Hole-Burning Study of Primary Photochemistry of Metalloporphyrins in Reactive Solvent Glasses

Indrek Renge*,† and Urs P. Wild

Physical Chemistry Laboratory, ETH-Zentrum, CH-8092 Zürich, Switzerland

Received: February 13, 1997; In Final Form: April 14, 1997⊗

Intermolecular photoprocesses in glassy solutions of magnesium octaethylporphine (MgOEP) and zinc tetrabenzoporphine (ZnTBP) have been investigated under one- and two-color irradiation between 8 and 80 K. The simultaneous exposure to the pulsed laser light in resonance with the 0−0 $S_1 \leftarrow S_0$ transition and the continuous blue light absorbed by the $T_n \leftarrow T_1$ transitions leads to a much faster hole burning than the irradiation with the laser light alone. This photon gating effect is observed in many reactive solvent glasses or the mixtures of a reactive component and the inert diluent. In solvent glasses containing electron acceptors (alkyl halogenides, *tert*-butyl peroxybenzoate, ethyl diazoacetate) the two-quantum photooxidation results in the bleaching of porphyrin absorption bands and formation of cation radical absorption at 650−700 nm (in the case of MgOEP). In the presence of electron donors (triethylamine) and alkenes the photoreaction can be observed only in the hole-burning regime because upon broad-band irradiation the intensity and position of the 0−0 band remain unchanged. The hole burning in these systems stems from sensitized photoprocesses leading to the rearrangement of pigment environment. The microscopic solvent shift of the zero-phonon transition frequency of the pigment following *cis*−*trans* isomerization of the alkene molecules or reversible electron transfer results in the formation of a dip in absorption. In this case "antiholes" are observed as a result of intensity redistribution within the 0−0 band. Depending on the height of the triplet level of the alkene, the sensitization can take place by means of triplet energy transfer from either the T_n or T_1 state (to cyclooctatetraene) of the pigment. The influence of concentration, chemical structure, reduction potential, and the height of triplet energy level of activators as well as the matrix properties on the efficiency of gated hole burning has been investigated. The reactivities of aliphatic halocarbons and amines, aromatic electron acceptors and donors, cyclic and linear olefins with and without electron-accepting substituents, and other compounds have been studied. The most efficient sensitizers have been selected and doped in the polymer films which are more convenient for the applications of spectral hole burning in optical data storage.

Introduction

The photoinduced redox reactions of porphyrin complexes with closed-shell metal ions in solid solutions have been considered initially as model systems of the primary processes in photosynthesis.[1] Extensive studies of photoionization of Mg and Zn porphyrins in frozen solvent glasses containing halocarbon acceptors have been performed by Khairutdinov et al.[2−8] and Gasyna et al.[9−11] at 77 K. The sensitized decomposition of alkyl iodides in the presence of Zn tetraphenylporphine has been found to be a two-quantum process.[12] On the contrary, it has been concluded[2,6,10] that the photooxidation of the pigment by CCl_4 and $C_2H_2Cl_4$ is a one-quantum process taking place in the first excited singlet level. In rather similar systems, the Mg and Zn *meso*-tetratolyltetrabenzoporphine solutions in poly(methyl methacrylate) films containing large amounts of halomethanes, the photon-gated hole burning (HB) has been realized with large gating ratios at liquid He temperatures.[13] It was proven that the green light absorbed during the lifetime of the T_1 state of the pigment leads to the photoionization which obviously takes place in the highly excited triplet state. In striking contrast to the conclusions of refs 2−11, the photon gating unequivocally indicates that the photooxidation of metalloporphyrins is a two-quantum process involving the triplet state, similar to classical two-quantum reactions of polycyclic arenes and aromatic amines under ultraviolet excitation.[14,15]

The paper by Carter et al.[13] triggered intensive research of gated hole-burning materials in Japan[16−27] and more recently in China.[28−33] Unfortunately, as compared to ref 13, little improvement of hole-burning characteristics has been achieved. The only exception is the azido polymer matrix showing the gating ratio more than 10^3.[21] However, the HB process remains rather inefficient in this system.

Efficient photon gating is indispensable in most of the HB applications.[34] This goal can be achieved by carefully optimizing the parameters of the HB activators as well as their concentration and the matrix properties.

With the purpose to clarify whether the modification of the pigment, the matrix, and the temperature can cause the above-mentioned dramatic changes in photochemical mechanisms, we started our studies with alkyl halogenide additives. In an attempt to correlate the HB rate with the electron affinities of acceptors, it was found that weak acceptors (cinnamaldehyde, cyclooctatetraene (COT)) can be efficient activators of both one- (COT) and two-color HB. Moreover, aliphatic amines can also induce gated HB. On the other hand, typical electron acceptors (nitrobenzene, benzoquinone) and donors (*N*,*N*-dimethylaniline) did not support HB. Fairly large sets of compounds were tested in a standard system of zinc tetrabenzoporphine (ZnTBP) in a toluene−benzene (2:1 v/v) mixture containing 1.3 M activators. Strong evidence was obtained that the HB mechanisms other than electron transfer can be operative. The preliminary results have been published in refs 35 and 36. Efficient acceptors were discovered among the polyhalogenated hydrocarbons (C_2Cl_6, DDT) and applied to achieve nondestructive readout of time

---

[†] Permanent address: Institute of Physics, Riia 142, EE2400 Tartu, Estonia.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

and space domain holograms written in the polymer films doped with these compounds.[34]

The present report deals with quantitative aspects of the mechanism and kinetics of induced HB processes in the presence of various activators. At the same time, the photoproducts and the reaction kinetics were investigated by using the broad-band irradiation and recording over a broad spectral range on a spectrophotometer. The interrelationship between the earlier broad-band studies at 77 K[1−11] and the HB data will be analyzed in detail. The inconsistencies existing in the literature will be pointed out.

Experimental Section

Magnesium octaethylporphine (MgOEP), activators, and solvents were purchased from Aldrich and used as received. Zinc tetrabenzoporphine (ZnTBP) was a generous gift from Dr. A. M. Shulga (Minsk). The solutions were prepared by adding an aliquot of ZnTBP (10^{-3} M) in pyridine to the mixture of activator and solvent. The solution was placed in a 0.5 mm cell (Hellma/Kontron) or in ∼1 mm thick glass "spades", cooled rapidly in liquid N_2 and loaded in the Oxford Instruments continuous flow cryostat CF1204 where the constant temperature (±1 K) was maintained. The concentration of solutes increases by about 30% upon cooling because of the contraction of the medium.

Holes were burned with pulsed light (pulse duration ∼10 ns, spectral width 2.5 ± 0.5 GHz, frequency 20−100 Hz) of the Lambda Physik dye laser LPD 3002E pumped with LPX 100 excimer laser. The sample was irradiated with circularly polarized light in order to avoid the photoselection effect. A 500 W incandescent lamp (Intralux 500-H, Volpi AG, Urdorf-Zürich) supplied with a light guide and a combination of filters (ZhS-12 and M575, transmission maximum 490 nm, 10% transmission cutoff limits at 450 and 580 nm) was used as a gating source. In some HB and photochemical studies the Osram mercury vapor lamp HBO 100W/2 was used. Holes were explored in transmission by scanning of the same dye laser with attenuated energy. In this case the detection was accomplished in a two-channel setup using Molectron JD2000 joulemeter ratiometer with a sensitive J3S-10 (1 kV/μJ) probe in the sample channel and a less sensitive one, J3-09 (1 V/mJ) as a reference. Laser was operated with the frequency of 40 Hz. Signals of the two channels were divided, averaged (over 10 Hz) and fed into the SUN computer. Typically, 400 data points per scanning interval were collected. The transmission signal was converted to logarithmic units and fitted with the Lorentzian function. Absorption spectra in broad wavelength intervals were recorded on a Perkin-Elmer Lambda-9 spectrophotometer.

The quantum yield of one-quantum HB process Φ_1 was calculated by dividing the number of out-burned molecules by the amount of absorbed quanta. Bearing in mind that the Q-band of metalloporphyrins consists of two transitions with similar intensities and by taking the Debye−Waller factor equal to 0.7 and the extinction coefficient of ZnTBP equal to $\epsilon = 1.3 \times 10^5$ M^{-1} cm^{-1} (pyridine, 295 K),[37] it was found that the unit hole area in the optical density scale ($D \times$ nm) corresponds to the depleaching of 9×10^{14} molecules/cm^2. The effective triplet−triplet absorption cross section in the gating wavelength interval (450−580 nm) was calculated by assuming that the average ϵ is about the half of the $T_n \leftarrow T_1$ absorption peak value at 490 nm ($\epsilon = 7.4 \times 10^4$ M^{-1} cm^{-1} [38]) and found to be equal to 1.4 Å^2. On the other hand, during the triplet-state lifetime of 40 ms,[39] only 0.035 quanta pass this area at the gating light intensity of 4 mW/cm^2. Because the triplet quantum yield is close to unity (∼0.85[39]), one can estimate the phototransformation probability, if the triplet molecule has absorbed a gating quantum (absolute yield of the two-quantum reaction, Φ_2). Under our standard conditions the triplet reaction yield Φ_2 is by a factor of 30 larger than the two-quantum burning yield with respect to the first photon. The gating ratio (G) was defined as a ratio of areas of the holes burned under identical conditions, with and without the gating light incident on the sample, respectively.

Results and Discussion

1. Mechanisms of One- and Two-Color Hole Burning in Solvent Glasses. The hole-burning behavior of ZnTBP in different frozen neat solvent glasses at 10 K is illustrated in Figure 1. Glass-forming solutions of allyl bromide and cyclooctatetraene (COT) (1 M at room temperature) in toluene−benzene (2:1 v/v) were used since these solvents crystallize upon freezing. The sample was first exposed from the opposite sides to 10 mJ cm^{-2} of selective red light (pulse frequency 40 Hz, pulse energy 4 μJ cm^{-2}) and 3 mW cm^{-2} of blue light for 60 s. The first hole at the relative position of 0.3 nm was burned at 0.5−1 nm longer wavelength from the 0−0 maximum, corresponding approximately to the maximum of inhomogeneous site distribution function.[34] Then the wavelength of the laser was shifted to the red by 0.3 nm, and the irradiation was carried out with the red light only. If no one-color hole was created, the red exposure was repeated for 120 s. Trace 1 shows these two-color and one-color holes burned consecutively. Trace 2 is scanned over the same 1 nm interval after a second two-color burn with reduced red light intensity (pulse energy 1 μJ cm^{-2}) at the relative position of 0.8 nm. A comparison of traces 1 and 2 reveals, on one hand, to what extent the saturation occurs (in a linear regime the second two-color hole should have 4 times smaller area) and, on the other hand, the extent of filling of the previously burned holes under the blue gating exposure. The influence of laser light on the existing holes was studied separately and found to be negligible at the comparable doses and spectral shifts of 0.2−0.3 nm. Both the saturation and the hole filling induced by the gating light ought to be taken into account when calculating the photochemical yields. By the term "saturation" two phenomena are meant. First, the ground-state bleaching occurs when the number of quanta per pulse is not small enough as compared to the number of molecules whose 0−0 transition is in resonance with the laser light. Second, because the photoreaction yield may depend on the degree of conversion (dispersiveness of kinetics), the growth of the hole gradually approaches the depth that can be considerably less than pure zero-phonon absorption at the burning wavelength.

