Photosensitized Oxygenation of Olefins with Zinc Tetraphenylporphine-1,4-Diazabicyclo[2.2.2]octane Complex

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In the presence of a proper amount of amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and piperidine, zinc tetraphenylporphine (ZnTPP) works as a not only apparently more effective but also more photoresistant sensitizer for singlet-oxygen oxygenation of olefins than in the absence of the amines. This is ascribed to the facts that ZnTPP forms a 1 : 1 complex with DABCO, and that DABCO coodinated to ZnTPP has no ability to quench singlet oxygen, as revealed by detection of singlet oxygen phosphorescence and product distributions in oxygenation of *d*-limonene, 1,2-dimethylcyclohexene, and 1-phenylcyclobutene.

Photooxygenation of organic compounds with singlet oxygen is usually quenched by amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO), and the quenching property of DABCO has been widely studied.¹⁾ DABCO has a moderately high quenching rate of singlet oxygen, but is not consumed in the physical quenching. This is also the case for dye-sensitized photooxygenation,²⁾ and there is no appreciable interaction between DABCO and most sensitizers. Porphyrins and metalloporphyrins are among the most popular and important sensitizers.³⁾ These have been used not only as energy-transferring sensitizers in photooxygenation to generate singlet oxygen⁴⁾ but also as electron-transferring sensitizers in photodecomposition of water in combination with methylviologen.⁵⁾ Recently, much interest has been focused on their use for phototherapy of cancer.⁶⁾

In the course of our investigation on photosensitized oxygenation of organic compounds, we have found that addition of a proper amount of DABCO does not quench but apparently accelerates zinc tetraphenylporphine (ZnTPP)-sensitized oxygenation of olefins such as *d*-limonene, 1,2-dimethylcyclohexene, and 1-phenylcyclobutene. Here, we wish to report behavior of a DABCO–ZnTPP complex which works as a more stable triplet sensitizer than ZnTPP itself to generate singlet oxygen but not as a singlet oxygen quencher.

Experimental

UV spectra were recorded on a Shimadzu UV-220 recording spectrophotometer. NMR spectra were recorded on a JEOL GSX-270 (270 MHz) and a Nicolet NMC-1280 (360 MHz) NMR spectrometer. GLPC analysis was performed on a Hitachi 163 gas chromatograph equipped with a flame ionization detector. Fluorescence and phosphorescence spectra were measured with a Hitachi MPF4 spectrofluorimeter.

Materials. Zinc tetraphenylporphine (ZnTPP) and tetraphenylporphine (TPP) were purified by means of column chromatography on alumina eluting with chloroform. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was crystallized from a hexane–benzene mixture and other amines were purified by distillation. 1,2-Dimethylcyclohexene (DMCH)⁷⁾ and 1-phenylcycrobutene (PCB)⁸⁾ were prepared according to the references and purified by distillation. *d*-Limonene (L, 1-methyl-4-isopropenylcyclohexene) was distilled before use. Special grade or spectrograde solvents were used.

cis- and *trans*-1-Methyl-4-isopropenyl-2-cyclohexen-1-ol⁹,¹⁰⁾ and *cis*- and *trans*-2-methylene-5-isopropenylcyclohexanol⁹,¹⁰⁾ were obtained from TPP-sensitized oxygenation of L in benzene followed by treatment with triphenylphosphine.

1-Methyl-2-methylenecyclohexanol and 1,2-dimethyl-2-cyclohexen-1-ol were prepared by irradiating a benzene solution of DMCH (0.36 g) and ZnTPP (0.03 g) with light of wavelength longer than 360 nm for 55 min and by subsequent treatment of the irradiation mixture with triphenylphosphine.⁷⁾

2-Phenyl-2-cyclobuten-1-ol, 4-oxo-4-phenylbutanal, and 1-(2-hydroxyphenyl)cyclopropanecarbaldehyde were prepared by oxygenation of PCB with singlet oxygen (photooxygenation) according to the reference.⁸⁾

Sensitized Oxygenation. Benzene solutions of L (2×10^{-3} M, M=mol dm^{-3}) and ZnTPP (8×10^{-4} M) were irradiated for 3 h under air in the absence and presence of DABCO (8×10^{-4} M) with light of 427±6 nm from a JASCO CRM-FA spectro-irradiator equipped with a 2-kW xenon lamp as a light source and a grating monochromator. After treatment with triphenylphosphine, the reaction mixture was analyzed by GLPC to determine the product distributions.

