information is available on the site configuration for dehydrated samples. For dehydrated mordenites two cationic sites S_{IV} and S_{VI} are occupied by monovalent cations in the channels.[24] They are both in distorted elliptical rings, eight-membered for S_{IV} and six-membered for S_{VI}. Only the big Cs cations are centered in the middle of the rings. The S_{VI} cations have a very one-sided coordination to oxygen. The systems appear to be much more asymmetrical than the S_{II} sites in faujasite. They should generate higher dipole moments. The contribution of these dipoles in any step dealing with adsorption of molecules in a cage appears not to be quantitatively related to the acid–base strength but to be strongly structure dependent. Even for the same acido-basic character (same chemical composition giving same zeolite electronegativity and same average oxygen and cation charges), two different cation–oxygen ring configurations will polarize differently an adsorbed molecule. Those considerations may explain the high NH shift of pyrrole in mordenite, not in line with the absence of combination bands and with the average overall oxygen charges.

In summary, the results presented allow a better understanding of the dual character of zeolites. For cation-containing zeolites it is relevant to think in terms of acido-basicity. In addition to chemical properties, dipoles are generated on the oxygen rings bearing cations. They are structure dependent. Both the acido-basic pairs and the resulting dipole have to be considered in interaction of a molecule with an adsorption and/or catalytic site.

Acknowledgment. We thank Dr. Roger Hulme and H. Suciu for discussions and for the gift of many samples and Mr. Frank Paciullo for the experimental work.

Registry No. Pyrrole, 109-97-7.

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[24] Smith. J. V. "Proceedings of the 5th International Conference on Zeolites"; Rees, L. V., Ed.; Heyden: London, 1980; p 194 and references therein.

Photoexcited Triplet State of Oxotitanium(IV) Tetraphenylporphyrin Studied by ESR and Laser Photolysis. Proton-Induced Quenching of the Triplet State

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Absorption spectroscopic studies of TPPTi=O (oxotitanium(IV) tetraphenylporphyrin) in ethanol solution at room temperature revealed that TPPTi=O is in equilibrium with TPPTi=O(EtOH) in which an ethanol molecule, EtOH, is coordinated in the axial position of TPPTi=O. ESR spectra of the triplet TPPTi=O in ethanol, MTHF (2-methyltetrahydrofuran), and toluene solutions were measured at 77 K. The zero-field splitting parameter, D, of TPPTi=O(EtOH) was found to be smaller than that of TPPTi=O free from axial ligand. Laser photolysis studies of acid ethanol solution of TPPTi=O at room temperature showed that the triplet TPPTi=O is efficiently quenched by proton with a rate constant of 3.4×10^9 M^{-1} s^{-1}. The result suggests that the Ti=O bond in the triplet TPPTi=O is polarized like $Ti^{\delta+}{=}O^{\delta-}$.

Introduction

Photochemical reactions of synthetic metalloporphyrins have been the subject of numerous studies.[1-6] Particular attention has been paid to the photoreaction of magnesium(II) and zinc(II) porphyrins[2,7,8] because of their importance as a model for chlorophylls which dominate the primary photochemical charge separation in photosynthesis.

Recently, the photochemistry of various metalloporphyrins, efficient absorbers of sun light, has been extensively studied for the purpose of solar energy conversion and storage.[9,10] Therefore, the understanding of the photochemical and photophysical properties of the porphyrins becomes important more than before.

Metalloporphyrins are known to possess their own characteristic properties which depend on the central metal. It is recognized, for example, that the luminescence properties of metalloporphyrins are dependent on the magnetism, the atomic number, and the size of the incorporated metal.[11]

In the present paper, we report studies on the absorption, the fluorescence, and the triplet ESR spectra as well as photoinduced triplet quenching in an ethanol solution studied by the laser-flash photolysis technique.

Experimental Section

Crude TPPTi=O prepared according to the literature[12] was purified ten times on alumina columns by using 1:1 mixture of benzene and chloroform as developing solvent. Toluene and MTHF were purified by fractional distillation and stored on Na-K alloy in vacuo in order to remove traces of water. Ethanol was used without further purification.

Absorption and fluorescence spectra were recorded on a Cary 14 or a Hitachi 200-20 spectrophotometer and a Hitachi MPF 4 spectrofluorimeter, respectively. X-Band ESR spectra were measured by a Jeol JES-FE 3AX spectrometer. Magnetic fields and microwave frequencies were calibrated by using Mn(II) in MgO powder and DPPH, and a Takeda Riken TR 5501 frequency

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[1] Engelsma, G.; Yamamoto, A.; Markham, G.; Calvin, M. *J. Phys. Chem.* **1962**, *66*, 2517–31.

