Molecular Orbital Calculations for Discoloration of Titanylphthalocyanine and Titanylporphyrin by Silyl Radical

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The reactivities of a silyl radical and porphyrins or phthalocyanines were studied using the index, ΔN, derived from "hard and soft acids and bases" concept. The silyl radical and titanyl derivatives were assigned as an electron donor and acceptors, respectively, in the reaction system. The order of the value of ΔN was in well agreement with the experimental result of the discoloration reaction.

Ab initio molecular orbital calculations were performed to reveal the reaction mechanism of the discoloration of titanylphthalocyanine (TiOPc) on the phenylmethylpolysilane (PMPS) thin film. A new recording method was proposed by the use of this discoloration reaction.[1] It was suggested that the discoloration was caused by cleavage of TiOPc ring and the cleavage was initiated by silyl radicals formed by thermo-decomposition of the UV (300-400 nm) irradiated PMPS.[1] This thermo-decomposition of the film occured only when the film was heated at up to 250°C (higher than Tg of PMPS). The ESR measurement suggested silyl radical species resulting from cleavage of the Si-Si backbone of the polysilane. On the PMPS thin film, we observed same phenomena of the oxo(5,10,15,20-tetraphenylporphinato)titanium (TiOTPPr),[2] oxo[5,10,15,20-tetra(4-pyridyl)porphinato]titanium (TiOTPyPr) and vanadyl-phthalocyanine, but not of the free base phthalocyanine (PcH_2), copperphthalocyanine and 5,10,15,20-tetraphenylporphine ($TPPrH_2$). In toluene suspension or solution too, the absorption bands of TiOPc, TiOTPPr and TiOTPyPr were drastically decreased by the irradiation of 300-400 nm or 335 ± 20 nm light, which corresponds to the absorption maximum of PMPS, in the presence of PMPS. These spectral changes were inhibited by adding methanol, chemical trap for radical species, to the solution. On the other hand, such spectral change was not observed in the toluene solution of $TPPrH_2$ or 5,10,15,20-tetraphenylporphine copper (CuTPPr). When the toluene solution of CuTPPr or $TPPrH_2$ was irradiated in the presence of PMPS by visible light of 420 ± 10 nm, corresponding to the Soret band of these two porphyrins, no spectral change was observed. In the case of TiOTPyPr, the absorption spectrum was slightly changed by the visible light irradiation. However, the change was so slow that the reaction caused from the excited state of TiOTPyPr can be negligible during the discoloration reaction caused by the UV irradiation. The spectral change of TiOTPyPr in toluene solution, including excess PMPS, by irradiation of 335 ± 20 nm light was shown in Figure 1. The concentration of silyl radical should be kept constant due to the excess amount of PMPS, accordingly the decrease of the absorbance at 423 nm obeyed good first-order kinetics, as shown in the plot superimposed in the Figure 1. The isosbestic points were also observed. From these results, we assumed that the thin films of TiOPc and TiOTPPr were discolored during the same reaction mechanism as that in solution, and that the reaction was initiated by the attack of silyl radical to the titanyl derivatives.

In this paper, we estimate the reactivities of a silyl radical

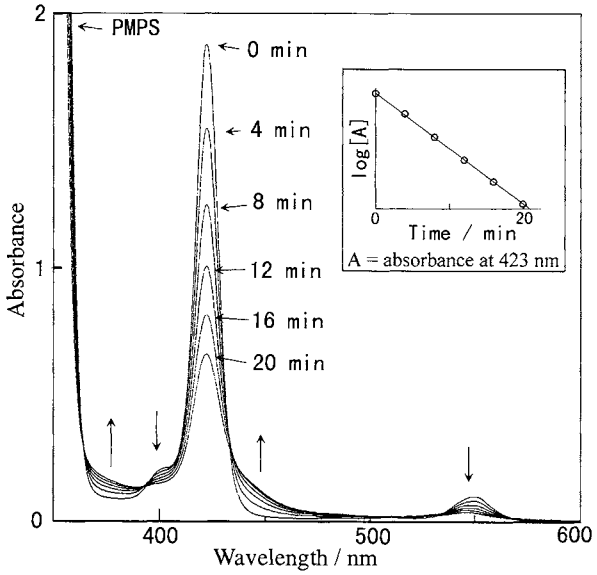
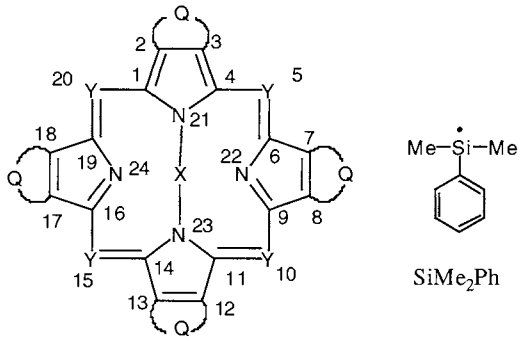


Figure 1. Absorption changes in toluene solution of TiOTpyPr of 1.4×10^{-4} mol dm^{-3} and PMPS of 0.4 wt% due to UV irradiation (335 ± 20nm).