Similarly, DMCH (2×10^{-3} M) and PCB (2×10^{-3} M) were irradiated with ZnTPP (8×10^{-4} M) for 3 and 60 min, respectively, in benzene in the absence and presence of DABCO (8×10^{-4} M), and the reaction mixtures were analyzed by GLPC after reduction with triphenylphosphine to determine the product distributions.

Quantum-Yeild Measurements. The exciting light for quantum-yield measurements was furnished from the JASCO CRM-FA spectro-irradiator. The light intensity was determined by potassium tris(oxalato)ferrate(III) actinometry.¹¹⁾ A benzene solution containing L (2.2—8.0×10^{-3} M), ZnTPP (8×10^{-4} M), and DABCO (0 or 8×10^{-4} M) was irradiated with 427±6-nm light for 25 min. Conversion of L was 9—11% as determined by GLPC. To the reaction mixture triphenylphosphine (2×10^{-3} M in benzene, 0.6—2.4 ml) was added and the solution was kept overnight at room temperature. The amounts of six alcohols formed were determined by GLPC analysis using phenol as an internal standard. The total yield of alcohols was 80—97% based on L consumed.

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Measurements of Singlet-Oxygen Emission. Near-infrared emission at 1.27 μm from singlet oxygen was observed by a germanium photodiode (Hamamatsu Photonics B2144) with a silicon window on irradiation of benzene solutions of ZnTPP (6×10^{-5} M) or TPP (2×10^{-4} M) with DABCO (0—2×10^{-3} M) with 555-nm laser pulses from an excimer laser (Lambda Physik LPX-100, XeCl, 308-nm, 10-ns fwhm)-pumped dye laser (Lambda Physik FL-3002, Coumarin 153 dye, 10-ns fwhm).[12] The response time of this system is less than 3 μs.

Photofatigue of the ZnTPP–DABCO Complex. Benzene solutions of ZnTPP (1×10^{-5} M) were irradiated in the absence and presence of DABCO (1×10^{-5} or 4×10^{-5} M) with light of 427±3 nm from the JASCO CRM-FA spectro-irradiator. The absorption spectrum of the solution was measured at appropriate intervals.

Results and Discussion

ZnTPP-Sensitized Oxygenation of Olefins in the Presence of DABCO. Photosensitized oxygenation of *d*-limonene (L) with ZnTPP was accelerated by addition of an equal amount of DABCO and piperidine. Thus, when a solution of L (0.01 M) and ZnTPP (8×10^{-4} M) in benzene (4 ml) was irradiated with a 500-W xenon lamp through a glass filter (Corning 0-75, $\lambda>340$ nm) for 30 min, L was consumed by 12% as determined by GLPC. In the presence of DABCO (8×10^{-4} M) under otherwise the same conditions, 24% of L reacted. When piperidine was added instead of DABCO to a similar solution of L and ZnTPP, 26% of L reacted.

In the presence of these amines the reaction products detected by GLPC showed, after treatment of the reaction mixture with triphenylphosphine, the same retention times as those of authentic samples obtained in ZnTPP-sensitized oxygenation. The product distribution in the presence of DABCO was identical with that for ZnTPP-sensitized oxygenation and that reported for Rose Bengal-sensitized oxygenation,[9,10] but was not equal to that from autoxidation of L (Table 1).[13] In those cases, singlet oxygen was suggested to be the reactive species since DABCO in a large excess amount quenched the photooxygenation.