[2] Harriman, A.; Porter, G.; Seale, N. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1515–21.

[3] Whitten, D. G.; Wildes, P. D.; DeRosier, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 7811.

[4] Mercer-Smith, J. A.; Sutcliffe, C. R.; Schmehl, R. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 3995–7.

[5] Harel, Y.; Manassen, J. *J. Am. Chem. Soc.* **1977**, *99*, 5817–8.

[6] Bizet, C.; Morliere, P.; Brault, D.; Delgado, D.; Bazin, M.; Santus, R. *Photochem. Photobiol.* **1981**, *34*, 315–21.

[7] Seely, G. R. *Photochem. Photobiol.* **1978**, *27*, 639–54.

[8] Shakhverdov, P. A. *Dokl. Akad. Nauk SSSR* **1967**, *174*, 1141–3.

[9] Lever, A. B. P.; Ramaswamy, B. S.; Licoccia, S. *J. Photochem.* **1982**, *19*, 173–82.

[10] Borgarello, E. B.; Kalyanasundaram, K.; Okubo, Y.; Graetzel, M. *Helv. Chim. Acta* **1981**, *64*, 1937–42.

[11] Allison, J. B.; Becker, R. S. *J. Chem. Phys.* **1960**, *32*, 1410–7.

[12] Fournari, P.; Guilard, R.; Fontesse, M.; Latour, J. M.; Marchon, J. C. *J. Organomet. Chem.* **1976**, *110*, 205–17.

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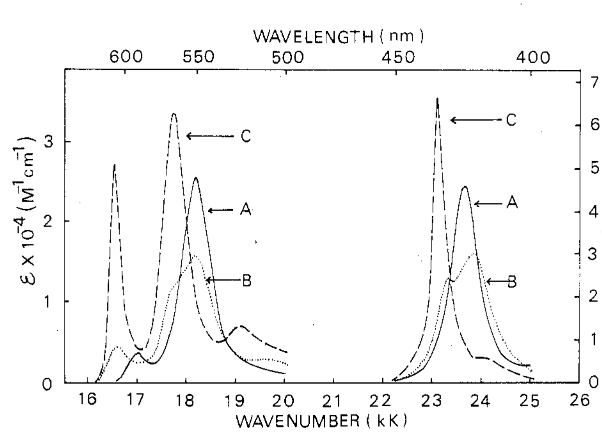


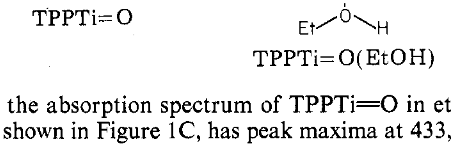
Figure 1. Absorption spectra of TPPTi=O (A) in chloroform at room temperature and (B) in ethanol at room temperature and (C) at 77 K. Right-hand scale is for the Soret band, and left-hand scale, for the red band.

counter. Photoexcited triplet states for the ESR measurements were created by illuminating the sample tube plunged in a dewar vessel filled with liquid nitrogen; the light source was a high-pressure mercury lamp (Phillips SP 500 W).

Conventional laser photolysis was carried out by using a Nd:YAG laser, Model HY 500 from JK Lasers Ltd., equipped with the second, third, and fourth harmonic generators. The second harmonic (532 nm), ca. 100 mJ/cm^2 and a flash duration of 20 ns, was used for excitation of the sample solutions throughout this study. Analyzing light beams from a xenon lamp (Ushio UXL-150D, 150W) were intensified by a factor of ca. 20 during the detection of the transient spectra. The light beam, after passage through a sample cell, came into the entrance slit of a monochromator (Model MC-20N from Ritsu Appl. Opt. Co.). The output from a Hamamatsu photomultiplier (R 758) attached to the exit slit of the monochromator was displayed on a Tektronix oscilloscope Model 7904.

