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Photochemical Reaction in Chlorinated Solvents in the Presence of Halogenated *p*-Benzoquinones. I

Photochemically Induced Acidification of Solution and Protonation on Octaethylporphyrin in Dichloromethane or Chloroform

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Irradiation of *visible* light on a dichloromethane or chloroform solution in the presence of halogenated *p*-benzoquinones, such as fluoranil, chloranil, and bromanil, caused the formation of an acid, HCl. In the presence of octaethylporphyrin in those solutions, the photoinduced protonations of porphyrins were observed. Stepwise spectral changes suggested the formations of monocationic and dicationic species and an "intermediate" which had a spectrum with maximum wavelength at 717 nm. The unstable intermediate was suggested to be octaethylphlorin. But the trial to isolate the intermediate gave octaethylbilindione. Dioxygen was found to exert both negative and positive effects on the acidification of solvents and on the protonation on porphyrin in the octaethylporphyrin–bromanil systems. The mechanisms of these photochemically induced reactions are discussed.

Since the configuration of the multi-chlorophyll system was revealed by Deisenhofer et al.,[1] the studies of electron and energy transfer mechanism have made significant advances. Attempts have focused on the trial of forming the systems where the charge separation between porphyrin and quinone will occur when irradiated by light, in systems where these two species were connected to or located near each other. In many cases, the quinone derivatives used were ubiquinone and its analogs, and in a few cases halogenated quinones were used.[2,3] We observed some phenomena in the systems of octaethylporphyrin (H_2OEP) and halogenated *p*-benzoquinones in dichloromethane and chloroform. These results indicated that the rather quick acidification of these solutions occurred under the irradiation of light, resulting in protonated porphyrins.[4] Here we report some phenomena which revealed the photochemical production of monocationic and dicationic porphyrins, and protonated porphyrin, phlorin, and the resulting ring opening of porphyrin at a *meso*-position of H_2OEP. Though the present reactions were much slower than the charge separation in the photosystems, these phenomena should be kept in mind when the photoreaction systems are applied.

The halogenated *p*-benzoquinones used here were fluoranil, chloranil, and bromanil. In the presence of bromanil, the reaction was faster than for the other two cases, so most of the study was done in the H_2OEP–CH_2Cl_2–bromanil system.

Chloranil and it's analog, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), are oxidizing reagents which have been used in oxidation of chlorin to porphyrin during porphyrin syntheses.[5] It is noteworthy that halogenated *p*-benzoquinones can catalyze the photoinduced reduction of the porphyrin ring.

The mechanistic details of the photoreaction in the systems of halogenated solvent in the presence of halogenated *p*-benzoquiones will be described elsewhere.

Experimental

Materials. 2,3,7,8,12,13,17,18-Octaethylporphyrin (H_2OEP) was obtained from Strem Chem. and was purified by SiO_2 column chromatography and recrystallization. 5,10,15,20-Tetraphenylporphyrin (H_2TPP) was purchased from Aldrich Chem. and was purified in the same manner. Tetrafluoro-1,4-benzoquinone (fluoranil: Aldrich Chem.) and tetrachloro-1,4-benzoquinone (chloranil: Wako Pure Chem. Ind.) were purified by repeated sublimation. Tetrabromo-1,4-benzoquinone (bromanil: Merck-Schuchardt) was purified by repeated sublimation after the recrystallization from dichloromethane. Freshly opened spectro-grade dichloromethane (Dojindo Lab.) was used for recording the spectral change. TLC plates of silica gel and polyethyleneimine (PEI)–cellulose were obtained from Wako Pure Chem. Other chemicals were of reagent grade. Nitrogen gas was deoxygenated by passing through Oxisorb (Messer Griesheim). Argon gas with a purity of 99.99% was supplied commercially.

Apparatus. We used a Hitachi 220A spectrophotometer with a water circulator attached. The spectrometer was connected to the computer to record spectra and to calculate the spectral data.

The sources of the irradiation light were tungsten and halogen lamps of 100 W and 200 W/100 V. The illuminances of the light were about 7300 and 10000 lx, respectively, measured at the distance of the cuvettes. The light from tungsten lamps was checked to have negligible intensity beyond 350 nm.

Reactions for recording the spectral change were performed in long-necked glass cuvettes with silicone stoppers or vacuum cocks.

Laser flash photolyses were performed using XeF excimer laser at 351 nm. The apparatus for measurements of transient absorption spectra was previously reported.[6]

The effect of dioxygen was examined by the spectral change recorded using vacuum line technique in an atmosphere of mixed gas of argon and oxygen.[7] The sample solution was deaerated by several freeze-pump-thaw cycles.