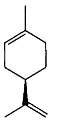
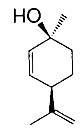
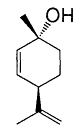
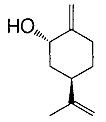
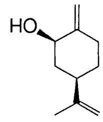
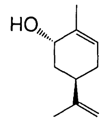
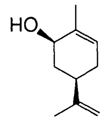
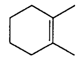
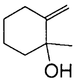
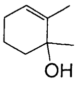
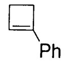
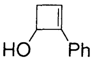
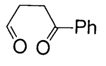
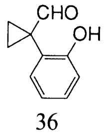
A similar acceleration effect of amines (DABCO and piperidine) was observed on photooxygenation of 1,2-dimethylcyclohexene (DMCH) with ZnTPP in benzene on irradiation with light longer than 510 nm. However, the effect was smaller than that on L oxygenation. The product distribution was not altered in the presence and absence of the amines (Table 1), and the reaction can be ascribed to singlet oxygen.

In the singlet-oxygen reaction with both L and DMCH, the "ene" reaction is predominant. As an example of other groups of reactions, 1-phenylcyclobutene (PCB) was oxygenated with ZnTPP-DABCO-sensitization. Addition of DABCO in ZnTPP-sensitized oxygenation increased the yield of 1-(2-hydroxyphenyl)cyclopropanecarbaldehyde, a 1,4-addition product of singlet oxygen (Table 1). The product distribution in oxygenation of PCB with singlet oxygen is known to be varied with sensitizers and solvents.[8,14] This finding will be discussed elsewhere.[15]

Behavior of metal-free tetraphenylporphine (TPP) as sensitizer was found to be different from that of ZnTPP. Photooxygenation of L and DMCH sensitized with TPP was not accelerated but retarded by DABCO and piperidine regardless of the used amount.

ZnTPP has been reported to form complexes with Lewis bases having N, S, O, and P atoms as a donor

Table 1. ZnTPP–DABCO Sensitized Oxygenation of Olefins[a]

Olefins	Sensitizer	Products										
												
	ZnTPP–DABCO	40	:	10	:	19.5	:	21	:	7	:	2.5
	ZnTPP	39	:	9.5	:	20	:	22	:	7	:	2.5
	Rose Bengal[b]	34	:	10	:	20	:	21	:	10	:	5
												
	ZnTPP–DABCO					90	:	10				
	ZnTPP					91	:	9				
												
	ZnTPP–DABCO			46	:	18	:	36				
	ZnTPP			54	:	42.5	:	3.5				

a) Products of sensitized oxygenation followed by treatment with triphenylphosphine. b) Ref. 10.

atom.[16,17] In the present reaction system, ZnTPP apparently forms a kind of complex with DABCO (vide infra); however, the reaction of singlet oxygen was not retarded. Consequently, the ZnTPP–DABCO complex might absorb the light and its excited triplet state might transfer its energy to oxygen to produce singlet oxygen. The nature of ZnTPP–DABCO complex, for example, coordination number, formation constant, and yield of singlet oxygen, is worthy of a further study.

The superoxide is not involved in the ZnTPP–DABCO complex sensitization in benzene though the oxidation potential (E_{ox}) of the triplet ZnTPP–DABCO complex is estimated to be −0.92 V from the triplet energy (1.57 eV; vide infra) and E_{ox} of the complex (0.65 V in acetonitrile vs. SCE). On irradiation of the ZnTPP–DABCO complex in benzene with light longer than 510 nm for 30 min, 2-cyclohexen-1-one, a well-known superoxide trap, was not consumed.[18] On irradiation of a benzene solution containing both 2-cyclohexen-1-one (8×10^{-3} M) and PCB (8×10^{-3} M) under similar conditions, 2-cyclohexen-1-one was not consumed but 95% of PCB disappeared.

