The Zinc Tetraphenylporphin-sensitized Photoredox Reaction between N-Phenylglycine and p-Benzoquinone in Polar Solvents

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The photoredox reaction between N-phenylglycine (NPG) and p-benzoquinone (BQ) sensitized by zinc tetraphenylporphin (ZnTPP) has been studied in various solvents under nitrogen at 25 °C. Decarboxylation of NPG and reduction of BQ occurred equimolecularly to give N-methylideneaniline (NMA), carbon dioxide, and hydroquinone (BQH_2) when an acetonitrile solution of NPG and BQ was irradiated at $\lambda_{ex.} > 500$ nm in the presence of a catalytic amount of ZnTPP. ZnTPP was recovered almost quantitatively after the photoreaction. The conversion of NPG increased linearly with increasing the molar ratio of ZnTPP to NPG up to *ca.* 2×10^{-3}. The quantum yield for the ZnTPP-sensitized decarboxylation of NPG (Φ_{CO_2}) in nitrogen-purged acetonitrile solution was evaluated as 0.20. The sensitizing activity of ZnTPP was remarkably enhanced upon increasing the solvent polarity.

The enhanced electron-transfer reaction of zinc tetraphenylporphin (ZnTPP) in the electronically excited states with p-benzoquinone (BQ) in polar solvents has been well characterized.[1-6] Recently, considerable attention has been given to irreversible product formation arising from photoinduced electron transfer from ZnTPP to quinones.[7]

In this paper we report the finding that the decarboxylation of N-phenylglycine (NPG) and reduction of BQ occur by photosensitization of ZnTPP in acetonitrile solution under nitrogen at 25 °C. The purpose of the present study is to demonstrate the overall stoicheiometry of the photoreaction, the photosensitizing activity of ZnTPP, and the solvent effect on the quantum yield for the ZnTPP-sensitized decarboxylation of NPG.

Experimental

Materials.—Following the procedure reported by Adler *et al.*,[8] zinc tetraphenylporphin (ZnTPP) was prepared by the reaction of *meso*-tetraphenylporphin (Aldrich) with a four-fold molar excess of zinc chloride in boiling dimethylformamide and purified by column chromatography on alumina with benzene. The purity of the ZnTPP was checked by the simultaneous use of the electronic absorption spectrum and h.p.l.c. N-Phenylglycine (NPG) was purified by recrystallization from water and p-benzoquinone (BQ) by vacuum sublimation immediately before use. The methyl ester of NPG was prepared by a conventional method. A solution of NPG (5.2 g, 34 mmol) in methanol (30 ml) was refluxed for 1 h in the presence of a catalytic amount of H_2SO_4. The reaction mixture was dissolved in water (50 ml) and extracted three times with ether (25 ml). The extract was washed three times with 5 wt % aqueous $NaHCO_3$ solution (50 ml) and then evaporated to give methyl anilinoacetate (MNPG) as a solid (85%), m.p. 44.5—45.5 °C; $\nu_{max.}$ (KBr) 3 400 (N–H stretch), 1 740 (ester C=O stretch), 1 610, and 1 230 cm^{-1} (ester C–O stretch); δ (CD$_3$OD) 3.67 (3 H, s, CH$_3$O), 3.83 (2 H, s, CH$_2$), and 6.47—7.29 (5 H, m, ArH).

Acetonitrile was refluxed over phosphorus pentaoxide and then fractionally distilled before use. Benzene, ethyl acetate, dichloromethane, butan-1-ol, and ethanol were of spectroscopic grades and used without further purification. Hexan-1-ol was used as received. Potassium ferrioxalate for chemical actinometry was prepared with potassium oxalate and iron(III) chloride, recrystallized from water under a red photographic safelight, dried, and then stored in the dark.[9] 1,10-Phenanthroline was used as received.

Spectra and Analyses.—Electronic absorption spectra and i.r. spectra were recorded on Shimadzu UV-200S and JASCO A-302 spectrophotometers, respectively. [1]H N.m.r. spectra were measured by a JEOL PMX-60 spectrometer with tetramethylsilane as an internal standard. G.c. and h.p.l.c. analyses were performed with a Shimadzu GC-6A gas chromatograph (column Polapack Q, 3 m × 3 mm) and a TOYO SODA HLC-802UR high performance liquid chromatograph (gel permeation-type column: TSK-GEL GMH$_6$ and G2000H$_6$, 0.6 m × 2.5 mm × 2, eluted with tetrahydrofuran), respectively.