Measurement of Spectral Change of H_2OEP in Di-

chloromethane. Solutions of dichloromethane containing H_2OEP (4.9×10^{-5} mol dm^{-3}) and halogenated *p*-benzoquinone (8.8×10^{-3} mol dm^{-3}) were charged in glass cuvettes. N_2 gas was bubbled through at 0°C and then *visible* light was irradiated. The spectra were recorded at determined intervals. Figure 1 shows the typical spectral change in the system of H_2OEP and bromanil: Each spectrum was obtained by subtracting the bromanil spectrum from each original spectrum. In Fig. 2 we see the spectral changes obtained from the spectra in Fig. 1 by subtracting the spectrum of the residual porphyrin from each spectrum. The reaction conditions are in the figure captions.

The effect of dioxygen and the acid (HCl) was examined under an atmosphere of Ar–O_2 mixed gas, using vacuum line techniques.

Similar experiments were done in the case of H_2TPP.

Acidification of CH_2Cl_2 or $CHCl_3$ Solution Containing Halogenated *p*-Benzoquinones. Acidification of the target solutions was observed without H_2OEP. The acidity of the resulting solution after irradiation of light was checked by adding Methyl Yellow solution. In CH_2Cl_2, Methyl Yellow turned reddish with absorption maxima at 520 and 540 nm.

The effect of dioxygen on the acidification was examined under Ar–O_2 mixed atmospheres. The effect of the presence of H_2OEP in the solution was examined as well.

The T–T^* absorption spectra of halogenated *p*-benzoquinones in dichloromethane were observed under Ar–O_2 mixed atmosphere with different ratios of O_2 to clarify the mechanism of photoinduced acidification in these systems.

Isolation of Octaethylbilindione. H_2OEP (90 mg) and 665 mg of bromanil were dissolved in 700 ml of spectro-grade dichloromethane in a one liter three-necked flask with a reflux condenser, a nitrogen inlet needle and a stirrer. Irradiation of light was done from inside using a halogen lamp of 100 W/100 V in a glass tube which was placed in the center of the flask. Aliquots of the solution were taken to check the spectral change after suitable dilution. When the maximum formation of 717 nm species was reached, the solvent was removed to dryness. To the residue, a small amount of dichloromethane was added and then the undissolved bromanil was filtered off. The filtrate was evaporated to dryness and developed on TLC of silica gel, using dichloromethane and then dichloromethane/methanol (95 : 5). The blue compound was recovered by eluting with dichloromethane/methanol (80/20). The final separation was done on the PEI-cellulose plates. The isolated compound was identified to be octaethylbilindione.[8,9] This compound was fairly stable in dichloromethane for a week under the irradiation of light or under the ambient room light, but was decomposed easily in the presence of bromanil to a reddish material and then a colorless compound.

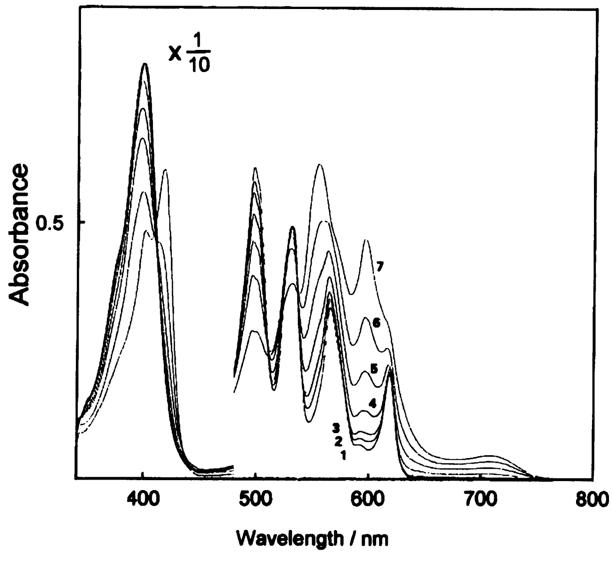

Fig. 1. The spectral change of the system of H_2OEP and bromanil in dichloromethane. Each spectrum was subtracted by that of bromanil. $[H_2OEP]=4.9\times10^{-5}$ mol dm^{-3}, $[\text{Bromanil}]=8.8\times10^{-3}$ mol dm^{-3}. Spectra were taken after **1**: 0 min, **2**: 30 min, **3**: 1 h, **4**: 2 h, **5**: 3 h, **6**: 4 h, **7**: 5 h of irradiation of visible light.