Coordination Number and Formation Constant (*K*) of the ZnTPP-DABCO Complex. The spectral change of benzene solutions of ZnTPP on addition of DABCO is shown in Fig. 1; the absorption maximum of the B band is shifted from 423 to 431 nm, and that of the Q band from 548 to 562 nm. The spectral shift is similar to that in the ZnTPP-pyridine complex,[19] and shows the formation of a ZnTPP–DABCO complex that is stabilized to a similar extent to the pyridine complex. The absorption maximum of ZnTPP at 590 nm is also shifted to 600 nm on addition of DABCO and the intensity of this band increases about two times. The aforementioned increase in oxygenation efficiency of L is presumably due to the increase in photon available for sensitization.

The coordination number of DABCO to ZnTPP was determined by the continuous variation method.[20]

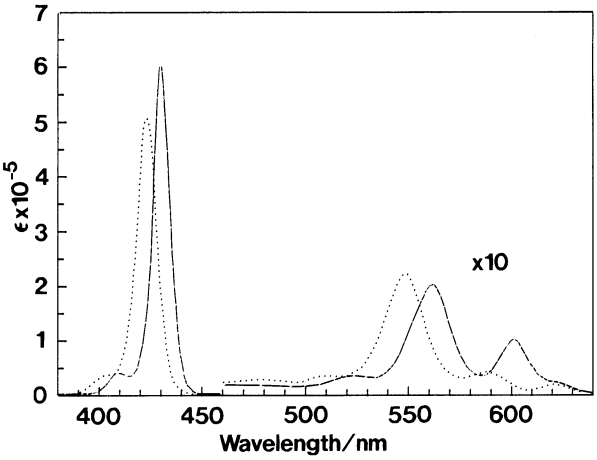


Fig. 1. UV spectra of ZnTPP and ZnTPP–DABCO complex. a) ZnTPP (1×10^{-6} M) and DABCO (4×10^{-4} M) in benzene (——); b) ZnTPP (1×10^{-6} M) in benzene (·····).

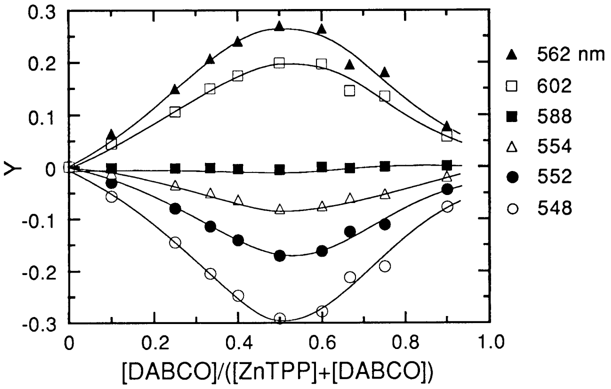


Fig. 2. Continuous variation method. Open circles: *Y* at 548 nm, closed circles: *Y* at 552 nm, open triangles: *Y* at 554 nm, closed triangles: *Y* at 562 nm, closed squares: *Y* at 588 nm, open squares: *Y* at 602 nm.

Benzene solutions of ZnTPP and DABCO in a summed concentration of 6×10^{-5} M with [DABCO]/[ZnTPP] molar ratios ranging from 0 to 9 were prepared and their absorption spectra were measured. *Y* values, as defined by Eq. 1, at six wavelengths, 548, 552, 554, 562, 588, and 602 nm, were plotted against [DABCO]/([ZnTPP]+[DABCO]) values. For 548, 552, and 554 nm the plots showed a minimum and those for 562 and 602 nm afforded a maximum at the point where the [ZnTPP]/[DABCO] ratio was unity (Fig. 2). However, at the point where the [ZnTPP]/[DABCO] ratio was 1/2 or 2/1 neither maximum nor minimum was observed.

$$Y = A_{1+2} - (A_1 + A_2) \qquad (1)$$

where A_{1+2}=(absorbance of a benzene solution containing ZnTPP and DABCO), A_1=(calculated absorbance of a benzene solution of ZnTPP in the same concentration as that of ZnTPP in the mixture), and A_2=(calculated absorbance of a benzene solution of DABCO in the same concentration as that of DABCO in the mixture). These findings indicate that in this dilute solution ZnTPP forms a 1 : 1 complex with DABCO but does not form a complex with a molar ratio of 1/2 or 2/1.