Besides the aliphatic halogenides (irreversible electron acceptors), the photon gating effect is also observed for electron donors (triethylamine, TEA) and polyenes (cycloheptatriene, CHT) and, in particular, for olefins carrying electron-withdrawing substituents (citral or *(cis + trans)*-3,7-dimethyl-2,6-octadienal). The triplet reaction yields Φ_2 can be as high as 0.01 in 1.3 M allyl bromide and citral. Efficient one-color reaction is observed in the presence of 1.3 M of COT ($\Phi_1 = 7 \times 10^{-4}$). The one-color hole in the COT solution is largely erased by the blue light. The one-color holes formed in a protic matrix, ethanol, with $\Phi_1 = 2 \times 10^{-5}$ are not influenced by the gating light. The two-color holes are also weakly filled with the gating light: the ratio of hole areas shown at 0.3 nm on traces 2 and 1 are 0.95, 0.9, 0.8, 0.8, and 0.75 for 1,1,2,2-tetrachloroethane, TEA, allyl bromide, citral and CHT, respectively.

Figure 1 a,b demonstrates considerable variations in the HB behavior of ZnTBP in different environments. Obviously, a

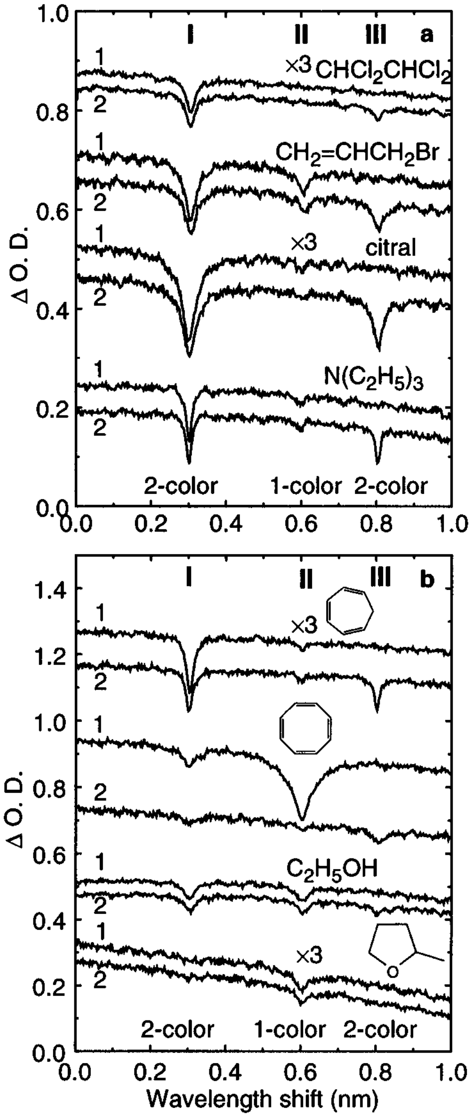


Figure 1. One- and two-color holes in the $S_1 \leftarrow S_0$ band of ZnTBP (optical density 0.7) in neat vitreous activators at 10 K. Trace 1 shows the two-color hole at the position of 0.3 nm (I) and the one-color hole at 0.6 nm (II). First, the two-color hole I was burned with simultaneous exposure to 10 mJ cm^{-2} resonant laser light (4 μJ cm^{-2} per pulse, 60 s, 40 Hz) and continuous blue light (3 mW cm^{-2}). The one-color hole II was burned for 1 or 3 min (×3) with the red-shifted (by 0.3 nm) laser light. Trace 2 shows the second two-color hole at 0.8 nm position (III) burned by 4 times attenuated selective light energy. Trace 2 serves as a check of the degree of saturation under relatively intense laser irradiation and filling of the already existing holes by gating light. COT and allyl bromide were studied as 1.3 M solutions in toluene−benzene glass (2:1). The systems with predominating electron-transfer mechanism are depicted in panel a.

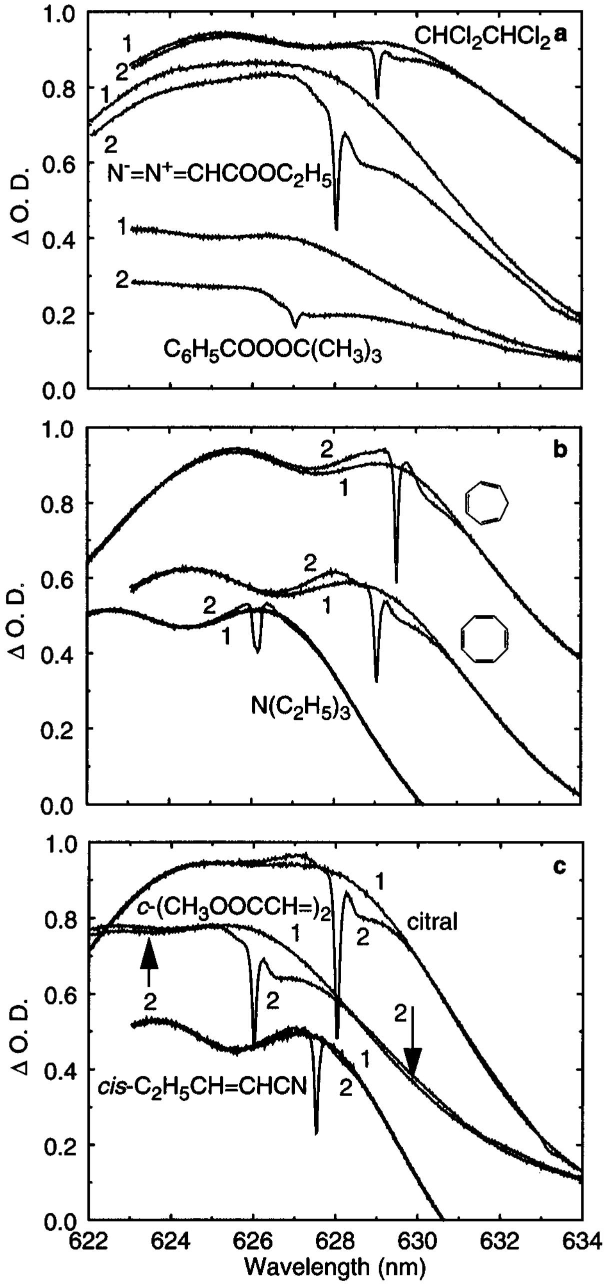


Figure 2. Absorption change of the $S_1 \leftarrow S_0$ band of ZnTBP (trace 1) after extensive hole burning (trace 2) in neat solvent glasses at 10 K: (a) electron acceptors; (b) triplet energy acceptors and an electron donor (TEA); (c) ethylenes with electron-accepting substituents. Holes were burned with saturating laser light (0.3 J cm^{-2}, 60 μJ cm^{-2}, 120 s, 40 Hz). The samples (except for COT) were simultaneously exposed to the gating light (3 mW cm^{-2}). Pairs of traces are arbitrarily shifted in the optical density scale. The initial O. D. at the burning wavelength was 0.5−0.9.

study of photoproducts is required for the understanding of the underlaying mechanisms. The intensity redistribution within the Q-band as a result of extensive (0.3 J cm^{-2} selective light dose) two-color burning is shown in Figure 2. The bleaching of the whole 0−0 absorption band in neat *tert*-butyl peroxybenzoate and ethyl diazoacetate is even much stronger than that in a reactive halocarbon, 1,1,2,2-tetrachloroethane (panel a). The former compounds act as the most efficient electron acceptors. On the other hand, there is practically no total loss of 0−0 absorption intensity in TEA and CHT glasses (panel b). The photoproduct ("antihole") accumulates mainly on the short-wavelength side of the $S_1 \leftarrow S_0$ maximum, where the overlap with the pseudowing is smaller. It seems that the reversible electron transfer resulting in structural changes in the matrix can be the mechanism of HB in an electron donor environment. It was already proposed by us[35,36] that in CHT and other olefins the *cis*−*trans* isomerization is sensitized by means of triplet energy transfer from the T_n state of the dye, leading to a microscopic solvent shift of the zero-phonon line and the creation of a hole. Efficient one-color process in COT solution results also in the redistribution of intensities within the 0−0 band. Ethylene derivatives containing electron-accepting π-electronic substituents show an integral loss of 0−0 band intensity, but there is also a clear-cut increase of absorption outside the hole region (panel c). The irreversible loss of intensity increases in the order *cis*-2-pentenenitrile (practically no loss) < citral < methyl maleate.

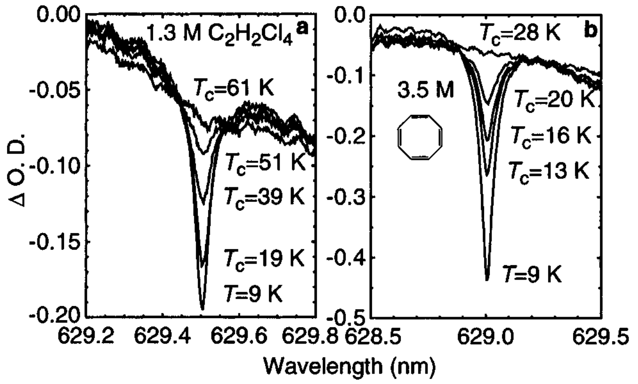


Figure 3. Influence of cyclic warm-up on two-color (a, 1,1,2,2,-tetrachloroethane) and one-color (b, COT) holes in the $S_1 \leftarrow S_0$ band of ZnTBP burned at 9 K. Holes were measured at 9 K. The solutions were prepared in toluene−benzene (2:1 v/v) mixture.

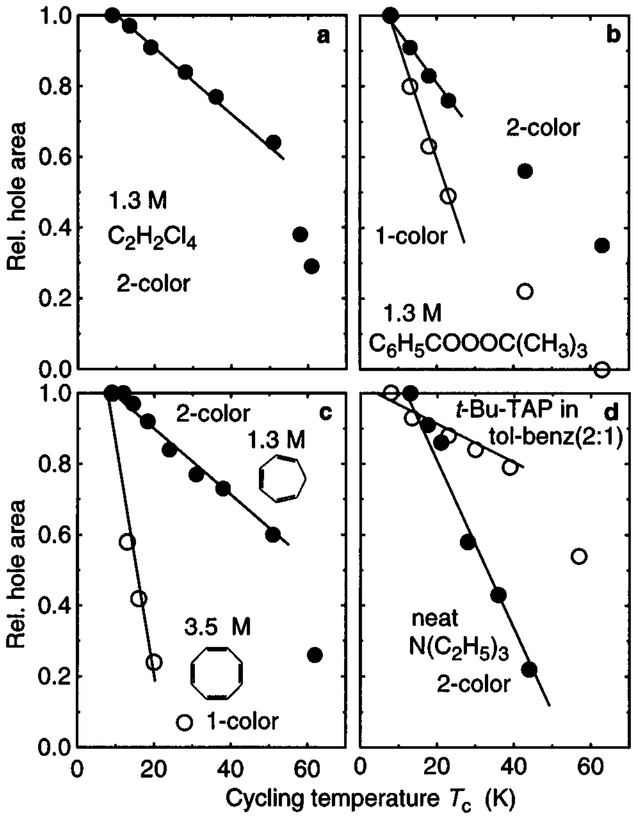


Figure 4. Temperature-induced filling of one- and two-color holes in the $S_1 \leftarrow S_0$ band of ZnTBP in toluene−benzene (2:1 v/v) mixture containing various activators as well as one-color holes in tetra-*tert*-butyltetraazaporphine in toluene−benzene (2:1 v/v).