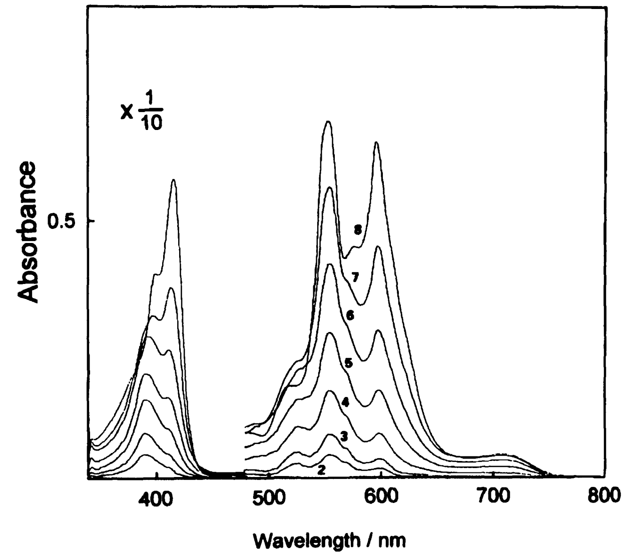

Fig. 2. The formation of protonated species in the system of H_2OEP and bromanil. The spectrum of remaining porphyrin was subtracted from each spectrum in Fig. 1. The conditions and spectrum identifications, **2**—**8** (**8**: after 6 h of irradiation) are the same as in Fig. 1.

The yield of octaethylbilindione was less than 1% based on the initial amount of H_2OEP.

Results and Discussion

Spectral Change of H_2OEP. The stepwise spectral changes in Figs. 1 and 2 show that three species were produced during the present photoreaction; namely monocationic porphyrin (H_3OEP^+), dicationic porphyrin (H_4OEP^{2+}) and an "intermediate" species with an absorption maximum at 717 nm (P_{717}).

The spectra attributable to the two acidic species, monocationic and dicationic, of H_2OEP were assigned by being compared with the reported spectra.[10,13] The latter were reproduced by adding dried hydrogen chloride into the solution without irradiation.

This spectral change in Fig. 2 reveals that in the early stage of the reaction, monocationic species appeared, and then dicationic species became dominant. It was also clear that P_{717} intermediately appeared and then finally disappeared, as shown in Fig. 3. A sharp Soret band at 400 nm suggested a small amount of a free porphyrin remaining or of a derivatized porphyrin which was not identified.

In the presence of chloranil and fluoranil, the acidification occurred similarly along with the formation of the P_{717}. The rates were in the order of bromanil> chloranil>fluoranil. The amount of the P_{717} produced was in the order of fluoranil>chloranil>bromanil.

A similar experiment showed that, in the case of H_2TPP, the spectrum of dicationic porphyrin was observed in the presence of halogenated *p*-benzoquinone (chloranil). The solution turned green; absorption maximum was 662 nm in dichloromethane, indicating the dicationic species. However no other species was observed during the irradiation (data not shown).

Acidification of the Solution and the Formation of Cationic Porphyrins. The main spectral change of H_2OEP indicates the acidification of the solution. The addition of Methyl Yellow solution into the irradiated solution actually revealed the acidity, which caused the acidic porphyrin. Moreover, in the system of $H_2OEP–CH_2Cl_2$ (or $CHCl_3$)–bromanil, chloride ions but no bromide ions were detected after the irradiation. Here chloride ions were precipitated as AgCl by the treatment with silver nitrate. The presence of bromide ions was checked by the method of oxidation using potassium permanganate in acidic media, followed by extraction into carbon tetrachloride. These results indicated that CH_2Cl_2 (or $CHCl_3$) decomposed to give HCl and possibly carbenes,[14] leading to acidity of the solutions.

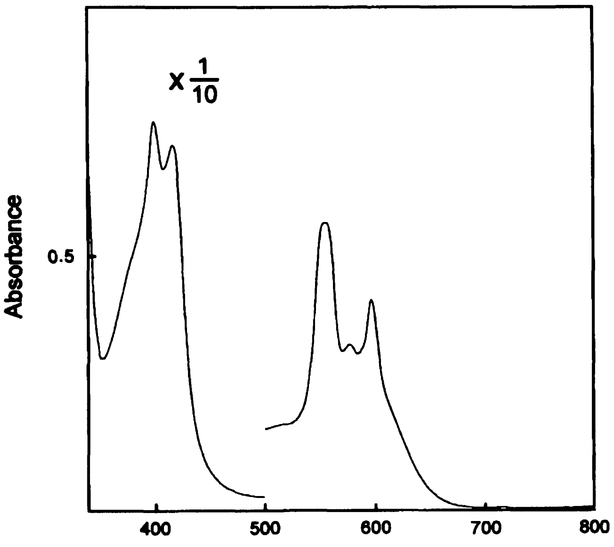

Fig. 3. The finally observed spectrum after irradiation of light for 7 h (No subtraction was made). The reaction conditions were the same as in Fig. 1. Dicationic porphyrin dominantly appeared.