Photoirradiation.—Typically, a solution containing 21μM-ZnTPP, 5mM-NPG, and 10mM-BQ in various solvents (8 ml) was prepared in a Pyrex glass tube (16 mm ϕ), purged with dry nitrogen for 30 min, and then sealed off before irradiation. Irradiation was performed with an Ushio UXL-500D xenon lamp (500 W) equipped with a Toshiba VO-52 cutoff glass filter ($\lambda_{ex.} > 500$ nm). Throughout the irradiation the sample solution was thermostatted at 25 ± 1 °C by a water stream through a glass jacket. The calibrated emission spectrum of the light source was obtained over the 380—700 nm wavelength range with a JASCO CT-25N monochromator and a vacuum thermopile. The absolute light intensity was determined as 1.93×10^{-8} einstein ml^{-1} min^{-1} at 405 nm with a ferrioxalate actinometer ($\Phi_{Fe(II)}$ 1.14 at 405 nm).[9] The light intensities at wavelengths >500 nm used in the present study were estimated from the emission spectrum by reference to the absolute value at 405 nm because the ferrioxalate actinometer is less photosensitive in this wavelength region.[9]

At appropriate time intervals during the irradiation, portions (0.1 ml) were withdrawn from the gas phase (14.3 ml) of the sealed sample to be subjected to g.c. analysis for carbon dioxide. The nonvolatile products in solution after irradiation were confirmed by i.r. spectroscopy. The photoreactions of NPG (0.30M) and BQ (0.25M) sensitized by ZnTPP (*ca.* 0.70mM) in deaerated [²H₃]acetonitrile (1 ml) were also followed as a function of irradiation time by [1]H n.m.r. measurements. The quantum yield for the ZnTPP-sensitized decarboxylation of NPG (Φ_{CO_2}) was obtained as the ratio of the number of NPG molecules decarboxylated to that of quanta absorbed by ZnTPP during the irradiation. The apparent Φ_{CO_2} value in nitrogen-purged acetonitrile solution was found to be constant up to a conversion of *ca.* 50% of NPG (see Figure 6).

Results and Discussion

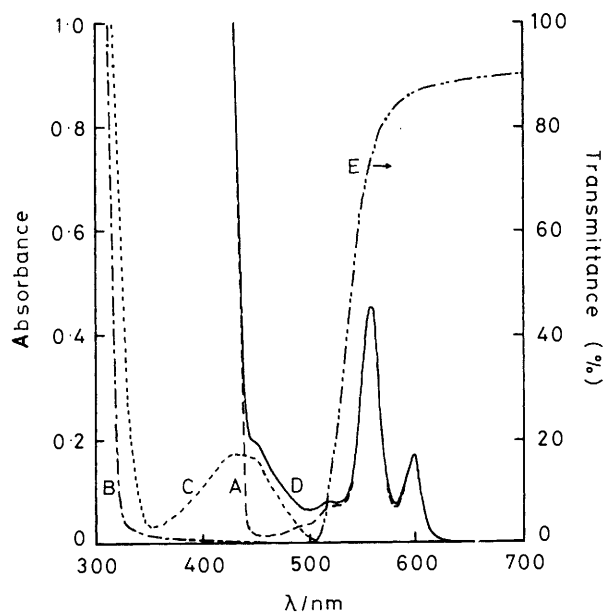*Decarboxylation of NPG by the Photosensitization of ZnTPP in the Presence of BQ.*—Figure 1 illustrates the