Results

Absorption Spectra of TPPTi=O. Figure 1A shows the absorption spectrum of TPPTi=O in chloroform at room temperature. The absorption peaks are located at 423, 550, and 588 nm. The absorption spectrum of TPPTi=O in toluene was nearly identical with that in chloroform. Since chloroform and toluene are noncoordinating solvents, the species giving the spectrum in Figure 1A is regarded as TPPTi=O free from an axial ligand. On the other hand, the absorption spectrum of TPPTi=O in ethanol, as shown in Figure 1B, exhibits extra peaks at 429 and 603 nm, and an absorption shoulder at 565 nm as well as the peaks at 419 and 550 nm due to TPPTi=O free from an axial ligand. We consider that the species showing these extra peaks and the absorption shoulder is ascribed to TPPTi=O(EtOH) which has an ethanol molecule in the axial position. The equilibrium between TPPTi=O and TPPTi=O(EtOH) is represented as



TPPTi=O TPPTi=O(EtOH)

At 77 K, the absorption spectrum of TPPTi=O in ethanol solution, as shown in Figure 1C, has peak maxima at 433, 564, and 603 nm. The locations of these peaks are in good agreement with those of the extra peaks and the absorption shoulder observed for ethanol solution at room temperature. This result implies that the equilibrium mentioned above shifts toward the right-hand side on going from room temperature to 77 K. The molar absorption coefficients of TPPTi=O(EtOH) at 77 K were obtained to be 6.70×10^5, 3.40×10^4, and 2.75×10^4 M^{-1} cm^{-1} at 433, 564, and 603 nm, respectively. By using the molar absorption coefficient at 603 nm, the concentration of TPPTi=O(EtOH) at room temperature can be evaluated approximately and the equilibrium constant (K_1 = [TPPTi=O(EtOH)]/[TPPTi=O]) is estimated to be ca. 0.2 at most.

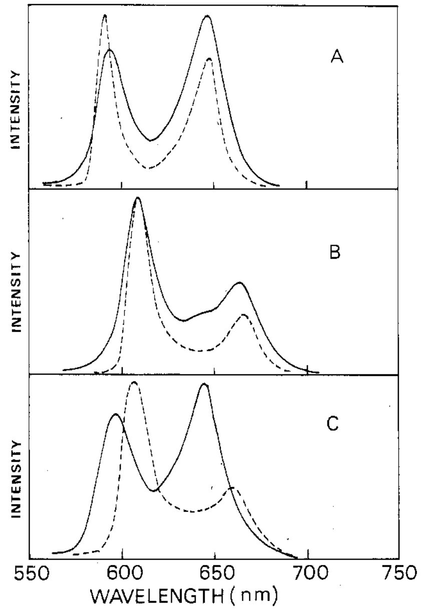


Figure 2. Fluorescence spectra of 6.5×10^{-6} M TPPTi=O solutions. (A) Fluorescence spectra of TPPTi=O in toluene at room temperature (—) and at 77 K (---). (B) Fluorescence spectra of TPPTi=O in ethanol at room temperature (—) and at 77 K (---). (C) Fluorescence spectra of TPPTi=O in MTHF at room temperature (—) and at 77 K (---).

An MTHF solution of TPPTi=O at room temperature gave an absorption spectrum similar to that of a chloroform solution. The spectrum at 77 K, however, closely resembles that of an ethanol solution, indicating that coordination of an oxygen atom of an MTHF molecule in the axial position of TPPTi=O takes place at 77 K as in the case of an ethanol solution. For a noncoordinating toluene solution of TPPTi=O, no substantial differences were observed between the absorption spectra measured at room temperature and at 77 K.

We consider that the aggregates of TPPTi=O are not formed because no spectral change was observed for TPPTi=O solution in MTHF, ethanol, or toluene over the concentration range from 2.0×10^{-6} to 2.6×10^{-5} M at room temperature and 77 K.

Fluorescence Spectra of TPPTi=O. Figure 2A shows the fluorescence spectra of a toluene solution of TPPTi=O measured at room temperature and at 77 K. The intensity maxima are located at 593 and 646 nm at room temperature, and at 591 and 647 nm at 77 K. If we take account of the absorption spectrum of TPPTi=O in a toluene solution, the luminescence species is undoubtedly TPPTi=O free from an axial ligand.

Figure 2B shows the fluorescence spectra of an ethanol solution of TPPTi=O measured at room temperature and at 77 K. The peak maxima of the spectrum at room temperature, in accordance with those at 77 K, are located at 608 and 663 nm. The strong resemblance of the two fluorescence spectra of Figure 2B indicates that the fluorescence originates from a common species, TPPTi=O(EtOH) in the excited singlet state, at room temperature and at 77 K. The excitation spectrum of the fluorescence at room temperature is in good agreement with the absorption spectrum of the ethanol solution. The fact implies that the identical fluorescence evolves from TPPTi=O and TPPTi=O(EtOH) upon excitation. Probably, an ethanol molecule attaches to the axial position of TPPTi=O in the excited singlet state:

$$[\mathrm{TPPTi{=}O}]^{1*} + \mathrm{EtOH} \rightarrow [\mathrm{TPPTi{=}O(EtOH)}]^{1*}$$