Some characteristic features observed here allow us to interpret the mechanism of the acidification. The reaction occurred only under the *visible* light in the presence of an excess of halogenated *p*-benzoquinone. When the solution was kept in the dark, no spectral change occurred. Without halogenated *p*-benzoquinones, degradation of H_2OEP was dominantly observed to result in only traces of acidified porphyrin under the irradiation of light. Moreover, when *p*-benzoquinone or duroquinone instead of halogenated *p*-benzoquinone was added to the above solution, no effect was observed.

It should be stressed that halogenated *p*-benzoquinones play essential roles in the photoreactions. The acidification was dependent on the concentration of bromanil. Even in the concentration of bromanil as low as equivalent of H_2OEP, the spectral changes occurred very slowly and no degradation of H_2OEP was observed. It was clear that bromanil protected H_2OEP from degradation. The rates of the photoinduced acidification were in the order of dichloromethane>chloroform. No reaction was observed, but decomposition occurred in carbon tetrachloride: Though CCl_4 might have reacted in the presence of halogenated *p*-benzoquinones under the irradiation of light, if there was no proton, neither acidification nor protonation occurred.

The Formation of Monocationic Porphyrin in the Early Stage and the Effect of Methanol or Ethanol during the Photoreaction. As shown before, in the course of the photoreaciton, the stepwise formations of monocationic and dicationic porphyrins were observed. The monocationic state of porphyrin is not generally observed[15] because of the deformed structure of the asymmetric cationic porphyrin, while some kinds of anions will help it to be stabilized.[12,16] Therefore the observaiton of monocationic species in the early stage of the present reaction is of interest.

We attempted to produce monocationic porphyrin under some different conditions. When a small amount of methanol or ethanol was added to the dichloromethane solution the spectra of monocationic type were observed. This would stay stable for a while and then turned dicationic under further irradiation of light. It seems that methanol or ethanol held monocationic species in the stable states. The monocationic spectrum with methanol after the irradiation of light is shown in Fig. 4: In this situation, no P_{717} appeared. The appearance of monocationic species was dependent on the concentration of alcohol present. When 2.5% of methanol was added, forming of the monocationic spectrum was completed, but at 0.25% of methanol the dicationic species was dominant and the formation of P_{717} was still observed during the photoreaction. Under the same conditions with methanol (2.5%) except for the presence of bromanil and the irradiation of light, the addition of small amounts of dry HCl caused the spectrum

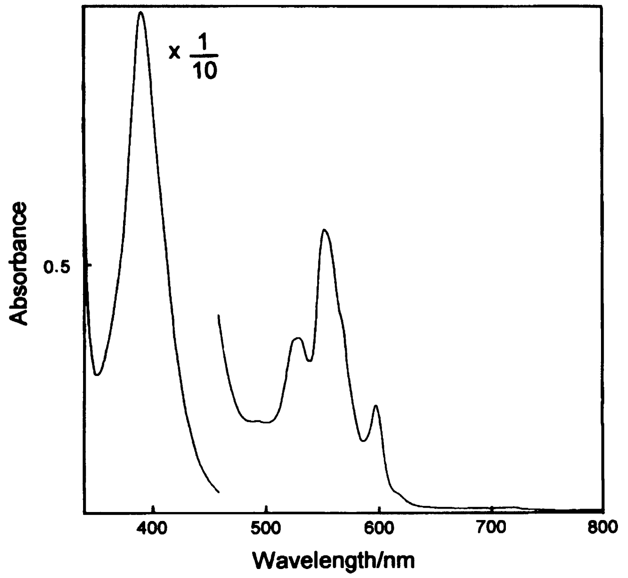

Fig. 4. The spectrum of monocationic octaethylporphyrin in the presence of methanol. $[H_2OEP]=4.9\times 10^{-5}$ $mol\,dm^{-3}$, $[Bromanil]=8.8\times10^{-3}$ $mol\,dm^{-3}$, $[Methanol]=2.5\%$.

of monocationic species. The counter ion here should be chloride ion.

It is noteworthy that when the monocationic species stably appeared, no P_{717} was observed in the presence of alcohol. Moreover, the monocationic spectrum of H_2OEP was also recorded in the presence of formic acid without irradiation,[17)] and again no P_{717} was observed under the further irradiation of light. Thus it is very likely that from the cationic species P_{717} was not formed photochemically under the present conditions. This was true for the dicationic species and for the monocationic species with alcohol or formic acid.

"Intermediate" Species, P_{717}. It was of interest that besides the acidic porphyrins, the "intermediate" species with absorption maximum at 717 nm (P_{717}) was observed during the photoreaction. This species appeared along with the formation of acidic porphyrins and disappeared just before the formation of dicationic porphyrin was completed. It was not clear whether this P_{717} became cationic porphyrin or was degradated to colorless compounds. The trial to isolate this species resulted in bilindione, as described in the experimental section.