Figure 1. Electronic absorption spectra of A, 21μM-ZnTPP, B, 5mM-NPG, C, 10 mM-BQ, and D, their mixture in acetonitrile, and transmission of E, a Toshiba VO-52 cutoff glass filter
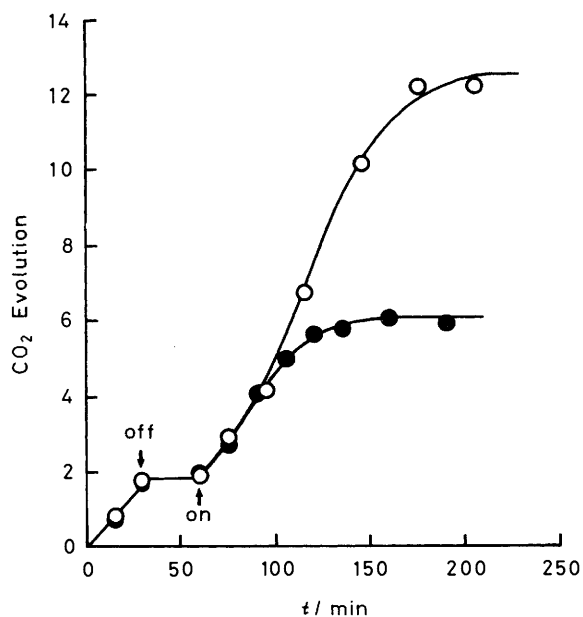

Figure 2. CO_2 Evolution as a function of time on irradiation of nitrogen-purged acetonitrile solutions containing 21μM-ZnTPP and 10mM-BQ at $\lambda_{ex.}$ > 500 nm and 25 °C: ●, 5mM-NPG in run 1; ○, 10mM-NPG in run 2

electronic absorption spectra of 21μM-ZnTPP, 5mM-NPG, 10mM-BQ, and their mixture in acetonitrile. These spectra indicate no specific interactions among the components of the ZnTPP–NPG–BQ system in their ground states. It is also seen from Figure 1 that ZnTPP exhibits the characteristic absorption maxima at 517, 556, and 595 nm, while neither NPG nor BQ absorbs light with wavelength longer than ca. 500 nm. Thus, only ZnTPP can be excited effectively under conditions of the irradiation at $\lambda_{ex.}$ > 500 nm.

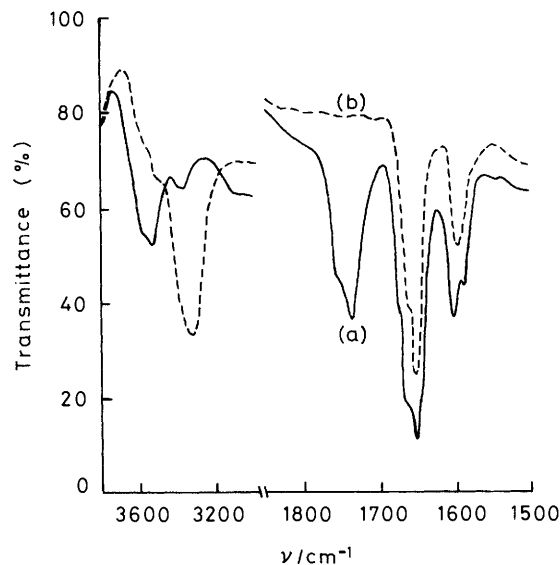Photoirradiation ($\lambda_{ex.}$ > 500 nm) of the ZnTPP–NPG–BQ

Figure 3. I.r. spectra of an acetonitrile solution of 21μM-ZnTPP, 5mM-NPG, and 10mM-BQ measured (a), before and (b), after irradiation up to the CO_2 yield of ca. 15% (see run 1 in Figure 2)

system in nitrogen-purged acetonitrile solution resulted in the evolution of carbon dioxide due to the decarboxylation of NPG, whereas no reaction occurred in the dark. As shown in Figure 2, the CO_2 evolution ceased completely in the absence of irradiation but proceeded again with the resumption of irradiation. The prolonged irradiation led ultimately to a maximum amount of evolved CO_2 depending on the initial concentration of NPG, e.g. 6.0 μmol (15.0% based on NPG) for [NPG] 5mM (run 1 in Figure 2) and 12.2 μmol (15.3%) for [NPG] 10mM (run 2). The maximum CO_2 yield of ca. 15% detected in the gas phase was found to correspond to the quantitative decarboxylation of NPG (see Figure 3).*

The CO_2 evolution was not observed on irradiation of the NPG–BQ system in nitrogen-purged acetonitrile solution at $\lambda_{ex.}$ > 500 nm, because neither component is photoexcited under these conditions as indicated by the electronic spectra (Figure 1). It is more remarkable that irradiation of the acetonitrile solution without BQ could not induce decarboxylation of NPG even in the presence of ZnTPP.