ZnTPP is known to form a 1 : 1 complex with amines,[21] and has also been found to form a similar 1 : 1 complex with DABCO in the low concentration range of 10^{-5} M, though DABCO has two nitrogen atoms capable of coordination in a molecule. Very recently, a zinc porphyrin with alkyl substituents (ZnAP) was reported to form a transient ternary complex of ZnAP–DABCO–ZnAP in porphyrin concentrations of more than 10^{-3} M in the presence of a less than one equivalent amount of DABCO.[17] Under the present photoreaction conditions of [ZnTPP]=8×10^{-4} M and [DABCO]=8×10^{-4} M, however, no evidence was obtained for formation of a ternary complex.

$$\text{ZnTPP} + \text{DABCO} \overset{K}{\rightleftarrows} \text{ZnTPP-DABCO} \qquad (2)$$

For DABCO, piperidine, and triethylamine the formation constants of the 1 : 1 complex, K, were determined in benzene by the Rose–Drago method.[22] The formation constant between ZnTPP and a donor is given by

$$K=\frac{C}{(A_0-C)(B_0-C)}, \tag{3}$$

where A_0 and B_0 are the initial concentrations of ZnTPP and the amine, respectively, and C is the equilibrium concentration of the ZnTPP complex. The total absorbance at a given wavelength where DABCO shows no absorption is given by

$$a=\varepsilon_C C+\varepsilon_A A, \tag{4}$$

where A is the concentration of free ZnTPP at the equilibrium, and ε_C and ε_A are the extinction coefficients of the complex and free ZnTPP, respectively. Combination of Eqs. 3 and 4 yields the Rose–Drago equation;

$$K^{-1}=\frac{a-a_0}{\varepsilon_C-\varepsilon_A}-A_0-B_0+A_0B_0\frac{\varepsilon_C-\varepsilon_A}{a-a_0}, \tag{5}$$

where $A=A_0-C$ and $a_0=\varepsilon_A A_0$.

UV spectra of benzene solutions of ZnTPP (2×10^{-5} M) and DABCO (5×10^{-6}—1×10^{-4} M) were measured at 25 °C. The K^{-1} values calculated according to Eq. 5 at 606 nm were plotted against assumed $\Delta\varepsilon$ ($=\varepsilon_C-\varepsilon_A$). K and $\Delta\varepsilon$ were determined graphically. Thus, the lines for the six solutions with various concentrations of DABCO intersect one another in a small region. From these points, K^{-1} was determined to be 6×10^{-6} M. In a similar manner, the formation constants of ZnTPP with piperidine and triethylamine were determined to be 1.1×10^5 and 13 M^{-1}, respectively. The determined log K values are summarized in Table 2.

The K value of ZnTPP with DABCO, 2×10^5 M^{-1}, is one of the largest values of K values of ZnTPP with amines.[21] From the obtained K value the concentration of ZnTPP–DABCO complex in the photooxygenation solution was calculated. In a solution of ZnTPP (8×10^{-4} M) and DABCO (8×10^{-4} M) 93% of ZnTPP is present as the 1 : 1 complex with DABCO.

Triplet State of ZnTPP-DABCO Complex. Phosphorescence spectra of ZnTPP (2×10^{-5} M) were measured at 77 K in methylcyclohexane in the absence and presence of DABCO (2×10^{-4} M) or piperidine (4.5×10^{-4} M) by exciting at 422 nm (with no amines) or 432 nm (with amines). The maximum wavelengths of phosphorescence spectra appeared at 776, 789, and 801 nm in the absence of amines, in the presence of DABCO, and piperidine, respectively.

The triplet energy of the ZnTPP–DABCO complex is estimated to be 36.2 kcal mol^{-1} from the above spectrum. This value is slightly lower than that of ZnTPP, 36.8 kcal mol^{-1}. ZnTPP is a well-known triplet sensitizer whose energy is transferred to oxygen to form singlet oxygen. The triplet energy of ZnTPP–DABCO complex is higher than the excitation energy of oxygen (22.5 kcal mol^{-1}),[23] and well suited for transferring its energy to oxygen to form singlet oxygen.