Several possible candidates for the P_{717} at this stage should be kept in mind: The first was phlorin salt, under the acidic conditions,[18)] in which a *meso*-position was diprotonated and four pyrrole nitrogens were protonated; the second was octaethylbilindione salt, if compared with the spectra of reported phlorins or bilindiones.[8,19,20)] Others were chlorin, oxophlorin, hydroxyporphyrin or halogenated porphyrins.

The formation of chlorins,[10)] oxophlorins,[21)] or hydroxyporphyrins[22)] were excluded by comparing spectra. The possibility of halogenation on the porphyrin by halogen from halogenated *p*-benzoquinones was also excluded because the same P_{717} spectra were observed with different halogenated *p*-benzoquinones.

The expected spectrum of phlorin is considered to be very similar to that of bilindione[8b)] as reported in the protoporphyrin cases.[19,20)] The absorption band at 717 nm which was observed in the middle stage of the reaction moved to around 630 nm when the reaction solution was neutralized by adding *N*,*N*-dimethylformamide; P_{717} was recovered again by adding HCl. Such a spectral change is expected in both phlorin and bilindione.

Nevertheless there exist some circumstantial evidence that the P_{717} is octaethylphlorin. Even in the strictly deoxygenated atmosphere using argon (99.99%), the P_{717} was formed. In forming P_{717}, oxygen is not necessarily required but the presence of protons (acidic media) is essential, while no bilindione should be formed without oxygenic sources. Under a pure argon atmosphere, the only oxygenic source is bromanil. The formation rates of the P_{717} relative to those of acidic porphyrins were not affected by the amount of dioxygen as shown in Fig. 5. Even under pure O_2 atmosphere, the amount of P_{717} formed did not significantly increase and P_{717} appeared in a manner which suggests that the acidification and the formation of P_{717} occur in parallel. The species was formed under the acidic media, suggesting that protons should be used in forming the P_{717}. In the solution of carbon tetrachloride, P_{717} was not observed.

Based on such evidence, we propose that P_{717} is phlorin rather than bilindione.

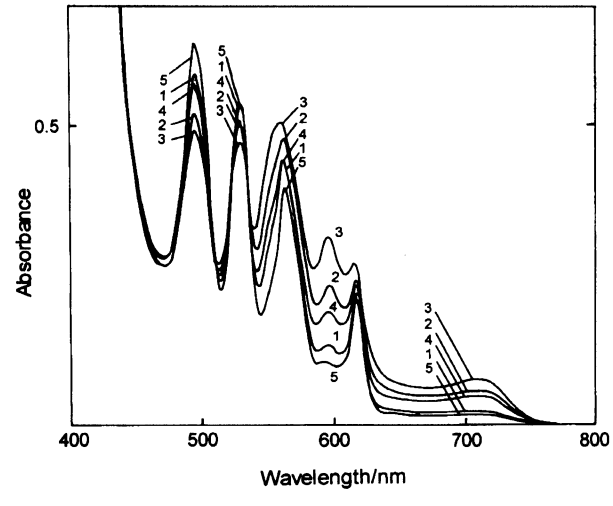

Fig. 5. The effect of dioxygen on the photochemical reaction. The spectra were taken after 4 h of irradiations of light. The reaction conditions are the same as in Fig. 1. The partial pressures of dioxygen were as follows. **1**: 0, **2**: 9, **3**: 40, **4**: 95, **5**: 610 mmHg under Ar–O_2 mixed gas (the total pressure was ca. 600 mmHg).

In the case of H_2TPP no P_{717} formation was observed. This also supports our proposal if we assume that no reaction except for acidification on porphyrin occurred because *meso*-positions were protected by phenyl groups.

The trial to isolate P_{717}, however, was unsuccessful, resulting in bilindione as described in the experimental section. It should be noted that oxygen or oxygenic species was necessary to cleave the porphyrin ring at the *meso*-position of phlorin to produce bilindione. This reaction might occur on the SiO_2 plate when TLC was performed using methanol in the air.

Effect of Porphyrin, Dioxygen, and Acid on Acidification and Formation of Phlorin. The present photoreaction was complicated with many factors: dioxygen, proton (acid), porphyrin, halogenated *p*-benzoquinones, solvents, and light. However, though these factors played their own roles in a complicated manner, the present reaction was reproduced well. Attempts to find out what was occurring lead to the conclusion that the reactions are to be divided into two categories: The first was the acidification of solvents and the second was the protonation on porphyrin, namely reduction. In both, all of the above materials and light were linked with each other. Detailed examinations of each factor revealed their functions as discussed below. The overall scheme is described in Fig. 6, along with the additional processes of the reaction.