These results indicate that the photoexcited ZnTPP is responsible for the decarboxylation of NPG only in the presence of BQ. It should also be noted that the ZnTPP is virtually invariant throughout the photoinduced decarboxylation of NPG as described below.

Stoicheiometry of the ZnTPP-sensitized Photoreaction between NPG and BQ.—Figure 3 shows i.r. spectra of the reaction mixture in acetonitrile measured before and after irradiation at $\lambda_{ex.}$ > 500 nm up to the maximum CO_2 yield in run 1 (see Figure 2). The absorption bands centred at 3 528 and 1 738 cm^{-1} assigned to OH and carbonyl groups of the acid NPG disappeared completely after the irradiation. The carbonyl band of BQ at 1 658 cm^{-1} also decreased by the irradiation and a new band assigned to OH stretching of hydroquinone (BQH$_2$) appeared at 3 325 cm^{-1}. Furthermore, the formation of N-methylideneaniline (NMA) as a fragment of NPG was suggested by the characteristic i.r. bands [11] at 2 800, 1 600, 1 495, and 695 cm^{-1} which were observed for the
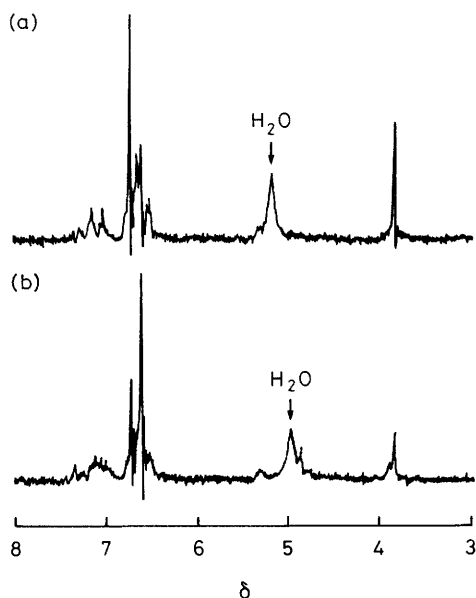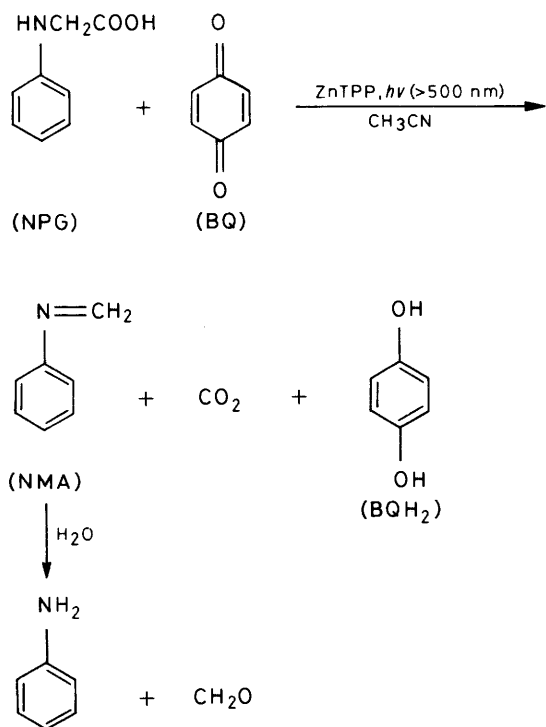
Figure 4. 60 MHz ^{1}H N.m.r. spectra of a deaerated [^{2}H$_3$]acetonitrile solution of ca. 0.7mM-ZnTPP, 0.30M-NPG, and 0.25M-BQ measured (a), before and (b), after 190 min irradiation at $\lambda_{ex.}$ > 500 nm and 25 °C
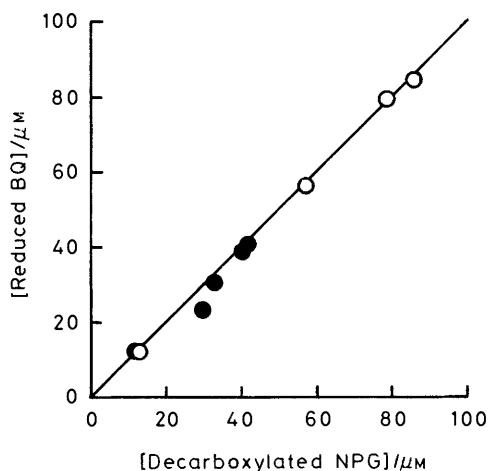

Scheme.

