の反応槽に芳香族炭化水素と、またもう一方の反応槽に消光剤であるBPO、フェン酸ジメチル、トリエチルアミンなどを入れて、光を照射した。電極としては白金および半導体電極である酸化スズを用いた。これらの系においてはいずれの場合にも数mA/cm²の光電流が観測された。
観察された光電流は光強度依存性および光剤の濃度依存性があるので、光照射下の芳香族多環性化水素の側と基底状態の電子受容体あるいは電子供与体の分子の側との間で電流が発生したことが明らかとなった。