The absorption spectrum of ZnTBP in neat vitreous activators was recorded in the 350−750 nm range in an attempt to observe the products after the exposure with visible light (Osram lamp, filter ZhS-12, $\lambda > 450$ nm, ∼100 mW cm^{-2}) at 10 K. After 1 min of photolysis the decrease of the 0−0 band amounted to 17% in ethyl diazoacetate, 12% in *tert*-butyl peroxybenzoate, 7% in $CHCl_2CHCl_2$, 3% in dimethyl maleate, and 0.5% in citral. In TEA, CHT, and COT (20% v/v in toluene−benzene glass) the absorption change was less than 0.2%. In electron-accepting environments an extremely weak and broad absorption appeared at 500 nm, and there was little decrease at the 410 nm band of the pigment whereas the 626 and 433−438 nm bands were subject to extensive bleaching. Little bleaching of the 410 nm band is in accordance with the fact that the spectrum of ZnTBP cation radical generated in methanol−dimethyl sulfoxide (10:1) by oxidation with iodine shows the strongest absorption at 415 nm.[40] It was noted already in ref 13 that the absorption of the product of gated HB in ZnTBP derivatives is weak and devoid of characteristic features.

The thermal stability of holes can also cast light to the burning mechanism. The deep holes were burned at 9 K and recorded at the same temperature after the warm-up of the sample to a certain temperature T_c (Figure 3). The temperature cycling results in broadening of the hole and a decrease of its area. The one-color hole that is formed with high efficiency at 9 K in COT/toluene−benzene mixture disappears completely after the temperature cycling up to 28 K (Figure 3b). In Figure 4 the normalized hole area is depicted as a function T_c for several acceptors, cyclic polyenes, and TEA. For the sake of comparison, the hole filling for tetra-*tert*-butyltetraazaporphine in a toluene−benzene mixture is displayed in Figure 4d. In this compound the photoinduced displacement of the pair of central protons in the tetrapyrrolic macrocycle leads to the formation of holes which are the most stable.[41] It follows from Figure 4 that the holes are relatively stable for $CHCl_2CHCl_2$ and CHT systems (half-filling temperature >55 K). The acceptors containing a π electronic fragment yield less persistent holes, with the half-filling temperatures at 47 (two-color hole) and 23 K (one-color hole) for both the 1.3 M *tert*-butyl peroxybenzoate and neat ethyl diazoacetate and 43 (two-color hole) and 35 K (one-color hole) for 1.3 M allyl bromide (data not shown), respectively. Photoproduct spectra and hole stability will be discussed in more detail in the following sections.

2. Electron Acceptors. The capability of several molecules with oxidizing properties to support the two-color HB in ZnTBP was already illustrated in Figures 1 and 2. There has been several attempts to correlate the HB efficiency with the free energy change of electron transfer,[16,24] but as a result of the limited number of investigated systems, the results remained inconclusive. The data obtained for a larger number of activators are reported here. The photoionization probability of the T_1 state of the dye upon absorption of the second quantum (Φ_2) was calculated as described in the Experimental Section. HB was performed in 7×10^{-5} M ZnTBP solutions in toluene−benzene (2:1 v/v) containing 7−10% of pyridine and 1.3 M activator. In a typical experiment the sample was first exposed for 100 s from the opposite sides with 5 mJ cm^{-2} (pulse frequency 20 Hz) of selective red light and 400 mJ cm^{-2} (4 mW cm^{-2}) of green light. The Φ_2 value characterizes the HB rate at the initial stage of transformation of about 10−20% molecules. At higher conversions the HB rate gradually decreases (see section 7).

The correlation of log Φ_2 with the irreversible reduction potentials (E_{red}) of halocarbons taken from refs 42 and 43 is poor (*N*, number of compounds, *r*, regression coefficient, *cis*-dichloroethylene and allyl bromide were excluded from the correlation) (Figure 5):

$$\log \Phi_2 = (-2.5 \pm 0.3) + (0.52 \pm 0.2)E_{red}; \quad N = 10, r = 0.65 \quad (1)$$

The slope of the eq 1 is very shallow: $0.52 \pm 0.2\ V^{-1}$ (or eV^{-1}).

For the quenching reactions of T_1 states of metalloporphyrins[44] and polycyclic hydrocarbons[45] by electron acceptors (nitrobenzenes, quinones) in liquid solutions, the slope of the plot of log k_q (k_q is the second-order quenching constant) vs E_{red} is as large as 8−11 eV^{-1}. This value is in accordance with the theoretical prediction for thermally activated electron transfer $^1/_2(2.3RT)^{-1} = 8.5\ eV^{-1}$.[44] The rate dependence of essentially barrierless electron transfer at 10 K may have a different slope, but it is expected to show at least a smooth dependence on the

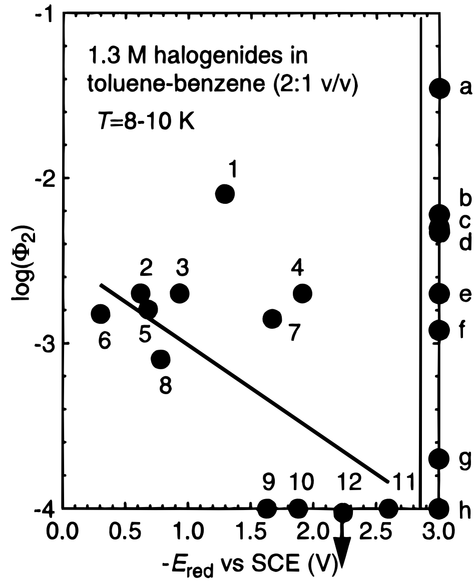
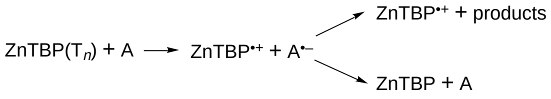


Figure 5. Dependence of the absolute two-color hole-burning yield for ZnTBP/toluene−benzene glass in the presence of 1.3 M halocarbons as a function of irreversible reduction potential of the acceptor (from refs 42 and 43): 1, allyl bromide; 2, C_2Cl_6; 3, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT); 4, allyl chloride; 5, $C_6H_5CCl_3$; 6, CBr_4; 7, $CHCl_3$; 8, CCl_4; 9, CH_3I; 10, C_2Cl_4; 11, *cis*-$C_2H_2Cl_2$; 12, CH_2Cl_2. The log Φ_2 values for substances with unknown E_{red} are depicted on the right-side panel of the figure: a, *trans*-1,4-dibromo-2-butene; b, CCl_3CN; c, hexachlorobutadiene; d, ethyl trichloroacetate; e, γ-hexachlorocyclohexane (0.8 M in polystyrene); f, 1,1,2,2-tetrachloroethane; g, 9-bromoanthracene (20% in polystyrene); h, 9-chloroanthracene (0.5 M). No gating effect was observed for C_6F_6, 1,2-dichloroethane (not shown) and CH_2Cl_2.

free energy change of reaction. The absence of such a dependence means that the HB yield may by determined by the structural features of halocarbon acceptors, rather than by the free energy of electron transfer. The rate-limiting step can be the irreversible transformation of the halocarbon anion radical, preventing the ion pair from recombination. Dissociation of the halocarbon anion radical can be strongly dependent on structure. Therefore, the following reaction scheme can be proposed (A, electron acceptor):



$$\mathrm{ZnTBP(T}_n\mathrm{)} + \mathrm{A} \longrightarrow \mathrm{ZnTBP}^{\bullet+} + \mathrm{A}^{\bullet-} \begin{cases} \nearrow \mathrm{ZnTBP}^{\bullet+} + \text{products} \\ \searrow \mathrm{ZnTBP} + \mathrm{A} \end{cases} \quad (2)$$

Probably the unimolecular reaction of the anion radical limits the overall rate of HB by rendering electron transfer irreversible.

The weak dependence of Φ_2 on E_{red} may indicate that the recombination of radicals having a large driving force may obey the inverted Marcus relationship.[46,47] In other words, the recombination rate may increase when the free energy gap between the ground state and the ion pair state decreases. Therefore, fast ionization in the presence of a strong acceptor resulting in a low-lying ion-pair state is followed by a fast recombination, which in turn leads to inefficient HB even in the case of good acceptors.

The activators that form transparent glasses on cooling, such as 1,1,2,2-tetrachloroethane, can be mixed with a neutral diluent, and the influence of the activator concentration can be studied over a broad range. The gating efficiency grows linearly between the 1 and 25% (3 M) content of the reactant and then reaches practically a limiting value (Figure 6). Evidently, the electron transfer requires nearly van der Waals contact of the pigment and activator molecules. In this case the reaction rate should increase linearly with concentration, since the number of acceptor particles in the closest coordination sphere of the pigment molecule is proportional to concentration. As a result of fast relaxation of the T_n state (probably several picoseconds), the electron transfer by means of long-range (~15 nm) tunneling in the sense expressed in refs 2−8 has no time to occur. The yield of permanent hole formation is not further increased when the pigment becomes fully surrounded by acceptor molecules. Possibly, a very fast recombination of the contact ion-radical pair may compete with the structural changes in the halocarbon anion radical (e.g., the halogen ion detachment) which are needed to render the process irreversible.

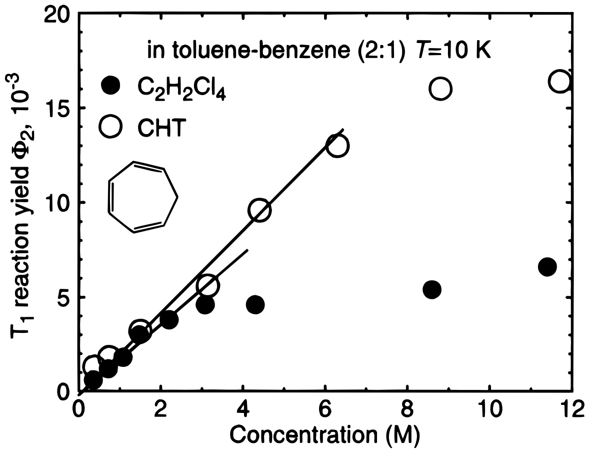


Figure 6. Dependence of the absolute yield of two-quantum reaction on the concentration of activator. The two-color holes were burned for 60 s with simultaneous exposure to the selective laser light (5 mJ cm^{-2}, 2 μJ cm^{-2} per pulse, 40 Hz) at 629.3 nm and continuous blue light (3 mW cm^{-2}).