Figure 5. Relationship between the amount of reduced BQ and that of decarboxylated NPG in the ZnTPP-sensitized photoreaction under deaerated conditions: ●, i.r. data in acetonitrile (see Figure 3); ○, ^{1}H n.m.r. data in [^{2}H$_3$]acetonitrile (see Figure 4)

reaction mixture dissolved in tetrachloromethane after the irradiation in acetonitrile and evaporation of the solvent.

Similar results were obtained by ^{1}H n.m.r. measurements. Both NPG, δ 3.83 (s, CH$_2$), and BQ, δ 6.73 (s, ArH), decreased whereas BQH$_2$, δ 6.55 (s, ArH), corresponding to a reduction product of BQ increased with the progress of the photo-reaction in deaerated [^{2}H$_3$]acetonitrile solution containing a catalytic amount of ZnTPP (Figure 4). Another new signal

appeared at δ 4.83 (s) in agreement with the =CH$_2$ group of NMA.

When the irradiated [^{2}H$_3$]acetonitrile solution was permitted to stand overnight in the dark, the =CH$_2$ signal of NMA disappeared completely to give an alternative broad signal centred at δ 4.08. It appears likely that NMA as the Schiff's base undergoes hydrolysis with the formation of aniline,[12] δ (CD$_3$CN) 4.01br (NH$_2$), as shown in the Scheme.* The ^{1}H n.m.r. measurements also indicated that a signal assigned to water is progressively shifted upfield with irradiation time (Figure 4). This behaviour is consistent with the decarb-oxylation of NPG resulting in successive destruction of the hydrogen bond between the acid and water.

Figure 5 shows that the amount of reduced BQ is equal to that of decarboxylated NPG. Similarly, the decrement of BQ was approximately equal to the yield of BQH$_2$. These stoich-eiometric relationships demonstrate that the decarboxylation of NPG to NMA with CO$_2$ evolution and the reduction of BQ into BQH$_2$ proceed equimolecularly by photosensitiz-ation of ZnTPP at $\lambda_{ex.}$ > 500 nm (Scheme). Since methyl anilinoacetate (MNPG) as the methyl ester of NPG was not decarboxylated under the same conditions, the labile proton of NPG should play an important role in the ZnTPP-sensi-tized photoreaction between NPG and BQ.

Photosensitizing Activity of ZnTPP.—As shown in the Table, the conversion of NPG reached 80% after 30 min irradiation ($\lambda_{ex.}$ > 500 nm) of ZnTPP being 238-fold less than NPG in nitrogen-purged acetonitrile solution containing BQ. On the other hand, the 2 h irradiation under the same conditions led to complete decarboxylation of NPG with the substantially quantitative (94.5%) recovery of ZnTPP. These results indicate that the catalytic amount of ZnTPP photosensitizes the decarboxylation of NPG in the presence of BQ without undergoing permanent structural change throughout the irradiation.

The Table also shows that the NPG conversion increases

* While the formation of formaldehyde could not be confirmed by ^{1}H n.m.r., it was suggested by the appearance of a probable car-bonyl band at 1 800 cm^{-1} in the i.r. spectrum of the ZnTPP–NPG–BQ system on standing overnight after the irradiation in nitrogen-purged acetonitrile at $\lambda_{ex.}$ > 500 nm.

Table. Photosensitizing activity of ZnTPP for the decarboxylation of 5mM-NPG in the presence of 10mM-BQ at 25 °C [a]

10^8[ZnTPP]/M	$10^4 I_{abs.}$ [b]/ einstein	Conversion of NPG (%)	10^5 Decarboxylated [NPG]/10^{-5}M	Turnover number [c]
0	0	0	0	
1.69	0.33	24.8	0.99	589
4.24	0.76	47.2	1.88	450
8.00	1.31	65.0	2.60	325
8.40	1.36	67.2	2.69	320
16.8	2.20	80.0	3.20	190
25.9	2.76	82.2	3.29	127