The Role of the Triplet State of Bromanil for the Acidification of Solvents. For the acidification of halogenated solvents, bromanil and light were necessary, as mentioned above. Addition of dioxygen to the system without H_2OEP strongly affected the formation of acid. Under oxygen-free argon atmosphere, the acidification was fastest; the rate was considerably decreased if dioxygen was added. In the experiments in which the Ar–O_2 ratio was varied, the rate of the acidification of bromanil solution that was checked after 60 min of irradiation of light by mixing with Methyl Yellow decreased drastically as the content of dioxygen increased.

To clarify the mechanism for the acidification, we measured the transient absorption spectra. In a preliminary experiment of laser flash photolysis in dichloromethane, the irradiation of a laser of 351 nm on the halogenated *p*-benzoquinones resulted in the formation of the triplet states, triplet–triplet absorption spectra of which had broad maxima around 450–500 nm. While the yield of the triplet was not affected by dioxygen, the lifetime of the triplet was extremely shortened by adding dioxygen. In addition, transient absorptions were observed due to semiquinone radicals, though in bromanil case such contributions were weak. Hence, the triplet state of bromanil was suggested to be essential to attack dichloromethane and to degrade it so as to produce HCl.

Effect of H_2OEP as a Photoabsorber and O_2 as a Mediator of Energy in the Acidification Process. On the other hand, the absorption band of H_2OEP was found to shield the visible light available for exciting bromanil to the triplet state. Actually when H_2OEP solution was placed as a filter between the bromanil solution in dichloromethane and the irradiating light, the rate of the acidification was extremely slowed down. The situation is shown in Fig. 7: We can see that the intensive Soret band covered up the bromanil peak. Thus we suggested that in H_2OEP–CH_2Cl_2–bromanil system the main photoabsorber might be H_2OEP. However, if we focused on the fact that without bromanil H_2OEP caused far less acidification, resulting in the degradation of porphyrin under the irradiation of light, it was indicated that there must be some kind of interaction between H_2OEP and bromanil which mediated the energy transfer from the excited H_2OEP to bromanil. The existence of this interaction can be supported by the following results: The quenching of fluorescence of H_2OEP by bromanil and the remarkable retarding of photodegradation of H_2OEP in the presence of a small amount of bromanil.

More importantly in these circumstances we must emphasize the role of dioxygen. This was demonstrated in the spectral changes with dioxygen shown in Fig. 5. The formations of mono- and dicationic porphyrins as well as P_{717} species were very slow under pure argon atmosphere, but the acidification rapidly occurred in bromanil–CH_2Cl_2 solution without H_2OEP. Under pure dioxygen atmosphere the reaction was also very slow, but under Ar–O_2 mixed gas (ca. 1 atm) containing the appropriate content of dioxygen (5×10^3 Pa) the reaction occurred at the maximum rate. The prompt decay of the bromanil triplet induced by dioxygen as shown before could explain the reason for the very slow reaction in pure dioxygen.

Thus, though both of dioxygen and H_2OEP separately prohibited the formation of acidity of solution, the effect of both materials resulted in recovering acidification of the solution under Ar–O_2 mixed gas with a small amount of O_2. The actually observed reaction suggested that the effect of oxygen can be considered in two categories; one is the acceleration of decay of triplet state of bromanil and the other is the excitation of bromanil to the triplet state in the presence of H_2OEP. In the second category, the function of dioxygen must be a mediator in the energy transfer from the excited H_2OEP to bromanil in the manner of accelerating an intersystem crossing process from the excited singlet of porphyrin to the triplet. As a result of a balancing of the two effects, the maximum situation was observed. Further details are under investigation.

Remarks on the Mechanism of the Formation of Phlorin. As mentioned, the spectra of P_{717} species were observed only when visible light was irradiated in the acidic solution in the presence of H_2OEP and bromanil. We proposed that this P_{717} was octaethylphlorin.