Figure 2C shows the fluorescence spectra of an MTHF solution of TPPTi=O observed at room temperature and at 77 K. The spectrum at room temperature shows intensity maxima at 598 and 645 nm, whereas at 77 K, the maxima are at 607 and 661

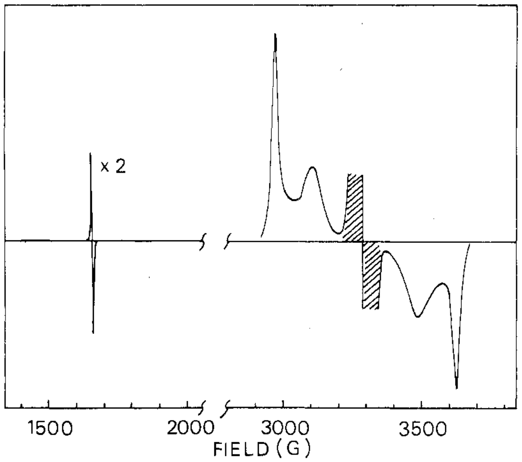


Figure 3. ESR spectrum of the triplet TPPTi=O in MTHF at 77 K. The concentration of TPPTi=O is ca. 10^{-6} M. The shaded absorption is due to the solvent radicals produced by light from a mercury lamp.

TABLE I: Zero-Field Splitting Parameter, D, of the Triplet TPPTi=O Obtained at 77 K

solvent	$10^{-4}D$, cm^{-1}
toluene	322 ± 2
EtOH	310 ± 2
MTHF	306 ± 2

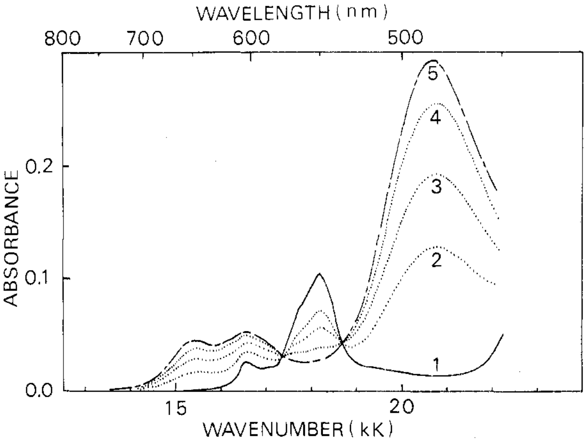


Figure 4. Absorption spectra of 6.5 × 10^{-6} M TPPTi=O solutions in acid ethanol (1) in the absence of hydrogen chloride, and at (2) 4.3 × 10^{-5}, (3) 8.6 × 10^{-5}, (4) 3.2 × 10^{-4}, and (5) 3.5 × 10^{-3} M hydrogen chloride.

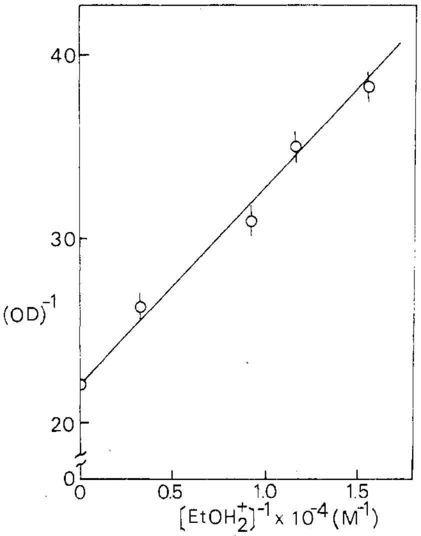


Figure 5. A plot of reciprocal optical densities at 650 nm against reciprocal concentrations of proton.

nm. On the basis of the absorption spectroscopic studies on an MTHF solution of TPPTi=O, we concluded that the luminescence species at room temperature is regarded as $[TPPTi{=}O]^{1*}$ while that at 77 K is $[TPPTi{=}O(MTHF)]^{1*}$, in which an MTHF molecule is coordinated in the axial position. It should be noted that the fluorescence spectra of TPPTi=O(EtOH) or TPPTi=O(MTHF) shift ca. 10 nm toward longer wavelengths than that of TPPTi=O free from an axial ligand.