[a] On irradiation of nitrogen-purged acetonitrile solutions (8 ml) for 30 min at $\lambda_{ex.} > 500$ nm. [b] Total number of quanta absorbed by ZnTPP. [c] Defined as the ratio of the total number of NPG decarboxylated during the irradiation to the initial amount of ZnTPP on the basis of the substantially quantitative recovery of the sensitizer.
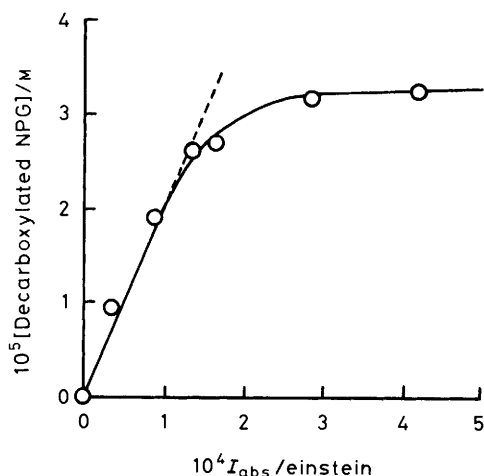

Figure 6. Variation in amount of decarboxylated NPG as a function of total number of quanta ($I_{abs.}$) absorbed during 30 min irradiation of 21μM-ZnTPP in nitrogen-purged acetonitrile solution containing 5mM-NPG and 10mM-BQ at $\lambda_{ex.} > 500$ nm

Figure 7. Variation in quantum yield for the ZnTPP-sensitized decarboxylation of NPG (Φ_{CO_2}) in the presence of BQ with dielectric constant of solvent (ε) at 25 °C: A, acetonitrile; B, ethanol; C, 50% v/v acetonitrile-benzene; D, butan-1-ol; E, hexan-1-ol; F, dichloromethane; G, ethyl acetate

with the initial amount of ZnTPP. It is however important to note that the turnover number of ZnTPP in the sensitized decarboxylation of NPG increases monotonically with decreasing ZnTPP, whereas the overall rate of the conversion is reduced (Table). This behaviour is associated with the conventional light-absorption property, i.e. the total number of photoexcited ZnTPP (ZnTPP*) arising from irradiation at a given time decreases but their fraction relative to the whole ZnTPP increases with the decreased ZnTPP. Thus, a maximum turnover number should be obtained at infinitely small amount of ZnTPP, which can be estimated by extrapolation to be more than 700 under the conditions studied (see footnote to the Table).

As is seen from Figure 6, the amount of decarboxylated NPG increases in proportion to the total number of quanta absorbed by ZnTPP ($I_{abs.}$) up to a conversion of ca. 50% (20 μmol) of NPG. From the slope of this linear relationship, the quantum yield for the ZnTPP-sensitized decarboxylation (Φ_{CO_2}) in the presence of BQ was evaluated as 0.20 in nitrogen-purged acetonitrile at 25 °C.

Decarboxylation of NPG on Shorter Wavelength Irradiation without ZnTPP.—While no reaction occurred on irradiation of the NPG-BQ system in acetonitrile at $\lambda_{ex.} > 500$ nm, irradiation with wavelengths shorter than 500 nm (at $\lambda_{ex.} > 450$ nm transmitted by a Toshiba VY-48 cutoff glass filter) was found to induce decarboxylation of NPG in this system even in the absence of ZnTPP. A similar result has been
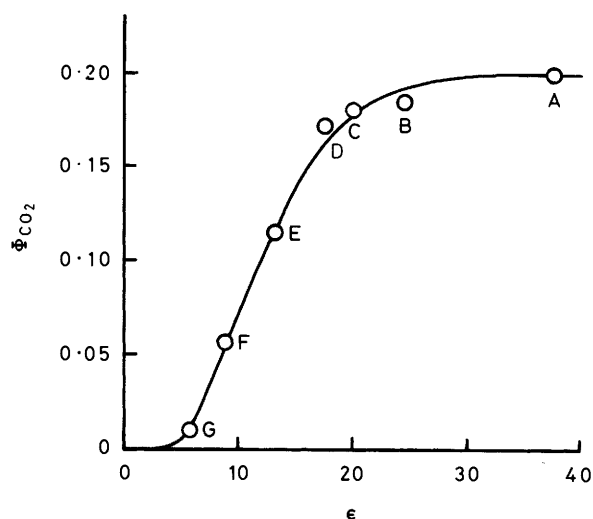
reported by Davidson et al. for the benzene solution containing N-(o-chlorophenyl)glycine and tetrachloro-p-benzoquinone.[12]