Weak reversible π-electronic acceptors (benzophenone, nitrobenzene, phthalonitrile, isophthalonitrile) fail to induce any HB (Tables 1 and 2). The triplet energies of these compounds are well below the T_n level (~4 eV) of ZnTBP.[48] Thus, both the electron and triplet energy transfer to the additive molecules are possible. Because of either the rapid charge recombination or the absence of isomerization in the T_1 state, there is practically no permanent change in the system capable of leading to HB. Moreover, 1.3 M "inert" compounds, such as nitrobenzene and benzophenone, can quench the gated hole burning in the presence of 1.3 M crotonaldehyde by ~50% due to the energy or reversible electron transfer. Upon the addition of 0.5−1 M of stronger π-acceptors (1,3-dinitrobenzene, 2-nitrobenzaldehyde, benzoquinone, 1,4-naphthoquinone, 2-methylnaphthoquinone, and maleic anhydride) the Q-band of ZnTBP broadens and shifts bathochromically, indicating that a charge-transfer complex is formed at low temperatures.[36]

3. Electron Donors. The efficiencies of one- and two-color hole formation measured under standard conditions (5 mJ cm^{-2} of selective light, 1.3 M solution in toluene−benzene mixture) for different aliphatic and aromatic electron donors as additives are given in Table 3. The triplet reaction yield Φ_2 is the highest in tertiary aliphatic amines. The largest effect appears in the presence of a high density of electron-donating *tert*-amino groups in *N,N′*-dimethylpiperazine, neat glassy bis(dimethylamino)methane $CH_2[N(CH_3)_2]_2$ ($\Phi_2 = 10^{-2}$, $G = 27$), and TEA ($\Phi_2 = 4 \times 10^{-3}$, $G = 8$)). The influence of much stronger π-electronic donors *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine ($G = 3$) and tetrathiafulvalene ($G = 2.5$) is rather small. Quinuclidine, 1,4-diazabicyclo[2.2.2]octane, and β-carotene were found to be completely inert.

TABLE 1: Quantum Yields of Gated Hole Burning in ZnTBP in the Presence of Aldehydes and Ketones as Activators at 8 K[a]

compound	name	Φ_1, 10^{-5}	Φ_2, 10^{-3}	G
	Aldehydes			
$CH_3CH{=}CHCHO$	crotonaldehyde	0.8	17	70
(*cis* + *trans*)-$(CH_3)_2CH{=}CHCH_2CH_2C(CH_3){=}CHCHO$	citral	1.4	15	35
$CH_2{=}C(CH_3)CHO$	methacrolein	<0.6	10	>16
trans-$C_6H_5CH{=}CHCHO$	cinnamaldehyde	0.6	7	40
$C_6H_5CH{=}C(CH_3)CHO$	α-methylcinnamaldehyde	1.2	2.3	7
$CH_2{=}CHCHO$	acrolein	0.6	1.6	10
o-$C_6H_4(CHO)_2$	phthalaldehyde	0.5	1.2	10
$CH_3CH{=}CHCH{=}CHCHO$	sorbic aldehyde	0.5	1.0	6
$C_6H_5CH{=}C(Cl)CHO$		0.3	0.8	9
p-HOC_6H_4CHO[b]	*p*-hydroxybenzaldehyde	0.5	<0.1	1.2
C_3H_7CHO	butanal	3.7	<0.1	1.2
α-$C_{10}H_7CHO$	α-naphthaldehyde	0.6	<0.1	0.9
	Ketones			
$(CH_3)_2C{=}CHCOCH_3$	mesityl oxide	0.7	1.6	9
$C_9H_{15}CH{=}CHCOCH_3$	α-ionon	1	1	4
$CH_3COCOCH_3$	diacetyl	1	1	4
$C_6H_5CH{=}CHCOCH_3$	benzalacetone	1.3	0.4	2
trans-$C_6H_5CH{=}CHCOC_6H_5$	chalcone	0.85	<0.1	1.2
(±)-camphorquinone		1.1	<0.1	1.2
$(C_6H_5CH{=}CHCH{=}CH)_2CO$[c]	dicinnamalacetone	0.5	<0.1	1.1
$C_6H_5COC_6H_5$	benzophenone	1.1	<0.1	0.9
$C_6H_5COCOC_6H_5$	benzil	1.3	<0.1	0.9

[a] 1.3 M activator in toluene−benzene (2:1 v/v) solvent glass with 10% of pyridine added: Φ_1, one-color burning yield; Φ_2, absolute two-color burning yield; G, gating ratio, errors ±30%. [b] In 90% propylene carbonate. [c] 0.65 M of activator.

TABLE 2: Quantum Yields of Gated Hole Burning in ZnTBP in the Presence of Esters and Nitriles as Activators at 8 K[a]

compound	name	Φ_1, 10^{-5}	Φ_2, 10^{-3}	G
	Esters			
$C_6H_5COOOC(CH_3)_3$	*tret*-butyl peroxybenzoate	11	15	5
$N^-{=}N^+{=}CHCOOC_2H_5$	ethyl diazoacetate	1	12	40
cis-$CH_3OOCCH{=}CHCOOCH_3$	dimethyl maleate	1.8	7	14
cis-$C_2H_5OOCCH{=}CHCOOC_2H_5$	diethyl maleate	0.4	1.7	15
cis-$C_3H_5OOCCH{=}CHCOOC_3H_5$	diallyl maleate	0.7	1	6
$CH_3COCOOCH_3$	ethyl pyruvate	0.4	0.7	6
trans-$C_2H_5OOCCH{=}CHCOOC_2H_5$	diethyl fumarate	0.8	0.2	2
$C_6H_5CH{=}CHCOOCH_3$	methyl cinnamate	1.4	0.1	1.4
propylene carbonate		1	<0.1	1
$CH_2{=}C(CH_3)COOCH_3$	methyl methacrylate	1	<0.1	0.6
	Nitriles			
cis-$C_2H_5CH{=}CHCN$	*cis*-2-pentenenitrile	20	24	5
$CH_2{=}C(Cl)CN$	chloroacrylonitrile	2	13	22
$NC(CH_3)_2CN{=}NC(CH_3)_2CN$[b]	AIBN	0.8	3	14
$CH_2{=}CHCN$	acrylonitrile	2	3	6
$C_6H_5CH{=}CHCN$	cinnamonitrile	0.7	1.7	9
trans-$NCCH{=}CHCN$	fumaronitrile	0.16	0.5	11
m-$C_6H_4(CN)_2$[c,d]	isophthalonitrile	0.6	0.1	2
$CH_2(CN)_2$[d]	malononitrile	0.8	0.1	1.3
o-$C_6H_4(CN)_2$[d]	phthalonitrile	0.55	<0.1	0.9
CH_3CN	acetonitrile	0.5	<0.1	0.8
cis,cis-$NCCH{=}CHCH{=}CHCN$[c,d]	mucononitrile	13	<0.1	0.25

[a] 1.3 M activator in toluene−benzene (2:1 v/v) solvent glass with 10% of pyridine added: Φ_1, one-color burning yield; Φ_2, absolute two-color burning yield; G, gating ratio, errors ±30%. [b] In 90% propylene carbonate. [c] 0.65 M of activator. [d] In 50% propylene carbonate.

The spectral change in TEA after an extensive gated HB by scanning the laser over 626−626.2 nm is displayed as the lowest trace in Figure 2b. Characteristic narrow antiholes (<1 nm) appear on both sides of the burning region. The overall decrease of the integrated absorption intensity is by a factor 5−10 smaller than the zero-phonon hole area. Therefore, the dominating process responsible for HB is the redistribution of centers within the inhomogeneously broadened 0−0 contour. The photoproduct absorption lies very close to the burning wavelength. The hole is relatively easily filled upon raising the temperature, demonstrating that the photoprocess is reversible (Figure 4d). Note that the holes created by means of irreversible electron transfer to $C_2H_2Cl_4$ are more stable (Figure 4a). Under extensive photolysis with an Osram lamp (filter SZS-25, transmission limits 300−800 nm, 100 mW cm^{-2}, 15 min) at 10 K, a shallow hump ($\Delta D = 0.03$) appears in neat bis(dimethylamino)methane at 500 nm. This band can be assigned to the ZnTBP anion radical absorption, in accordance with the published spectrum of chemically generated ZnTBP$^{\bullet-}$.[51]

Consequently, the HB process induced by aliphatic amines (D) can be summarized as follows (ZnTBP′ denotes the pigment molecule with shifted 0−0 frequency):

$$\mathrm{ZnTBP(T}_n\mathrm{)} + \mathrm{D} \longrightarrow \mathrm{ZnTBP}^{\bullet-} + \mathrm{D}^{\bullet+} \longrightarrow \begin{cases} \mathrm{ZnTBP}^{\bullet-} + \text{products} \\ \mathrm{ZnTBP}' + \mathrm{D} \\ \mathrm{ZnTBP} + \mathrm{D} \end{cases} \qquad (3)$$

A small number of ions may escape recombination after the deprotonation of the TEA cation radical.[5] The structural change

TABLE 3: Quantum Yields of Gated Hole Burning in ZnTBP in the Presence of Electron Donors as Activators at 8 K[a]

compound	$\Phi_1, 10^{-5}$	$\Phi_2, 10^{-3}$	*G*	IP(eV)[b]
bis(dimethylamino)methane $CH_2[N(CH_3)_2]_2$[c,d]	1.3	10	27	
N,N′-dimethylpiperazine	1.6	3.4	8	
triethylamine (TEA)[c]	2	4	8	7.37
triethylamine (TEA)	2	2	4	
N,N,N′,N′-tetramethyl-*p*-phenylenediamine	2.2	1.4	3	6.2
tetrathiafulvalene (TTF)	0.4	0.2	2.5	6.4
N.N-dimethylaniline (DMA)	0.15	0.1	2.7	7.1
1,4-diazabicyclo[2.2.2]octane	0.2	<0.1	1.2	7.52[e]
β-carotene	1.6	<0.1	1.1	6.5
quinuclidine	1.5	<0.1	0.9	

[a] 1.3 M activator in toluene−benzene (2:1 v/v) solvent glass with 10% of pyridine added: Φ_1, one-color burning yield; Φ_2, absolute two-color burning yield; *G*, gating ratio, errors ±30%. [b] Ionization potential from ref 49. [c] Neat activator. [d] At 18 K. [e] Reference 50.