Singlet-Oxygen Emission. In order to examine the evolution of singlet oxygen from the ZnTPP–DABCO system and to clarify the effect of DABCO as the singlet oxygen quencher in this system, singlet-oxygen emission at 1.27 μm was measured for benzene solutions of ZnTPP and TPP in the presence of varying concentrations of DABCO by irradiating with 555-nm laser pulses under air. In this experimental technique the exact yield of singlet-oxygen evolution is not measured but the lifetime of singlet oxygen is exactly measured. At this wavelength ZnTPP and the ZnTPP–DABCO complex have identical molar absorptivities, while DABCO has no absorptivity. Therefore, increase in DABCO concentration increases the concentration of the complex, but the quantity of light absorbed by the mixture remains unaltered.

In a solution of ZnTPP in a concentration of 6×10^{-5} M only the 1 : 1 complex is formed with DABCO. Judging from the formation constant, when 6×10^{-5} M of ZnTPP and 2×10^{-3} M of DABCO are dissolved in benzene, almost all ZnTPP molecules are complexed with DABCO. The intensity of singlet-oxygen emission immediately after 555-nm laser irradiation of this solution was in the same order as that from a solution of ZnTPP in the absence of DABCO. This fact shows that singlet oxygen is produced on irradiation of the ZnTPP–DABCO complex.

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \tag{6}$$

$$^1O_2+\mathrm{DABCO} \xrightarrow{k_q} {}^3O_2+\mathrm{DABCO} \tag{7}$$

$$1/\tau=k_1=k_d+k_q[\mathrm{DABCO}] \tag{8}$$

The lifetime of singlet oxygen from the TPP solution decreased continuously with increasing DABCO concentration. A plot of the reciprocal lifetime ($1/\tau=k_1$) of singlet oxygen as a function of the concentration of DABCO showed a linear correlation (Fig. 3). From the slope of this plot the quenching rate constant (k_q) of singlet oxygen by DABCO was estimated to be

Table 2. Formation Constants for ZnTPP–Amine Complexes in Benzene

Ligand	log K	pK_a of ligand[a]
DABCO	5.2	8.60, 2.90
Piperidine	5.05	11.12
4-Aminopyridine	4.65[b]	9.11
Pyridine	3.78[b]	5.17
Triethylamine	1.1	10.87

a) "Lange's Handbook of Chemistry," 13th ed, ed by J. A. Dean, McGraw-Hill, New York (1985), 5-18.
b) Ref. 19.

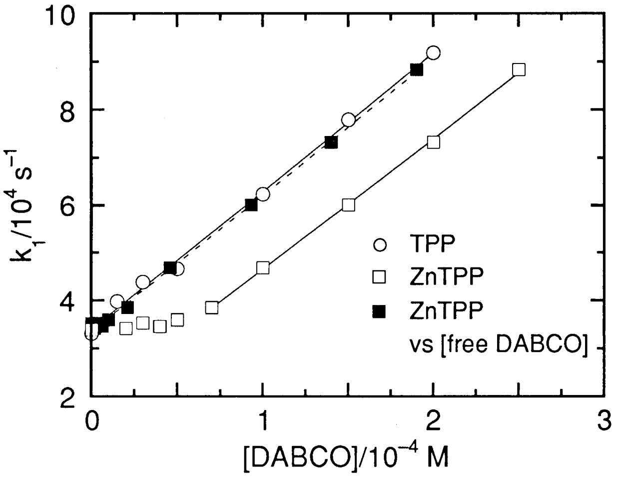


Fig. 3. Plot of the reciprocal lifetime ($1/\tau = k_1$) of singlet oxygen as a function of the concentration of DABCO on irradiation with 555-nm laser pulses in benzene. Open circles: [TPP]=2×10^{-4} M and [DABCO]=0—2×10^{-4} M. Open squares: [ZnTPP]=6×10^{-5} M and [DABCO]=0—2.5×10^{-4} M. Closed squares: [ZnTPP]=6×10^{-5} M and [DABCO]=0—2.5×10^{-4} M; the reciprocal lifetimes are plotted against the concentrations of uncoordinated DABCO.