Photoexcited Triplet State of TPPTi=O Studied by ESR. Figure 3 shows the X-band ESR spectrum of the photoexcited triplet state of TPPTi=O in an MTHF solution at 77 K. From the $\Delta M_s = 1$ transitions, the zero-field splitting parameter (zfs), D, was determined to be (306 ± 2) × 10^{-4}. In Table I are listed D values of the photoexcited triplet state of TPPTi=O in ethanol, MTHF, and toluene solutions at 77 K. These values are very close to those of the photoexcited triplet state of zinc(II) and magnesium(II) tetraphenylporphyrin.[13] It appears that the D value obtained with an ethanol solution is almost the same as that with an MTHF solution, and D with ethanol or MTHF solutions is smaller than that with a toluene solution. These results are interpreted by considering the coordination of an electron-donating molecule, an ethanol or an MTHF molecule, in the axial position of TPPTi=O at 77 K as will be discussed later.

Absorption Spectra of TPPTi=O in Acid Ethanol. Figure 4 shows the absorption spectra of TPPTi=O in an ethanol solution containing hydrogen chloride at various concentrations. New absorption peaks appear at 650, 605, and 483 nm with increasing concentration of hydrogen chloride. Since oxotitanium(IV) porphyrins undergo protonation in acid solutions,[12,14] the new peaks are ascribed to the formation of an acid form of TPPTi=O, i.e., $TPPTi^+$-OH. The acid-base equilibrium of TPPTi=O in acid ethanol is represented as

$$TPPTi{=}O \rightleftarrows TPPTi{=}O(EtOH) \qquad \text{(i)}$$

$$TPPTi{=}O + EtOH_2^+ \rightleftarrows TPPTi^+\text{-}OH + EtOH \qquad \text{(ii)}$$

$$TPPTi{=}O(EtOH) + EtOH_2^+ \rightleftarrows TPPTi^+\text{-}OH + 2EtOH \qquad \text{(iii)}$$

where $EtOH_2^+$ stands for a protonated ethanol molecule. From reactions i–iii, the equilibrium constants K_1, K_2, and K_3 are expressed by

$$K_1 = [TPPTi{=}O(EtOH)]/[TPPTi{=}O] \qquad (1)$$

$$K_2 = [TPPTi^+\text{-}OH]/[TPPTi{=}O][EtOH_2^+] \qquad (2)$$

$$K_3 = [TPPTi^+\text{-}OH]/[TPPTi{=}O(EtOH)][EtOH_2^+] \qquad (3)$$

From eq 1–3, we can obtain

$$[TPPTi^+\text{-}OH]/(C_0 - [TPPTi^+\text{-}OH]) = K_2[EtOH_2^+]/(1 + K_1) \qquad (4)$$

where $C_0 = [TPPTi{=}O] + [TPPTi{=}O(EtOH)] + [TPPTi^+\text{-}OH]$. Equation 4 is transformed to

$$1/D - 1/D_\infty = (1 + K_1)(K_2D_\infty)^{-1}[EtOH_2^+]^{-1} \qquad (5)$$

where D and D_∞ are the absorbances of $TPPTi^+$-OH measured at 650 nm at $[EtOH_2^+]$ and at an infinite concentration of $[EtOH_2^+]$, respectively.

Figure 5 shows a plot of reciprocal absorbances of $TPPTi^+$-OH at 650 nm against the reciprocal concentrations of hydrogen chloride under the condition that $C_0 << [EtOH_2^+]$. Because of the low concentration (ca. 3.2 × 10^{-4} M at most) hydrogen chloride is assumed to be completely dissociated:

$$HCl + EtOH \rightarrow EtOH_2^+ + Cl^-$$

From the slope and line of Figure 5, $K_2(1 + K_1)^{-1}$ is obtained to be 2.1 × 10^4 M^{-1}. Since $K_1 \sim 0.2$, $K_2 \sim 2.5 \times 10^4$ M^{-1}. This value is in good agreement with the reported one (2.8 × 10^4 M^{-1})

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[13] van der Waals, J. H.; van Dorp, W. G.; Schaafsma, T. J. In "The Porphyrins"; Dorphin, D., Ed.; Academic Press: New York, 1978; Vol. IV, Chapter 5.

[14] Fuhrhop, J. H. *Tetrahedron Lett.* **1969**, 3205–8.