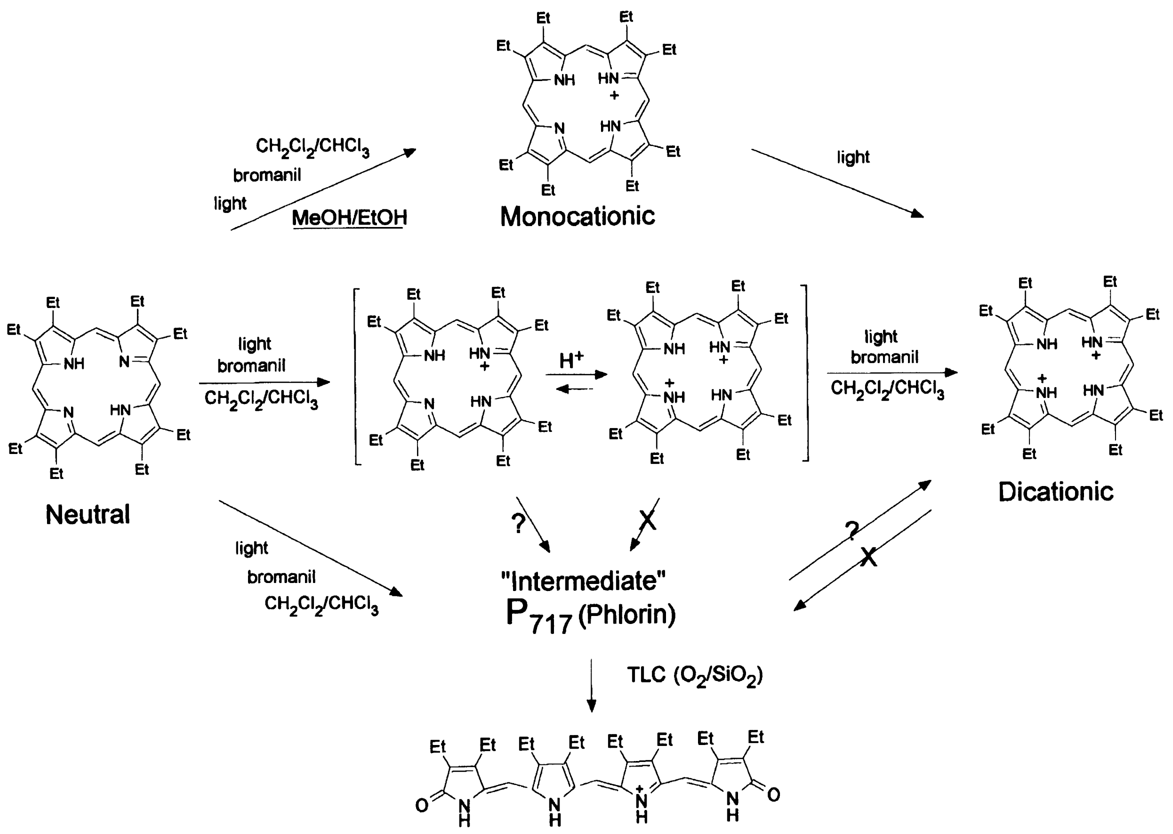

Fig. 6. Overall process of photoinduced protonation of H_2OEP in the presence of bromanil.

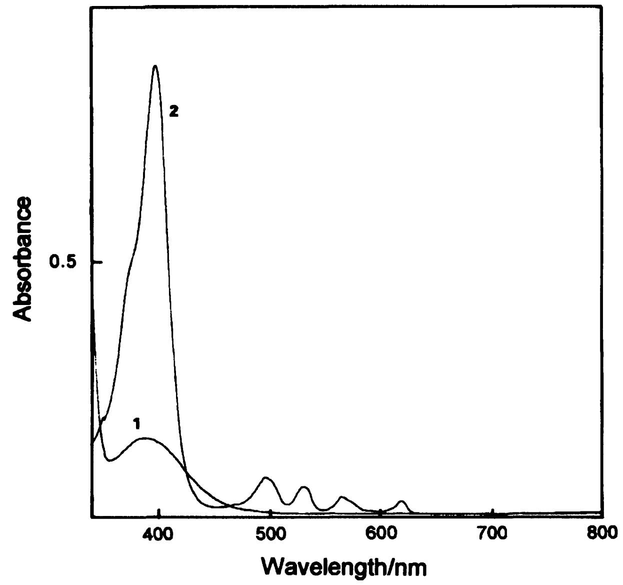

Fig. 7. Coverage of the spectra of H_2OEP and bromanil. The concentrations were those of the present reaction conditions. 1; Bromanil, 2; H_2OEP. $[H_2OEP] = 5.75\times10^{-5}$ mol dm^{-3} and [Bromanil] = 5.9×10^{-3} mol dm^{-3}.