2.9×10^8 M^{-1} s^{-1}. This is in good agreement with the reported value (4.9×10^8 M^{-1} s^{-1}).[1)]

In the case of ZnTPP, the lifetime of singlet oxygen in benzene was little affected by the presence of DABCO whose concentration was lower than that of ZnTPP (6×10^{-5} M). When the concentration of DABCO was higher than that of ZnTPP, the emission lifetime decreased with increasing DABCO concentration (Fig. 3).

When ZnTPP (6×10^{-5} M) and DABCO (5×10^{-5} M) are dissolved in benzene, the solution contains 4.2×10^{-5} M of ZnTPP-DABCO formed, 1.8×10^{-5} M of ZnTPP, and 8×10^{-6} M of DABCO. The singlet-oxygen lifetime measured for this solution was nearly equal to that of ZnTPP solution in the absence of DABCO. This observation indicates that the complexed DABCO has no ability to quench the singlet oxygen. This is confirmed by the following findings. A plot of the reciprocal lifetime of singlet oxygen against the concentration of uncomplexed DABCO gave a linear correlation, and the intrinsic decay rate (k_d) of singlet oxygen, 3.4×10^4 s^{-1}, is equal to that estimated from the plot for TPP. Under these conditions the quenching rate constant of singlet oxygen by free DABCO is estimated to be 2.9×10^8 M^{-1} s^{-1}, which is identical to that for TPP-sensitized evolution of singlet oxygen. Although DABCO is an efficient singlet-oxygen quencher, it does not quench singlet oxygen when coordinated to ZnTPP.

Quantum Yield for Singlet Oxygen Production by ZnTPP-DABCO Complex. The quantum yield (ϕ_{HP}) for hydroperoxide (HP) formation from *d*-limonene (L) was measured by irradiating benzene solutions of L (2.2—8.0×10^{-3} M), ZnTPP (8×10^{-4} M), and DABCO (0 or 8×10^{-4} M) with 427±6-nm light. In the solutions containing DABCO, 93% of ZnTPP is present as the complex with DABCO, and the light is absorbed predominantly by the ZnTPP-DABCO complex.

The reciprocal quantum yield is written by Eq.11;

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \tag{6}$$

$$^1O_2 + L \xrightarrow{k_r} HP \tag{9}$$

$$\phi_{HP} = \phi_{^1O_2} \frac{k_r[L]}{k_r[L]+k_d} \tag{10}$$

$$\frac{1}{\phi_{HP}} = \frac{1}{\phi_{^1O_2}}\left(1 + \frac{k_d}{k_r[L]}\right), \tag{11}$$

where $\phi_{^1O_2}$ is the quantum yield for singlet oxygen formation from sensitizer. ϕ_{HP} is obtained as a function of L concentration. In order to compare the quantum yield for $^1O_2$ generation from ZnTPP with that for ZnTPP-DABCO, $1/\phi_{HP}$ was plotted against 1/[L] (Fig. 4).

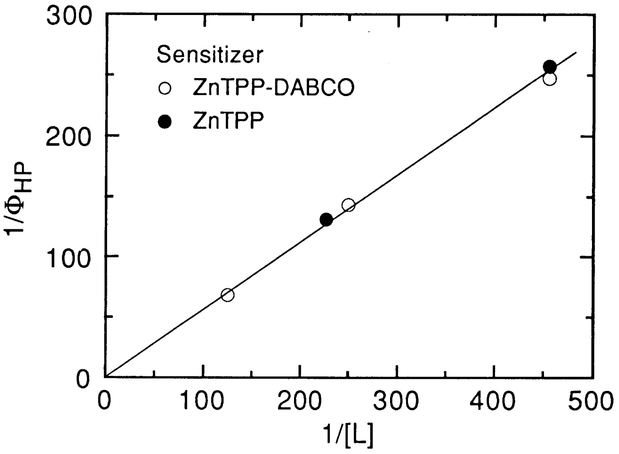


Fig. 4. Efficiency of sensitizing action of ZnTPP-DABCO complex in oxygenation of *d*-limonene.