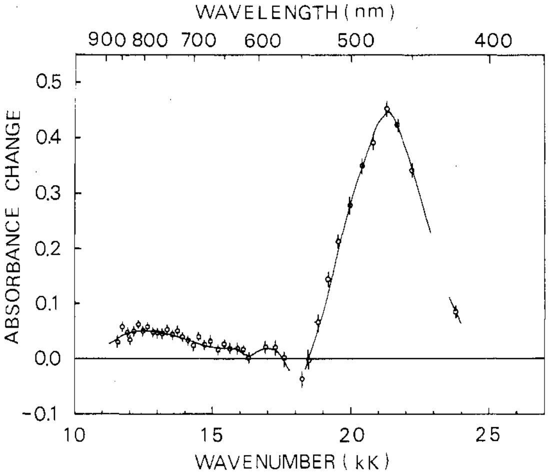

Figure 6. T–T absorption spectrum of TPPTi=O in ethanol measured at 200 ns after a laser flash. The concentration of TPPTi=O is 6.5×10^{-6} M.

which was determined in a chloroform solution of TPPTi=O.[12] The value of K_3 is obtained to be 1.25×10^5 M^{-1}.

Fluorescence Quenching by Proton in Acid Ethanol. Fluorescence of TPPTi=O in an ethanol solution is efficiently quenched by protons. The fluorescence quenching study was carried out with hydrogen chloride of which concentrations were varied in the range of 0–3.2×10^{-4} M. The acid form of TPPTi=O, $TPPTi^+$–OH, was found to be nonfluorescent. Fluorescence quenching by protons was ascertained to be due solely to the formation of $TPPTi^+$–OH by the measurements of fluorescence intensities at various concentrations of hydrogen chloride.

Proton-Induced Quenching of TPPTi=O in the Triplet State. Figure 6 shows the transient spectrum observed for a degassed ethanol solution 200 ns after a laser flash. An intense absorption peak is located at 465 nm, and a weak and broad absorption covers from 600 to 900 nm. This spectrum is very similar to the triplet–triplet (T–T) absorption spectra of other metallotetraphenylporphyrins which have diamagnetic metal.[15] The transient spectrum decays according to first-order kinetics over the entire wavelength region studied. The lifetime is obtained to be 35 ± 1 μs. In an aerated ethanol solution of TPPTi=O, the lifetime of the transient becomes as short as 1.2 μs due to quenching by oxygen. These results indicate that the transient is regarded as the photoexcited triplet state of TPPTi=O.

Although the two triplet species, $TPPTi{=}O^{3*}$ and $TPPTi{=}O(EtOH)^{3*}$, are expected to be in equilibrium in an ethanol solution, no information is obtained in the present study.

In an acid ethanol solution, the decay of the T–T absorption spectrum of TPPTi=O becomes faster and the initial yield of the triplet state decreases with increasing concentration of hydrogen chloride. Therefore, static and dynamic quenching processes are concluded to be involved for the proton-induced quenching of the triplet state. Since no transient spectrum was observed by laser photolysis of an acid ethanol solution containing only $TPPTi^+$–OH, static quenching is considered to be due to the formation of $TPPTi^+$–OH in the ground state. The triplet state of $TPPTi^+$–OH, if observable, should have a lifetime shorter than the duration (20 ns) of a laser flash. No stable photoproducts were detected after several flashes irrespective of the presence or the absence of hydrogen chloride in an ethanol solution of TPPTi=O.

Figure 7 shows a plot of the decay rate, $1/\tau$, of the triplet TPPTi=O against the proton concentration in ethanol solutions. The decay rate is expressed by

$$1/\tau = 1/\tau_0 + k_q[EtOH_2^+]$$

where $\tau_0 = 35 \pm 1$ μs. The slope of the line in Figure 7 gives $k_q = 3.4 \times 10^9$ M^{-1} s^{-1}. This value is very close to that for the diffusion-controlled process.

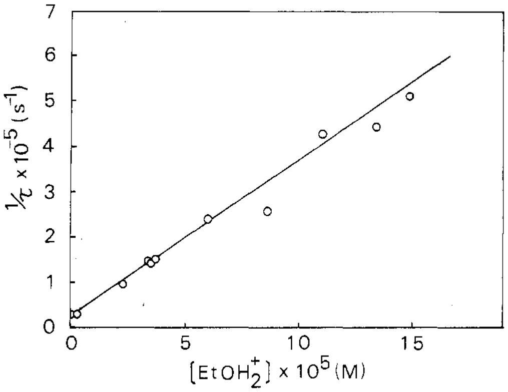

Figure 7. A plot of reciprocal lifetimes of the triplet TPPTi=O in acid ethanol against the concentrations of proton.

The decay rate of the triplet TPPTi=O was investigated by adding water (10 vol %) in an acid ethanol solution. Water is expected to accelerate the ionic dissociation of hydrogen chloride. However, no effect was observed for the triplet decay. Thus, most of hydrogen chloride molecules are considered to be dissociated in the concentration range used in the present study.