TABLE 4: Quantum Yields of Gated Hole Burning in ZnTBP in the Presence of Alkenes as Activators at 8 K[a]

compound	name/abbr	$\Phi_1, 10^{-5}$	$\Phi_2, 10^{-3}$	*G*
cis-2,4,5-$(CH_3O)_3C_6H_2CH{=}CHCH_3$	asarone	2	18	30
4,4′-*bis*[2-(1-propenyl)phenoxy]benzophenone (mixture of *cis* and *trans*)		<2	10	
trans-4-$CH_3OC_6H_4CH{=}CHCH_3$	anethole	1	6	20
cycloheptatriene	CHT	1.2	3	11
(cis + trans)-$CH_3CH{=}CHCH{=}CHCH_3$		3.5	2.3	3
(cis + trans)-$CH_2{=}CHCH{=}CHCH_3$[b]	piperylene	0.5	1.8	13
cis-$C_6H_5CH{=}CHC_6H_5$	*cis*-stilbene	0.3	0.8	3
$CH_2{=}CHC(CH_3){=}CH_2$	isoprene	0.8	0.36	2.5
$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$		0.9	0.1	1.4
$C_6H_5CH{=}CH_2$	styrene	0.8	0.1	1.4
cis-$HOCH_2CH{=}CHCH_2OH$		2.5	0.1	1.2
$(CH_3)_2C{=}C(CH_3)_2$[b]		1	0.1	1.2
cis,cis-cyclooctadiene		10	<0.1	0.9
(cis + trans)-$CH_2{=}CHCH{=}CHCH{=}CH_2$[b]		0.8	<0.1	0.7
cyclooctatetraene	COT	70	<0.1	0.15

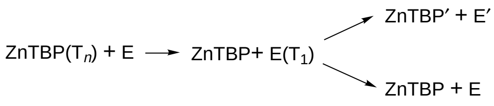
[a] 1.3 M activator in toluene−benzene (2:1 v/v) solvent glass with 10% of pyridine added: Φ_1, one-color burning yield; Φ_2, absolute two-color burning yield; *G*, gating ratio, errors ±30%. [b] In 50% propylene carbonate.

following the recombination of radicals may produce a microscopic solvent shift and lead to HB. It is not clear, however, whether the electron-transfer step or the matrix rearrangement limits the HB rate. Several aliphatic donors with low ionization potentials,[49,50] such as quinuclidine and 1,4-diazabicyclo[2,2,2]-octane, do not support the gated HB process. Plausibly, in these rigid molecules the electron transfer proceeds reversibly and without structural changes. The π-electron donors *N,N*-dimethylaniline and tetrathiafulvalene are also inefficient because they can quench the T_n state of the dye, and the structural changes following the triplet energy or electron transfer have a small probability in aromatic systems.

The two-quantum mechanism has been reported for the photoinduced charge separation in the Zn etioporphyrin−TEA system at 77 K, where TEA acts as an electron donor.[5] It has been surmised that a short-lived ion-radical pair is formed already upon absorption of the first quantum, and the second quantum promotes the electron from the primary pigment anion radical to some other neutral pigment molecule by means of a long-range tunneling process. However, the existence of such a transient ion radical has not been proven.[5]

4. Olefins. Numerous olefinic compounds devoid of appreciable electron affinity can induce HB in the 0−0 bands of ZnTBP and MgOEP. Fairly efficient gated HB with Φ_2 values reaching 10^{-2} (Table 4) can be observed after adding substituted alkenes and cycloalkenes to the matrix (Figure 1b; see also Figure 1 in refs 35 and 36). The spectra recorded after an extensive burning show practically no decrease in the absorption intensity integrated over a broad wavelength interval (Figure 2b).

Olefins capable of *cis*−*trans* isomerization, such as cycloheptatriene and 1-propenyl-substituted benzenes (asarone, anethole), support the gating to a larger extent than those without isomers: 2-methyl-1,3-butadiene (isoprene), 1,6-dimethyl-2,4-hexadiene, and styrene. A large π-electronic system seems to suppress HB in *cis*-stilbene and 1,3,5-hexatriene. *cis*-1,4-Dihydroxy-2-butene is inactive because the triplet level of a compound with only one double bond is probably too high to accept energy from the T_n level of ZnTBP.[48] Both the high activity of *cis*-alkenes and the spectral distribution of the product within the inhomogeneously broadened band contour can be rationalized in terms of isomerization of alkenes (E) sensitized by highly excited triplet porphyrin (E′ denotes the structural isomer of alkene):



(4)

The structural rearrangement of alkene in the close vicinity of pigment molecule can give rise to a solvent shift of zero-phonon transition frequency of the latter and, as a consequence, create a resonant hole.

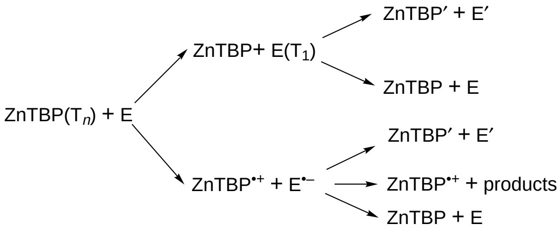
Remarkably, it has been already observed that naphthalene-d_8 can sensitize the conversion of matrix molecules to the *trans* form in neat glassy *cis*-2-pentene at 77 K as a result of energy transfer from the higher triplet level of naphthalene.[52]

The concentration dependence of the two-quantum photochemical yield for toluene−benzene glass containing various amounts of cycloheptatriene (CHT) is plotted in Figure 6. The Φ_2 dependence remains linear up to the CHT content as high as 6 M (50%). For CHT the relationship is somewhat steeper than that for the electron-transfer system containing 1,1,2,2-tetrachloroethane. Its conceivable that for the spectral redistribution mechanism the effect of activator concentration (c) is stronger because c enters the burning rate expression twice, by influencing both the rate of energy transfer and the magnitude of the solvent shift. The distance r between the reactants scales as $c^{-1/3}$. The rates of both exchange processes, the electron and triplet energy transfer, fall off exponentially with distance as $\exp(-r)$. On the other hand, the dispersive interaction energy has a distance dependence of r^{-6}. A multiplication of these factors ($c^2 \exp(c^{1/3})$) gives rise to a steeper concentration dependence in case of spectral redistribution mechanism (eq 4).

A peculiar behavior was observed in the presence of cyclooctatetraene (COT) which was initially utilized as a weak electron acceptor with a known value of electron affinity. COT (1.3 M) causes one-color bleaching with the quantum yield of $\Phi_1 = 7 \times 10^{-4}$ (Figure 1b). As a result of extensive hole filling under the green light exposure, the gating ratio is much less than unity ($G = 0.15$). The one-color holes are thermally unstable: after a temperature cycle up to 28 K the hole is completely erased (Figures 3b and 4c). By contrast, the thermal filling of gated holes in the presence of CHT occurs at much higher temperatures and may be limited mainly by spectral diffusion. Remarkably efficient one-color hole burning induced by COT may arise as a result of triplet energy transfer (or electron transfer, see the next section) from the T_1 level of ZnTBP followed by *cis*−*trans* isomerization of the polyene. Isomerization with respect to a single bond would account for the instability of the product. However, on the basis of a triplet quenching study at room temperature the T_1 level of COT can be located at 14 000−17 500 cm^{-1} (40−50 kcal/mol), depending on the degree of planarity of the molecule.[53] The T_1 level of the ZnTBP lies at 12 450 cm^{-1}.[39] Thus, the triplet energy transfer from ZnTBP to COT may require a considerable distortion (flattening) of COT molecule which is nonplanar in the free state.

5. Olefins with Electron-Accepting Substituents. The quantum yields and gating ratios have been measured under standard conditions for the following groups of HB activators: aldehydes, ketones (Table 1), esters, and nitriles (Table 2). Except for several electron acceptors (*tert*-butyl peroxybenzoate, ethyl diazoacetate), most of active compounds belong to substituted ethylene derivatives. The additives with the largest values of Φ_2 contain one or two double-bonded (>C=O) or triple-bonded (−C≡N) heteroatomic substituents conjugated with a single ethylenic fragment: *trans*-butenal (crotonaldehyde) ($\Phi_2 = 1.7 \times 10^{-2}$), a mixture of *cis*- and *trans*-dimethyl-2,6-octadienal (citral) (1.5×10^{-2}), 2-methyl-2-penten-4-one (mesityl oxide) (1.6×10^{-3}), dimethyl maleate (7×10^{-3}), *cis*-2-pentenenitrile (2.4×10^{-2}), and chloroacrylonitrile (1.3×10^{-2}).

As far as the spectral distribution of the photoproduct is concerned, these compounds occupy an intermediate position between halocarbon acceptors and unsubstituted alkenes (Figure 2c). After a strong HB both the bleaching and intensity redistribution within the 0−0 band of ZnTBP take place with different relative weights for every compound. For example, the dimethyl maleate seems to produce mostly the decay of the pigment whereas in case of *cis*-2-pentenenitrile the spectral redistribution mechanism largely prevails. It is probable that isomerization or less extensive structural change can occur not only in the T_1 state but also in the ionic (anion radical) state of the olefin. The following general reaction scheme may be proposed (E′ stands for the olefinic activator molecule with changed geometrical structure):



(5)

As in case olefinic hydrocarbons, the activators with possible *cis*−*trans* isomerism possess larger Φ_2, e.g., $CH_3CH{=}CHCHO$ ($\Phi_2 = 1.7 \times 10^{-2}$) vs $CH_2{=}C(CH_3)CHO$ ($\Phi_2 = 1.0 \times 10^{-2}$). The monosubstituted ethylenes, such as acrolein (1.6×10^{-3}) and acrylonitrile (3×10^{-3}), can also support HB, plausibly owing to the displacement of a substituent (quasi-isomerization) in the solid-state matrix. The activity of substituents attached to the same olefinic fragment increases in the following order: esters (least reactive) ketones < nitriles < aldehydes (most reactive), e.g., $C_6H_5CH{=}CHCOOCH_3$ (10^{-4}) < $C_6H_5CH{=}CHCOCH_3$ (4×10^{-4}) < $C_6H_5CH{=}CHCN$ (1.7×10^{-3}) < $C_6H_5CH{=}CHCHO$ (7×10^{-3}). Similarly to unsubstituted olefins, the reactivity seems to be reduced by a large size of π-electronic system in 2,4-pentadienal (sorbic aldehyde), *trans*-1-phenyl-1-buten-3-one (benzalacetone), chalcone, dicinnamalacetone, etc.

Gated HB was reported recently for ZnTBP in phenoxy resin containing 0.96 M crotonic acid ($CH_3CH{=}CHCOOH$).[20,32,33] In toluene−benzene glass the Φ_2 (2×10^{-3}) and gating ratio ($G = 8$) were found to be quite small in the presence of 1.3 M crotonic acid. In our system the carboxylic acid forms a pyridinate salt and dissolves in the nonpolar host as an ion pair which may be characterized by lower electron affinity and mobility. Undoubtedly, a combined mechanism (eq 5) can be valid in case of crotonic acid, which is a structural analogue of crotonaldehyde, dimethyl maleate, and 2-pentenenitrile (Tables 1 and 2).