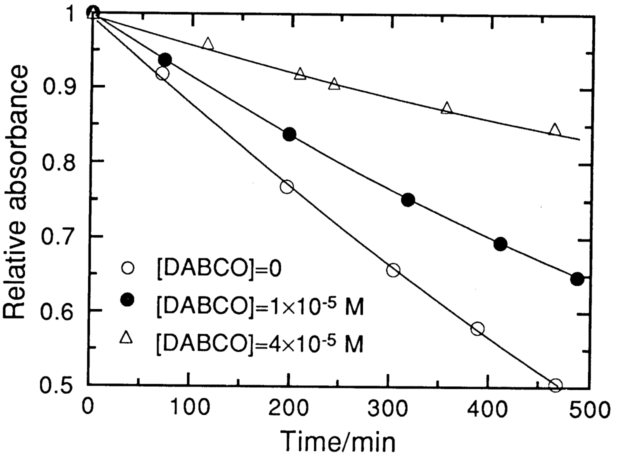


Fig. 5. Photobleaching of ZnTPP in benzene. Benzene solutions of ZnTPP (1×10^{-5} M) and DABCO were irradiated with 427±3 nm-light. Open circles: [DABCO]=0, closed circles: [DABCO]=1×10^{-5} M, triangles: [DABCO]=4×10^{-5} M.

The plot for ZnTPP–DABCO gave a straight line. This line agreed with that of ZnTPP-sensitized oxygenation of L. It may be concluded that the ZnTPP–DABCO complex is a sensitizer to produce singlet oxygen, and its efficiency of singlet oxygen production is nearly equivalent to that of ZnTPP.

Photoresistant Nature of ZnTPP in the Presence of DABCO. Addition of DABCO increased photoresistance of ZnTPP. Thus, a benzene solution of ZnTPP (1×10^{-5} M) with DABCO (1×10^{-5} or 4×10^{-5} M) or without DABCO was irradiated with 427±3-nm light. In the absence of DABCO 40% of ZnTPP was consumed during 400-min irradiation. In the presence of DABCO, only 10—30% of ZnTPP disappeared for the same period (Fig. 5).

Quantum yields for consumption of ZnTPP or ZnTPP–DABCO were measured to be 2×10^{-5}, 1×10^{-5}, and 6×10^{-6} for DABCO concentration of 0, 1×10^{-5}, and 4×10^{-5} M, respectively. When 1×10^{-5} M of DABCO is added to a solution of 1×10^{-5} M of ZnTPP, 5.9×10^{-6} M of free DABCO is present in the solution. This concentration of free DABCO decreased the lifetime of singlet oxygen very slightly from 3.0×10^{-5} s to 2.8×10^{-5} s in benzene. It may be a reason for the long lifetime of the ZnTPP–DABCO complex that the complex is less sensitive to singlet-oxygen attack compared to ZnTPP.

Conclusion

Zinc tetraphenylporphine (ZnTPP) forms a 1:1 complex with 1,4-diazabicyclo[2.2.2]octane (DABCO) with a large formation constant of 2×10^5 M^{-1}. Singlet-oxygen evolution properties of the ZnTPP–DABCO complex on irradiation under oxygen was clarified by means of $^1O_2$ phosphorescence measurements and product distributions in the complex-sensitized oxygenation of some olefins. The quantum yield for $^1O_2$ evolution from the complex is as high as that from ZnTPP itself, and DABCO coordinated to ZnTPP has no ability to quench $^1O_2$. ZnTPP is more photoresistant in the presence of DABCO than in its absence. The complexation effects of DABCO may be observed for other metal complexes.

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