The quenching of the triplet TPPTi=O by Cl^- was disregarded since the triplet decay was not influenced by the addition of 10^{-3} M tetraethylammonium chloride, $(C_2H_5)_4N^+Cl^-$, in an ethanol solution.

Discussion

It has been demonstrated that TPPTi=O in an ethanol solution is in equilibrium with TPPTi=O(EtOH). The absorption peaks of the latter spectrum are red shifted by ca. 15 nm both in the Soret and the red band regions compared with those of the former one. We concluded that the red shift is due to the coordination of an ethanol molecule in the axial position of TPPTi=O on the basis of the comparison of the absorption spectra measured for chloroform, toluene, and MTHF solutions at room temperature and at 77 K. The hydrogen bonding, which can be expected to act between TPPTi=O and an ethanol molecule, is considered to have a small contribution to the spectral shift because the absorption spectrum of TPPTi=O(MTHF) in MTHF at 77 K, which does not have an OH group, is nearly identical with that of TPPTi=O(EtOH).

Fluorescence study on TPPTi=O in an ethanol solution has revealed that an ethanol molecule attaches to the axial position of TPPTi=O in the excited singlet state at room temperature. This result suggests that the charge on the Ti atom of TPPTi=O becomes more positive in the excited singlet state than in the ground state.

The ESR spectrum of the photoexcited triplet state of TPPTi=O created in ethanol or MTHF solutions at 77 K considerably differs from that in a toluene solution. In particular, the zfs parameter, D, obtained in ethanol or MTHF solutions is smaller than that in a toluene solution. Since D is a measure of the dipole–dipole interaction, $\langle(3z^2 - r^2)/r^2\rangle$, the reduction of D implies that the distance, r, between two triplet spins in the triplet state increases with the axial coordination of an ethanol or an MTHF molecule. It is likely that the coordination of an electron-donating molecule causes a decrease in electron negativity of the central Ti atom and, therefore, pushes electrons toward the periphery of the porphyrin plane, resulting in a reduction of the D value. This explanation has been also given by Kooyman et al.[16] for the marked decrease in the D value of chlorophyll *a* with the axial coordination of an electron-donating molecule at the central magnesium atom.

Proton-induced quenching of excited singlet states has been reported for several aromatics. The quenching mechanism has been established to involve the electrophilic protonation at the ring carbon atom of the aromatics.[17-19] Systematic studies on the

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(15) Tsvirko, M. P.; Sapunov, V. V.; Solovev, K. N. *Opt. Spectrosc.* **1973**, *34*, 635–8.

(16) Kooyman, R. P. H.; Schaafsma, T. J.; Kleisbeuker, J. F. *Photochem. Photobiol.* **1977**, *26*, 235–40.

quenching mechanism have revealed that the excited states having intramolecular charge-transfer character are efficiently quenched by electrophilic attack of proton.[20] Shizuka et al.[21] investigated the proton-induced quenching of the excited singlet and triplet states of 9,9-bianthryl and reported that the quenching rate constants are 1.5×10^9 and 1.2×10^6 M^{-1} s^{-1} in the excited singlet and the triplet states, respectively. It appears that the quenching rate constant of the triplet state is extremely smaller than that of the excited singlet state.

The present study has shown that the quenching of the triplet TPPTi=O takes place by a diffusion-controlled process. Analogously with the case of aromatics, the quenching mechanism is considered to be due to the electrophilic protonation as represented by

$$\mathrm{TPPTi{=}O^{3*} + EtOH_2^+ \rightarrow TPPTi^+{-}OH^{3*} + EtOH}$$

$$\mathrm{TPPTi^+{-}OH^{3*} \rightarrow TPPTi^+{-}OH}$$

$$\mathrm{TPPTi^+{-}OH + EtOH \rightarrow TPPTi{=}O + EtOH_2^+}$$

where the lifetime of the triplet TPPTi$^+$–OH, TPPTi$^+$–OH^{3*}, is assumed to be very short because of the fact that no transient ascribable to TPPTi$^+$–OH^{3*} is observed during the proton-induced decay of TPPTi=O^{3*}. The efficient quenching of TPPTi=O^{3*} by protons suggests that the Ti=O bond is polarized like Ti$^{\delta+}$=O$^{\delta-}$, which may give access for a proton to the oxygen atom of TPPTi=O.

Registry No. TPPTi=O, 58384-89-7; TPPTi=O(EtOH), 87764-09-8; EtOH, 64-17-5; HCl, 7647-01-0; TPPTi$^+$–OH, 87764-10-1.