Finally, the sensitized photodecomposition of organic azides should be mentioned. Promising photon gating characteristics have been described for Zn tetratolyltetrabenzoporphine doped in aliphatic glycidyl azide polymer as well as in PMMA containing aromatic 4,4′-diazidodiphenyl sulfone at 20 K.[21] It was assumed that in both cases the triplet energy transfer from the T_n state of pigment to the $-N_3$ fragment is followed by its spontaneous splitting to a nitrene and N_2. As a result, the modification of the environment can lead to HB. Surprisingly, no gating effect was observed in the 1.3 M 1-azidoadamantane/toluene−benzene system ($\Phi_2 < 10^{-4}$). On the other hand, direct excitation of 1-azidopyrene leads to extremely fast burning of a broad hole at 385.3 nm.[36] The 130 fs decomposition rate obtained from the hole width indicates that the dissociation reaction proceeds in the S_1 state, because such a dramatic enhancement of S_1−T_1 interconversion rate appears to be improbable. If the singlet channel indeed prevails, the mechanism proposed in ref 21 should be reconsidered.

6. Photon-Gated Hole Burning in Polymer Matrices. Optical components can be manufactured from amorphous polymers, such as polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinyl butyral) (PVB) since they are isotropic and fully transparent in the visible range. The materials made in the form of solid films or plates are much easier to handle than frozen solvent glasses and, therefore, preferable as far as HB applications are concerned. The behavior of various HB activators in polymer carriers is shortly discussed in this section.

In Figure 7 the one- and two-color holes in 0.1−0.3 mm thick PS films are compared. As above (Figure 1), first the two-color hole was burned under simultaneous irradiation with

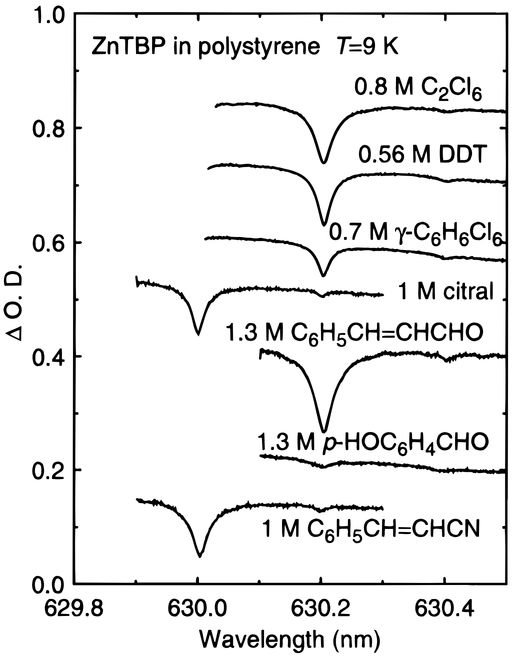


Figure 7. One- and two-color holes in the $S_1 \leftarrow S_0$ band of ZnTBP (optical density 0.7−1) in polystyrene matrix containing 0.56−1.3 M activators at 9 K. First, the two-color hole was burned at 630−630.2 nm with simultaneous exposure to 6 mJ cm^{-2} laser light (0.6 μJ cm^{-2} per pulse, 100 s, 100 Hz) and continuous blue light (4 mW cm^{-2}). Then the laser was tuned by 0.2 nm to the red, and the one-color hole was burned. The one-color hole is barely visible. The trace corresponding to *p*-hydroxybenzaldehyde additive is shifted to shorter wavelength by 1.2 nm. All traces are arbitrarily shifted in the optical density scale.

selective and gating light. The exposure to the same dose of the selective laser light results only in tiny holes which are barely visible on the right-hand side of every trace (gating ratio $G = 15-40$). For hexachloroethane the T_1 transformation yield Φ_2 is somewhat higher in PS (6×10^{-3}) than that in toluene−benzene glass (2×10^{-3}). On the contrary, the effect of citral is less in polymer ($\Phi_2 = 2 \times 10^{-3}$ and 1.5×10^{-2}, respectively). Cinnamonitrile is slightly more reactive in PS ($\Phi_2 = 3 \times 10^{-3}$ and 1.7×10^{-3}) whereas the influence of cinnamaldehyde remains the same in both environments ($\Phi_2 = 7 \times 10^{-3}$) (Tables 1 and 2). Thus, a small enhancement of the irreversible electron-transfer mechanism in polymers is observed. On the other hand, the HB processes based on structural isomerization of activator molecules (e.g., citral) seem to be suppressed by plausibly a more stiff macromolecular host matrix. The increase of polarity has negligible influence on HB in the presence of 1 M citral in the following set of polymers: low-density polyethylene, PS, PVB and PMMA ($\Phi_2 = (2 \pm 0.5) \times 10^{-3}$). Citral is characterized by both the electron transfer and isomerization pathways (eq 5, see the product redistribution in Figure 2c).

We have already applied the PS films activated by DDT for storage of time and space domain holograms.[34] Much more efficient materials require the utilization of stronger irreversible electron acceptors (*tert*-butyl peroxybenzoate, ethyl diazoacetate, *trans*-1,4-dibromo-2-butene, allyl bromide, etc.; see Figure 5 and Table 2). To avoid the spontaneous oxidation of pigment and the Menshutkin reaction under ambient conditions, the casting of films should be carried out at lower temperatures and under the exclusion of moisture and pyridine.

Dicyanobenzenes[28−30] and 4-hydroxybenzaldehyde[31] have been used as activators of gated HB in zinc complexes of meso-tetraaryl-substituted TBP derivatives in a PMMA matrix. The addition of these compounds (0.65−1.3 M) has negligible influence on HB in the case of ZnTBP in solvent glasses (Tables 1 and 2). In polystyrene matrix containing 1.3 M 4-hydroxybenzaldehyde a tiny gated hole ($G = 3$) could be burned (Figure 7). No additives have been reported to be introduced to the PMMA film which showed a fairly large gating effect in ref 54. The residual solvents ($CHCl_3$, CCl_4) in polymers may be responsible for the photon-gated HB observed in these studies.

Rather puzzling gated HB characteristics have been reported for free-base tetraphenylporphine (H_2TPP) in the presence of halogenated aromatic compounds[16] and *p*-benzoquinone[18] embedded in a PMMA host polymer (for a review, see ref 19). HB quantum yields with respect to the selective red light (645 nm) (Φ_1') much higher than unity have been obtained. Its easy to find out by integrating the 0−0 band of H_2TPP that the unit area ($D \times$ nm) corresponds to 1.5×10^{16} molecules/cm^2. (The extinction coefficient of H_2TPP in benzene is 3.4×10^3 M^{-1} cm^{-1}.[55]) The hole areas can be estimated from the figures in refs 16−19. It turns out that the number of quanta in the selective irradiation dose is considerably less than the number of out-burned molecules. For example, $\Phi_1' = 4$ in the case of β-bromonaphthalene additive (Figure 4 in ref 16) and $\Phi_1' = 10$ or even 100 in the presence of *p*-benzoquinone (Figures 1 and 2a in ref 17, respectively). In a PMMA copolymer containing covalently bound 9-chloroanthracene every red light quantum causes bleaching of 10 H_2TPP molecules (Figure 2 in ref 18). Obviously, the investigation of gated HB may be complicated by the one-quantum prototropic phototransformation in free-base porphyrins, which occurs in H_2TPP with a high quantum yield ($\Phi_1 = (1.3 \pm 0.5) \times 10^{-2}$ [56] or 4×10^{-3} [57]). Unfortunately, the measurements reported in refs 16−19 are difficult to reproduce since the details of sample preparation are not available in most cases. It is also likely that the light doses have been underestimated.

7. Spectrophotometric Study of MgOEP in the Presence of Electron Acceptors. Photooxidation of metalloporhyrins in solvent glasses containing electron acceptors at 77 K have been used as a model reaction of primary processes in photosynthesis.[1,6,7] It has been concluded that photoionization of Zn tetraphenylporphine in C_2H_5OH/1 M CCl_4[2] or 2-chlorobutane/CCl_4 (1:1 v/v)[11] and similar vitreous systems at 77 K takes place in the first excited singlet state as a result of the absorption of a single quantum. On the contrary, the photon-gated HB experiments suggest that the efficient electron ejection should occur from the highly excited triplet state, i.e., after absorption of a second light quantum by the molecule in the T_1 state.

In this section mainly the photoprocesses of MgOEP in a ethanol−CCl_4 mixture are described. The gated HB characteristics of ZnTBP and MgOEP are similar. In contrast to ZnTBP, the photoproducts of MgOEP possess a characteristic absorption at 650−700 nm. A nearly identical system, Mg etioporphyrin in ethanol glass containing 0.2−2 M CCl_4, has been investigated in refs 4 and 5.

A strongly nonlinear dependence of photochemical rate on the intensity of visible light which excites both the $S_1 \leftarrow S_0$ and $T_n \leftarrow T_1$ transitions becomes apparent in a simple experiment. The sample of 5×10^{-5} M MgOEP is exposed to a sequence of constant light doses with increasing intensities from 1 to 33 mW cm^{-2} by using the neutral density filters. The equality of doses is maintained by adjusting the irradiation times. The initial exposure at an intensity of 1 mW cm^{-2} for 30 min has a negligible effect on the Soret band intensity whereas the treatment with the same dose during 1 min produces a large loss of absorption (Figure 8), despite the concentration decrease during the previous exposures and the possibility that the remaining molecules may be less reactive.

By ignoring the dispersiveness (see below) of the reaction,

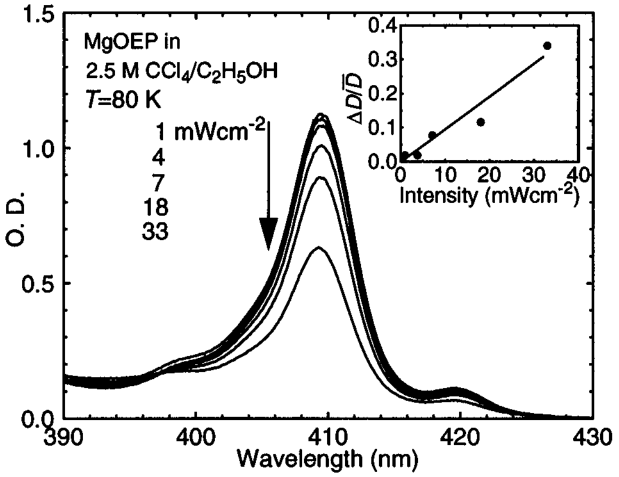


Figure 8. Photolysis of the 5 × 10^{-5} M solution of MgOEP in ethanol in the presence of 2.5 M CCl_4 at 80 K. The irradiation was carried out in the visible region (450−650 nm, filters ZhS-12 + SZS-21) consecutively with fixed doses of 1.3 J cm^{-2} for 30, 8.5, 4.3, 2, and 1 min with growing intensities of 1, 4, 7, 18 and 33 mW cm^{-2}, respectively. The Osram Hg lamp has strong lines at 547 and 578 nm nearly in resonance with the Q-bands of MgOEP. Optical densities of the spectra are set to zero value at 430 nm. Insert shows the dependence of the relative amount of reacted molecules as a function of light intensity (eq 8). Short exposures at high intensities led to stronger bleaching, revealing the two-quantum mechanism of the reaction.

one can write a formal expression for the time (t) dependence of the dye concentration c in the case of small optical densities

$$\mathrm{d}c/\mathrm{d}t = \mathrm{const}\cdot I^n c \qquad (6)$$

or

$$\Delta c = \mathrm{const}\cdot I^n c \Delta t \qquad (7)$$

where I is the light intensity and n is the number of quanta needed for the reaction. c and Δc can be replaced by the optical densities, and for a constant dose the $I\Delta t$ is constant:

$$\Delta D/[(D_i + D_{i+1})/2] = \mathrm{const}'\cdot I^{n-1} \qquad (8)$$

For simplicity, an average value of optical density before and after each exposure $\bar{D} = (D_i + D_{i+1})/2$ was used. An approximate linearity of the plot in the coordinates $\Delta D/\bar{D}$ vs I means that $n - 1 = 1$ or $n = 2$ (Figure 8, insert); i.e., we have a process requiring the absorption of two quanta.