Since BQ exhibits the $n-\pi^*$ transition band in the 350—500 nm wavelength region with $\lambda_{max.}$ 440 nm as shown in Figure 1, the photoinduced decarboxylation in the NPG-BQ system at $\lambda_{ex.} > 450$ nm is considered as occurring via the reaction of NPG with BQ in the $n-\pi^*$ excited state. In spite of this behaviour by BQ, the formation of the BQ excited states via energy transfer from the sensitizer ZnTPP is ruled out in the ZnTPP-NPG-BQ system (at $\lambda_{ex.} > 500$ nm), because both energy levels of the lowest excited singlet and triplet states of BQ (E_S 272 and E_T 222 kJ mol⁻¹) lie sufficiently above those of ZnTPP (E_S 198 and E_T 154 kJ mol⁻¹).[1,13]

Solvent Effect on the ZnTPP-sensitized Decarboxylation of NPG.—Polar solvents were found to favour the ZnTPP-sensitized decarboxylation of NPG in the presence of BQ at $\lambda_{ex.} > 500$ nm. As shown in Figure 7, the Φ_{CO_2} value varies in a sigmoidal form with dielectric constant of the solvent (ε). While the ZnTPP-sensitized decarboxylation is negligibly slow in nonpolar solvents with ε < 6, an approximately linear increase in Φ_{CO_2} with increased ε is observed in the region of 6 < ε < 18. At higher dielectric constant of ε > 18, the variation in Φ_{CO_2} is asymptotic to a maximum value of 0.20

which was attained in acetonitrile (ε 37.5). An essentially identical dependence on ε has been characterized by Harriman et al. for the yield of ZnTPP cation radical (ZnTPP$^{+\cdot}$) via electron transfer from photoexcited ZnTPP (most probably the triplet state) to BQ.[1]

The apparent similarity of the solvent dependence of Φ_{CO_2} to that of ZnTPP$^{+\cdot}$ yield may lead to a sensitization mechanism in which the electron-transfer quenching of ZnTPP* by BQ to produce ion radical intermediates is involved in the initial step of decarboxylation as follows. This mechanism is con-

$$ZnTPP \xrightarrow[>500\ nm]{hv} ZnTPP^* \qquad (1)$$

$$ZnTPP^* + BQ \longrightarrow ZnTPP^{+\cdot} + BQ^{-\cdot} \qquad (2)$$
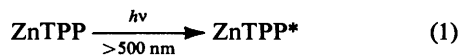
sistent with the observation that ZnTPP shows no sensitizing activity in the absence of BQ. Furthermore, from the large turnover number of ZnTPP, it appears rational to presume that the resulting ZnTPP$^{+\cdot}$ has the ability to oxidise NPG into the cation radical (NPG$^{+\cdot}$) with the efficient regeneration of ZnTPP as in equation (3). The conjugated aryl-nitrogen

$$ZnTPP^{+\cdot} + NPG \longrightarrow ZnTPP + NPG^{+\cdot} \qquad (3)$$

atom of NPG should favour such a one-electron oxidation as is the case for carboxylic acids having a common structure ArXCH$_2$CO$_2$H (X = O, S, or NH).[12,14]

It is likely that the back electron-transfer reaction between ZnTPP$^{+\cdot}$ and BQ$^{-\cdot}$ [reverse reaction of equation (2)] is depressed by either electron transfer from NPG to ZnTPP$^{+\cdot}$ [equation (3)] or proton transfer from NPG to BQ$^{-\cdot}$ with formation of the more stable semiquinone radical (BQH$^\cdot$). Similarly, the intermediate NPG$^{+\cdot}$ may be unstable and decompose spontaneously with CO$_2$ evolution, by which the back electron-transfer reaction between ZnTPP and NPG$^{+\cdot}$

[reverse reaction of equation (3)] is depressed. These properties of NPG are clearly favourable for its undergoing decarboxylation by the photosensitization of ZnTPP in the presence of BQ.

Photosensitizing activities of a series of metallotetraphenylporphins as well as reactivities of N-substituted glycines and quinone derivatives as a function of redox potential will be reported later.

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