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(17) Stevens, C. G.; Strickler, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 3922–8.
(18) Tsutsumi, K.; Shizuka, H. *Chem. Phys. Lett.* **1977**, *52*, 485–8.
(19) Shizuka, H.; Tsutsumi, K.; Takeuchi, H.; Tanaka, I. *Chem. Phys. Lett.* **1979**, *62*, 408–12.
(20) Tobita, S.; Shizuka, H. *Chem. Phys. Lett.* **1980**, *75*, 140–4.
(21) Shizuka, H.; Ishii, Y.; Morita, T. *Chem. Phys. Lett.* **1977**, *51*, 40–4.

Dielectric and Electron Spin Resonance Spectroscopic Studies of Glassy Crystalline States of Organic Compounds[1]

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Dielectric studies of the glassy crystalline states of cyclohexanol, cyclohexanone, and camphor obtained by supercooling the plastic crystalline phase demonstrate the presence of characteristic α- and β-relaxations. The parameters of the α-relaxation fit the Vogel–Tammann–Fulcher (VTF) equation. ESR spin-probe studies of the glassy crystalline phase of cyclohexanol show that there is a marked decrease in the correlation time above the glasslike transition temperature. The present studies suggest the similarity between glassy crystals having long-range orientational disorder and glasses which are known to be translationally disordered.

Introduction

It is well-known that glasses are formed by supercooling viscous liquids. It is interesting to ponder whether one may not form "glasses" wherein disorder, other than positional, is frozen in. Plastic crystals would be appropriate materials for such an enquiry and earlier work[2,3] indicates that orientationally disordered glasses or "glassy crystals" may indeed be formed by supercooling the plastic crystalline phase. Glassy crystals also seem to show glasslike transitions[2–6] occurring at a temperature T_g' similar to glass transitions at T_g.

Calorimetric studies[6] of glassy crystals have shown that an ideal glass (-like) transition temperature, T_0, may be described in these systems just as in the case of bona fide glasses. The variation of excess entropy with temperature is known to be similar in glasses as well as in glassy crystals[6] so that it seems reasonable to expect that a viable model of the glass transition can be easily extended to explain glasslike transitions in materials which may be positionally ordered.

Dielectric studies of glassy crystals have shown the presence of multiple relaxations, those at temperatures above T_g' being called α-relaxations and those below T_g' being called β-relaxations.[5] α-Relaxations have been associated with the activation of intermolecular modes, and β-relaxations with that of intramolecular modes.[5] In cyclohexanol, however, the β-relaxation has been attributed to hydrogen-bond flipping.[5] In order to elucidate the details of the glassy crystalline state we have carried out dielectric investigations on cyclohexanone and *dl*-camphor and have also reexamined the behavior of cyclohexanol. An ESR spin-probe study has been carried out on cyclohexanol, which is the first such study of the glassy crystalline state. We find that β-relaxations are likely to be found generally in glassy crystals. The present ESR study shows that the correlation times, τ_c, decrease at a temperature T_k ($T_k > T_g'$) as the glassy crystal is warmed. Such a behavior is reminiscent of the bona fide glasses studied earlier in this laboratory.[7] We have also explored the use of the recently developed cluster model[8] of the glass transition in order to explain our results.

Experimental Section

Samples of cyclohexanol and cyclohexanone were purified by fractional distillation while camphor was repeatedly sublimed before use. Dielectric measurements on liquids were carried out by using an annular cell while those of camphor employed a three-terminal setup. A General Radio null detector was used along with a GR 1615 A bridge for these measurements. The

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(1) Contribution No. 198 from the Solid State and Structural Chemistry Unit.
(2) H. Suga and S. Seki, *J. Non-Cryst. Solids*, **16**, 171 (1974).
(3) H. Suga and S. Seki, *Faraday Discuss. Chem. Soc.*, 69 (1980).
(4) H. Adachi, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.*, **41**, 1073 (1971).
(5) K. Adachi, H. Suga, S. Seki, S. Kubota, S. Yamaguchi, O. Yono, and Y. Wada, *Mol. Cryst. Liq. Cryst.*, **18**, 345 (1972).
(6) G. P. Johari, *Philos. Mag. Part B*, **41**, 41 (1981).
(7) R. Parthasarathy, K. J. Rao, and C. N. R. Rao, *J. Phys. Chem.*, **85**, 3085 (1981).
(8) K. J. Rao and C. N. R. Rao, *Mater. Res. Bull.*, **17**, 1337 (1982).

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