Evidence for quenching processes of porphyrins in the S_1 state in cryogenic solid solutions is scarce.[2,10,11,58] The intensity of ZnTPP fluorescence in frozen ethanol at 80 K was reported to decrease by a factor of ~4 in the presence of 0.3 M methylviologen.[58] It was noted that even in chemically bound porphyrin−viologen compounds connected with flexible chains the donor and acceptor moieties tend to reside in close proximity in the solid matrix.[58] The fluorescence decay profiles can reveal whether the S_1 quenching is accompanied by a gradual shortening of lifetime with the increase of the quencher concentration (dynamic quenching) or, alternatively, the deactivation occurs "instantaneously" in complexes or close pairs of molecules (static quenching). A slight increase of fluorescence decay rates of H_2TPP, MgTPP, and ZnTPP in 2-chlorobutane upon addition of large amounts of CCl_4 or CBr_4 has been ascribed to a dynamic quenching due to an electron-transfer process.[10,11] However, a nonspecific matrix effect on the excited-state lifetime cannot be ruled out in this case, because the acceptors CCl_4 and CBr_4 have markedly larger refractive indices (polarizabilities) than the matrix. Therefore, the existence of dynamic quenching of the S_1 state of porphyrins in solid environment needs further investigation.

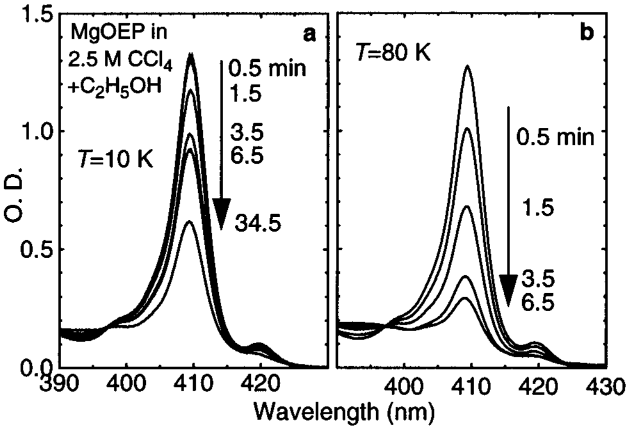


Figure 9. Photolysis of the 7 × 10^{-5} M solution of MgOEP in ethanol in the presence of 2.5 M CCl_4 at 10 (a) and 80 K (b). Irradiation was carried out in the visible region (450−650 nm, filters ZhS-12 + SZS-23) at the intensity of 37 mW cm^{-2}. The initial absorbed intensity was 2.2 mW cm^{-2}. The decrease of the Soret band after the irradiation for 0, 0.5, 1.5, 3.5, and 6.5 min is shown for both temperatures. At 10 K nearly a half of the dye remains unreacted after 34.5 min of irradiation (a).

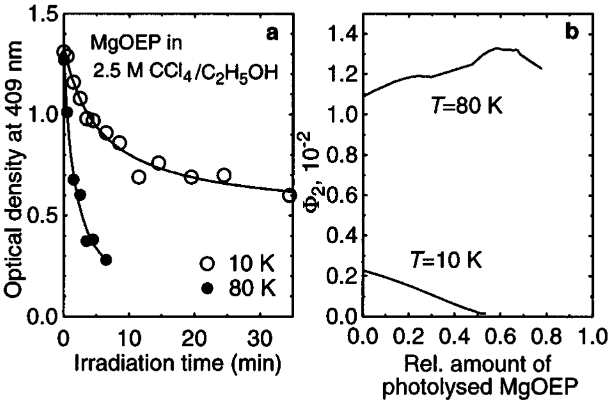


Figure 10. Kinetics of the photolysis of the 7 × 10^{-5} M solution of MgOEP in ethanol in the presence of 2.5 M CCl_4 at 10 and 80 K (see Figure 8). Fitting curves (stretched exponential functions) were used for smoothing the observed dependencies and have no direct physical meaning. The photoreaction probability for a dye in the T_1 state upon absorption of a quantum Φ_2 is depicted in panel b. Φ_2 has a much smaller initial value at 10 K and drops to zero value during the reaction.

The incorrect assumption that the relatively long-lived S_1 state participates in adiabatic electron transfer[2] has been unfortunately used later by the same authors[4] for calculating electron tunneling parameters. (See also reviews of the topic in refs 6−8).

The tunneling phenomena are characterized by their activationless character. By contrast, a comparison between the photobleaching kinetics of MgOEP in the presence of 2.5 M CCl_4 at 10 and 80 K shows a pronounced temperature dependence of the photochemical rate (Figure 9). The irradiation of 7 × 10^{-5} M solution of MgOEP at 80 K with 37 mW cm^{-2} of visible light (450−650 nm) during 6.5 min leads to fading of the Soret band by 80% (Figure 10a). Under comparable conditions at 10 K the decrease of absorption is only 40%. The remaining half of molecules have very low reactivity at 10 K. In Figure 10b the absorption kinetics is presented in terms of the probability of the T_1 state to undergo reaction after the absorption of a quantum (Φ_2) as a function of the relative amount of the decomposed dye. The calculation was done as described in the Experimental Section, bearing in

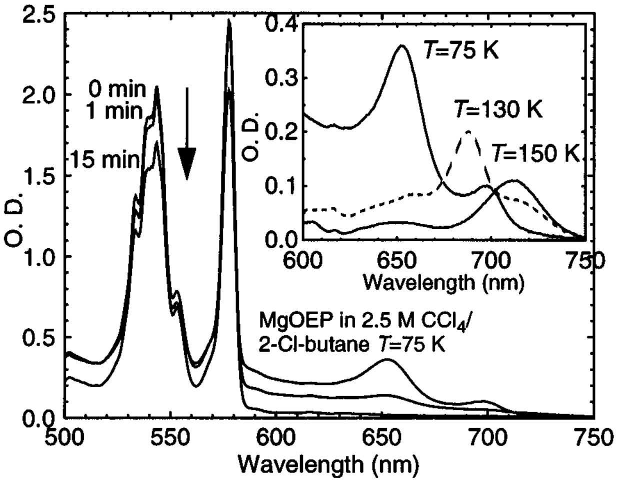


Figure 11. Accumulation of products during the photolysis of the 2 × 10^{-3} M solution of MgOEP in 2-chlorobutane glass in the presence of 2.5 M CCl_4 at 75 K. Irradiation was carried out in the visible region (450−650 nm, filters ZhS-12 + SZS-23) at the intensity of 37 mW cm^{-2} for 1 and 15 min, respectively. Insert shows irreversible red shifts of the product spectrum upon the increase of temperature of the irradiated sample.

mind that the initial $S_1 \leftarrow S_0$ absorption rate was 2.2 mW cm^{-2}, the triplet yield, lifetime and average extinction coefficient at the 547 and 578 nm lines of the Osram lamp are 0.75, 0.13 s,[39] and 7 × 10^3 M^{-1} cm^{-1},[59] respectively. Every one out of 100 molecules in the T_1 state reacts in its highly excited T_n state at 80 K ($\Phi_2 = 10^{-2}$). On the other hand, at 10 K the initial Φ_2 is by a factor of 5 lower, and it decreases fast in the course of the conversion of dye. In other words, at low temperature the kinetics is strongly dispersive, and a large amount of dye molecules practically cannot be converted.

The photoproduct formed from MgOEP in frozen solutions containing electron acceptors (CCl_4, $C_2H_2Cl_4$, *tert*-butyl peroxybenzoate) has two spectral maxima at 650 and 680−700 nm (Figure 11). The relative intensity of these maxima depends on matrix and temperature of photolysis. Spectral transformation of the product accumulated at 75 K in 2-chlorobutane−CCl_4 (2.5 M in the solid glass) mixture with increasing temperature is shown in the insert of Figure 11. At 130 K the two bands peaking at 652 and 697 nm are replaced by a single maximum at 688 nm. The original pigment absorption is partially recovered. At 150 K a single band appears at 713 nm. By contrast, ZnOEP in the 2-chlorobutane−CCl_4 (2.5 M) mixture gives rise to a single band at 652 nm which disappears at 130 K. Most probably these bands belong to pigment cation radicals which can have different maxima in various solvents (660 nm in CH_2Cl_2,[60] 683 nm in CH_3OH[61]). It is difficult to determine solely on the basis of optical data whether the spectra are modified by interactions with counteranions or radicals ($CCl_4^{\bullet-}$, $CCl_3^{\bullet}$, Cl^-), solvation of central Mg ion, or more extensive substitution and addition reactions at the π-radical itself. The electron spin resonance method may prove invaluable for proper characterization of the photooxidation products.[1−8,60] The efficiency of MgOEP photolysis in different media containing 2.5 M CCl_4 is somewhat dependent on the polarity of matrix. The highest value of Φ_2 (0.01) is observed in highly dipolar ethanol and propylene carbonate. Φ_2 is less in 2-chlorobutane (4 × 10^{-3}) and toluene−benzene glass (10^{-3}). The decomposition of the pigment is remarkably hampered ($\Phi_2 = 10^{-4}$) in triethylamine. It is possible that $MgOEP^{\bullet+}$ is reduced by TEA. The accumulation of $CCl_3^{\bullet}$ radicals in this system has been ascertained in refs 3 and 5, and it was concluded that the porphyrin can sensitize the reduction of many CCl_4 molecules by TEA in the TEA host matrix.