Decades ago, Mauzerall[19)] and Woodward[20)] observed the stoichiometric photo-reduction of protoporphyrin to phlorin or phlorin salt in the presence of weak reductants such as ascorbic acid or tertiary amines in aqueous solution: The rates were fairly quick if compared to those in the present reaction. In discussions of the formation of phlorins, it was reported that the proton exchange of *meso*-proton occurred rather more easily in neutral metalloporphyrins than in free porphyrins.[23)] A phlorin derivative which was obtained from tetraphenylphloringold(III) was reported to be very air-sensitive.[24)]

It is very important that we did not use reducing reagent apparently in the present system. We used halogenated *p*-benzoquinones, halogenated solvents, and visible light. The formation of phlorin seemed to occur in parallel to the acidification, except for the final stage of the spectral change, as shown in Fig. 2. As mentioned, protons were needed to produce phlorin; actually it was shown that when the solution of bromanil was preirradiated by light for 1 h before adding H_2OEP, the formation of phlorin was accelerated in the thus formed slightly acidified solution. However, when the irradiation was started in the acidic solution (HCl) without bromanil, no formation of phlorin was detected. On the other hand, the formation of phlorin increased under stronger light, suggesting that the excited H_2OEP reacts with protons (acid) to produce phlorin with the aid of bromanil. Thus in our systems, the presence of halogenated *p*-benzoquinone was essential to obtain phlorin.

If the formation of octaethyphlorin is accurate, the electron source should be clarified. As mentioned before in protoporphyrin cases,[19,20)] photoexcited H_2OEP reacted with weak reducing reagents such as ascorbic acid or tertially amines in aqueous media. In our present case, bromanil must have the role of producing a species in halogenated solvent which is able to reduce porphyrin under the irradiation of light. The combination of bromanil and CH_2Cl_2 (or $CHCl_3$) would produce radical species such as semiquinone radicals or possibly carbene (:CHCl or $:CCl_2$). It is plausible that these radicals reduced the photoexcited porphyrin to produce phlorin in the presence of protons (acid). The lifetime of these radicals should be long enough for the reduction of porphyrin. Thus the two processes of the acidification and formation of phlorin were connected. Some examples were reported for the reductions by radicals in the cases of hematoporphyrin and its zinc complexes.[25] The details of the reduction mechanism of the porphyrin ring are under investigation.

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7) Care should be taken in handling cuvettes in vacuum line technique: Sealing by a flare might cause the decomposition of chlorinated solvents, to give acidity to the solution.

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9) In the present study ^{1}H NMR (270 MHz) signals of isolated octaethylbilindione in $CDCl_3$ showed that the compound was a mixture of two stereoisomers: Isomer **1**: (4*Z*, 9*Z*,15*Z*)-Octaethylbilin-1,19-dione: $\delta=13.08$ (2H, s, NH), 10.12 (2H, s, NH), 6.99 (1H, s, CH), 6.01 (2H, s, CH), 2.72 (4H, qua, $J=7.5$ Hz, CH_2), 2.58 (8H, qui, $J=7.5$ Hz, CH_2), 2.42 (4H, qua, $J=7.5$ Hz, CH_2), 1.28—1.11 (24H, mul, CH_3): Isomer **2**: (4*Z*,9*E*,15*Z*)-Octaethylbilin-1,19-dione: $\delta=13.07$ (2H, s, NH), 10.10 (2H, s, NH), 6.64 (1H, s, CH), 5.90 (2H, s, CH), 2.63—2.45 (12H, mul, CH_2), 2.28 (4H, qua, $J=7.5$ Hz, CH_2), 1.25—1.02 (24H, mul, CH_3). UV-vis 650 and 368 nm (in CH_2Cl_2), 712 and 368 nm (in acidic CH_2Cl_2 (HCl)). MS m/z 554 (M^+).

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14) The following decomposition reactions are considered: $CH_2Cl_2(CHCl_3) \longrightarrow HCl+\ :CHCl\ (:CCl_2)$. These reactions are predicted to occur endothermically with about 340 (CH_2Cl_2) and 250 ($CHCl_3$) kJ mol^{-1} in the gas phase, where the following heats of formation at 298.15 K in kJ mol^{-1} are available: ΔH_f° (CH_2Cl_2(g))$=-95.5$, ΔH_f° ($CHCl_3$(g)$=-103$, ΔH_f° (CHCl(g))=335, ΔH_f° (CCl_2(g))= 239, ΔH_f° (HCl(g))$=-92.3$. Cf., *J. Phys. Chem. Ref. Data*, **14**, *Suppl. 1*, *JANAF Thermochemical Tables*, 3rd ed, ACS, Washington D. C. (1985). Although the formation of carbenes has not yet been confirmed, the above energetic relation suggests that those reactions could occur in the present photoreaction systems.

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17) The formation of monocationic porphyrin in a solution containing methanol or formic acid indicates that the stability of asymmetric monoacid is dependent on the concentration of acid. Any special kinds of anions were not needed. The reducing ability of formic acid did not affect the reaction under these conditions.

18) pK_a of phlorin was expected to be about 9 in aqueous solutions; in the present case of H_2OEP phlorin, should be acidified on pyrrole nitrogen. Cf. Ref. 19.

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