Conclusions

Both one- and two-color (step) matrix-induced photoreactions in ZnTBP and MgOEP were studied by spectral HB method in neat glassy solvents as well as three-component systems consisting of the pigment, the activator, and the frozen solvent or polymer host matrix. The main emphasis was placed on photon-gated processes because of their importance in creation of permanent optical memories. Absolute yields of phototransformation of the lowest triplet (T_1) state after the absorption of a gating light quantum (Φ_2) are reported for many systems. The primary event that triggers the transformations leading to HB can be either the triplet energy or electron transfer from the pigment molecule in the T_1 or T_n state. Porphyrins in their highly reactive T_n state can also accept an electron from a suitable donor (e.g., triethylamine).

In addition to irreversible photochemical changes of the pigment that can be monitored spectrophotometrically in a broad spectral range, the HB method enables one to detect subtle structural changes in the pigment environment. *Cis*−*trans* isomerization of olefins or even much smaller displacements of atomic groups in the host matrix can result in the shift of zero-phonon transition frequency and leave behind a hole at the wavelength of the selective laser light. It was confirmed that aliphatic halocarbons serve as irreversible electron acceptors relative to metalloporphyrins. It was found, in contrast to previous work carried out at 77 K,[2,6,10] that the photoionization from the S_1 level is inefficient at 10 and 80 K. The two-quantum photooxidation rate has a pronounced temperature dependence between 10 and 80 K and therefore cannot be regarded as a purely tunneling phenomenon. The linear dependence of the photon-gated HB rate on the concentration of activator in the range 2−30(50)% indicates that the reactants should be nearly in van der Waals contact. Several acceptors that are much more efficient oxidizers than halocarbons (*tert*-butyl peroxybenzoate, ethyl diazoacetate) were discovered.

Acknowledgment. Dr. A. M. Shulga (Institute of Physics, Minsk, Bielorus) is thanked for the generous gift of zinc tetrabenzoporphine.

References and Notes

(1) Bobrovskii, A. P.; Kholmogorov, V. Ye. *Biofizika* **1974**, *19*, 49.

(2) Strekova, L. N.; Brikenshtein, E. Kh.; Asanov, A. N.; Sadovskii, N. A.; Khairutdinov, R. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1227 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1981**, *30*, 965].

(3) Khairutdinov, R. F.; Brikenshtein, E. Kh.; Strekova, L. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 1504 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1982**, *31*, 1341].

(4) Khairutdinov, R. F. *Khim. Vys. Energ.* **1985**, *19*, 438 [*High Energy Chem.* **1985**, *19*, 355].

(5) Brickenstein, E. Kh.; Kozhushner M. A.; Penkov, D. N.; Strekova, L. N.; Khairutdinov, R. F. *Chem. Phys.* **1989**, *135*, 209.

(6) Khairutdinov, R. F.; Brickenstein, E. Kh. *Photochem. Photobiol.* **1986**, *43*, 339.

(7) Khairutdinov, R. F.; Zamaraev, K. I.; Zhdanov, V. P. Electron Tunneling in Chemistry. Chemical Reactions Over Large Distances; In *Comprehensive Chemical Kinetics*; Compton, R. G., Ed.; Elsevier: Amsterdam, 1989; Vol. 30.

(8) Zamaraev, K. I.; Khairutdinov, R. F. In *Photoinduced Electron-Transfer IV*; Mattay, J., Ed.; Top. Curr. Chem. Vol. 163; Springer: Berlin, 1992; pp 1−94.

(9) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chim. Acta* **1984**, *92*, 37.

(10) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1985**, *24*, 2440.

(11) Gasyna, Z.; Browett, W. R.; Stillman, M. J. In *Porphyrins. Excited States and Dynamics*; *ACS Symp. Ser.* Vol. 321; Gouterman, M., Rentzepis,

P. M., Straub, K. D., Eds.; American Chemical Society: Washington, DC, 1986; pp 298−308.

(12) Ryl′kov, V. V.; Kholmogorov, V. E.; Terenin, A. N. *Dokl. Akad. Nauk SSSR* **1966**, *169*, 1373 [*Dokl. Phys. Chem.* **1966**, *169*, 554].

(13) Carter, T. P.; Bräuchle, C.; Lee, V. Y.; Manavi, M.; Moerner, W. E. *J. Phys. Chem.* **1987**, *91*, 3998.

(14) Bagdasar′yan, Kh. S. *Sov. Sci. Rev., Sect. B* **1980**, *2*, 139.

(15) Lesclaux, R.; Joussot-Dubien, J. In *Organic Molecular Photophysics*, Birks, J. B., Ed.; Wiley: London, 1973; Vol. 1, pp 457−487.

(16) Suzuki, H.; Shimada, T.; Hiratsuka, H. *Chem. Phys. Lett.* **1991**, *183*, 570.

(17) Suzuki, H.; Shimada, T. *Appl. Phys. Lett.* **1991**, *59*, 1814.

(18) Suzuki, H.; Nishi, T.; Shimada, T.; Hiratsuka, H. *J. Lumin.* **1992**, *53*, 271.

(19) Suzuki, H. *Adv. Mater.* **1993**, *5*, 216.

(20) Horie, K.; Zhang, Z.-L.; Shi, L.-Q.; Machida, S.; Suzuki, T.; Yao, S.-M.; Zhang, M.-H. *Polym. J.* **1992**, *24*, 715.

(21) Machida, S.; Horie, K.; Kyono, O.; Yamashita, T. *J. Lumin.* **1993**, *56*, 85.

(22) Machida, S.; Horie, K.; Yamashita, T.; Furusawa, A. *J. Phys. Chem.* **1993**, *97*, 8234.

(23) Machida, S.; Kyono, O.; Horie, K.; Matsuno, R.; Yamashita, T. *Polymer* **1994**, *35*, 3915.

(24) Takahashi, J.; Tsuchiya, J.; Kawasaki, K. *Chem. Phys. Lett*. **1993**, *209*, 479.

(25) Suga, T.; Furusawa, A.; Uchikawa, K. *Chem. Phys. Lett*. **1993**, *210*, 411.

(26) Kishii, N.; Shirai, K.; Asai, N.; Tamura, S.; Seto, J. *J. Lumin*. **1993**, *56*, 79.

(27) Tamura, S.; Kishii, N.; Asai, N.; Seto, J. *J. Lumin*. **1993**, *56*, 93.

(28) Wang, D.; Hu, L.; He, H.; Rong, J.; Xie, J.; Zhang, J.; Zhao, L.; Lu, Z.; Zhang, X.; Zhang, D.; Mi, X.; Ni, Y.; Ye, P. *J. Opt. Soc. Am. B* **1992**, *9*, 800.

(29) Zhao, L.; Lu, Z.; Zhang, X.; Zhang, D.; Feng, B.; Nie, Y.; Wang, D.; Hu, L.; He, H. *Opt. Commun.* **1994**, *111*, 123.

(30) Wang, D. Y.; Hu, M. X.; Hu, L. Z.; He, H. Z.; Zhao, L. Z.; Lu, Z. Z.; Nie, X. Y. *J. Lumin.* **1995**, *64*, 155.

(31) Luo, B.; Tian, M.; Li, W.; Huang, S.; Yu, J. *J. Lumin*. **1992**, *53*, 247.

(32) Zhao, Y.; Pan, Y.; Yin, Y.; Chen, L.; Wang, R.; Li, F.; Yao, S.; Zhang, M. *J. Lumin*. **1995**, *64*, 161.

(33) Pan, Y.; Zhao, Y.; Yin, Y.; Chen, L.; Wang, R.; Li, F. *Opt. Commun.* **1995**, *119*, 538.

(34) Rebane, A.; Reiss, D.; Renge, I.; Wild, U. P. *Chem. Phys. Lett*. **1996**, *262*, 155.

(35) Renge, I.; Wild, U. P. *Mol. Cryst. Liq. Cryst*. **1996**, *283*, 265.

(36) Renge, I.; Wild, U. P. *Mol. Cryst. Liq. Cryst*. **1997**, *291*, 257.

(37) Gouterman, M. *J. Mol. Spectrosc*. **1961**, *6*, 138.

(38) Tsvirko, M. P.; Sapunov, V. V.; Solovev, K. N. *Opt. Spektrosk.* **1973**, *34*, 1094 [*Opt. Spectrosc. (USSR)* **1973**, *34*, 635].

(39) Gradyushko, A. T.; Tsvirko, M. P. *Opt. Spektrosk.* **1971**, *27*, 548 [*Opt. Spectrosc. (USSR)* **1971**, *27*, 291].

(40) Vogler, A.; Rethwisch, B.; Kunkely, H.; Hüttermann, J.; Besenhard, J. O. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 951.

(41) Renge, I. *J. Chem. Phys*. **1997**, *106*, 5835.

(42) Stackelberg, M. v.; Stracke, W. *Z. Elektrochem*. **1949**, *53*, 118.

(43) Rosenthal, I.; Lacoste, R. J. *J. Am. Chem. Soc.* **1959**, *81*, 3268.

(44) Renge, I. V.; Kuzmin, V. A.; Mironov, A. F.; Borisevich, Yu. E. *Dokl. Akad. Nauk SSSR* **1982**, *263*, 143 [*Dokl. Phys. Chem.* **1982**, *263*, 181].

(45) Kuzmin, V. A.; Renge, I. V.; Borisevich, Yu. E. *Chem. Phys. Lett*. **1980**, *70*, 257.

(46) Suppan, P. In *Photoinduced Electron-Transfer IV*; Mattay, J., Ed.; Top. Curr. Chem. Vol. 163; Springer: Berlin, 1992; pp 95−130.

(47) Barbara, B. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.

(48) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(49) Seki, K. *Mol. Cryst. Liq. Cryst.* **1989**, *171*, 255.

(50) Siegbahn, K.; Allison, D. A.; Allison, J. H. In *Handbook of Spectroscopy*, Robinson, J. W., Ed.; CRC Press: Cleveland, OH, 1974; Vol. 1, p 257.

(51) Dodd, J. W.; Hush, N. S. *J. Chem. Soc*. **1964**, 4607.

(52) Shekk, Yu. B.; Batekha, I. G.; Alfimov, M. V. *Khim. Vys. Energ.* **1971**, *5*, 297 [*High Energy Chem.* **1971**, *5*, 270].

(53) Forward, P. J.; Gorman, A. A.; Hamblett, I. *J. Chem. Soc., Chem. Commun*. **1993**, 250.

(54) Korotaev, O. N.; Donskoi, E. I.; Glyadkovskii, V. I. *Opt. Spektrosk.* **1985**, *59*, 492 [*Opt. Spectrosc. (USSR)* **1985**. *59*, 298].

(55) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Appendix; p 876.

(56) Renge, I. Unpublished data.

(57) Kishii, N.; Asai, N.; Kawasumi, K.; Tamura, S.; Seto, J. *Appl. Phys. Lett*. **1988**, *52*, 16.

(58) Harriman, A. *Inorg. Chim. Acta* **1984**, *88*, 213.

(59) Smalley, J. F.; Feldberg, S. W.; Brunschwig, B. S. *J. Phys. Chem.* **1983**, *87*, 1757.

(60) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451.

(61) Fuhrhop, J.-H.; Mauzerall, D. *J. Am. Chem. Soc.* **1969**, *91*, 4174.