Compound	X	Y	Q
PcH_2	H, H	N	-CH=CH-CH=CH-
TiOPc	Ti = O	N	-CH=CH-CH=CH-
PrH_2	H, H	CH	H, H
TiOPr	Ti = O	CH	H, H
VOPr	V = O	CH	H, H
CuPr	Cu	CH	H, H

Scheme 1. Structures of phathalocyanines and porphyrins studied

and porphyrins or phthalocyanines with a useful index, ΔN, of chemical reactivity derived from "hard and soft acids and bases" concept.[3,4]

For the two reactant molecules A and B in the composite reacting system, the net amount of the electron charge shifted from B to A in the interaction has been given by [3,4]

$$\Delta N = 1/2\ (\chi_A^0 - \chi_B^0) / (\eta_A^0 + \eta_B^0) \quad (1)$$

where N is the number of electrons, χ_A^0 and η_A^0 indicate the electronegativity and the hardness of A in an isolated state, respectively. The χ and η can be calculated by

$$\chi = (I + A)/ 2 = -(\varepsilon_{HOMO} + \varepsilon_{LUMO})/ 2 \quad (2)$$

$$\eta = (I - A)/ 2 = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/ 2 \quad (3)$$

where I, A, ε_{HOMO} and ε_{LUMO} are the ionization potential, the electron affinity and the orbital energies of the HOMO and LUMO of the system, respectively. The ab initio molecular orbital calculations for the compounds shown in Scheme 1 were carried out with the Gaussian 94 program.[5] The four phenyl groups in the porphyrin derivatives were omitted from the calculation due to decrease the computation time. VOPr was used as the model compound for vanadylphthalocyanine. We used $SiMe_2Ph$ radical as the model radical species generated from PMPS, and optimized the geometry of the radical by the UHF/ 3-21G* level. The calculated spin density indicated that a radical center was localized on the Si atom with cationic character. The electronic states of PcH_2[6], PH_2[6] and TiOPc[7] were calculated by the RHF/ 3-21G* level with the geometries adapted from the calculated and the crystallographic data. In this report, we used the molecular geometry of TiOPc in phase I, because the absorption spectrum of the TiOPc thin film was approximately equal to that of the evaporated film of the phase I.[8] Since the crystallographic structure of the phase I of the TiOPc shows approximate C_{4v} symmetry, the geometry of TiOPr was optimized by RHF/3-21G* level under constraint of C_{4v} symmetry. The geometry of VOPr and CuPr were optimized by UHF/3-21G* level under constraint of C_s and C_{2v} symmetries, respectively. The optimized geometry of CuPr showed approximate D_{2h} symmetry, though the one of VOPr retained C_s symmetry.

The calculated χ, η and ΔN are shown in Table 1. $SiMe_2Ph$ has the smallest χ value, suggesting that an electron shift occurs from $SiMe_2Ph$ radical to substrates. TiOPc, TiOPr and VOPr have larger χ values than CuPr, PcH_2 and PrH_2. This leads to larger ΔN for TiOPc, TiOPr and VOPr than for CuPr, PcH_2 and PrH_2, indicating that the silyl radical can donate more electrons to the former substrates than to the latter substrates. This electron donation should more stabilize the reacting composite system of the former substrates than that of the latter substrates, indicating that TiOPc, TiOPr and VOPr are more reactive than CuPr, PcH_2 and PrH_2. PcH_2 has also positive ΔN value, however, we estimated that the stabilization due to the electron shift from silyl radical to PcH_2 was too small to react. And then, the order of the values of ΔN is consistent the experimental result of the discoloration. Our result suggests that a radical having smaller electronegativity may react with TiOPc more quickly.

Silyl radicals have affinities for electronegative atoms, such as nitrogen, oxygen or halogens. For the reaction of a silyl radical and alkylhalides, it was suggested that the polar structure generated by an electron transfer from silyl radical to the substrate should be significant on the transition state.[9] In other word, silyl radical was regarded as an electron donor on the transition state due to the small electronegativity of silicon atom. Our result also supports this suggestion.

Since the χ in Table 1 are the values for the molecules not for the atoms in the molecule, the reaction site was not discussed in this report. The ΔN is useful to estimate the relative reactivity for isolated molecules in solution, but not to give a threshold in reactivity. To estimate the reactivity more precisely, the energy difference between the starting materials and the products should be calculated. The reaction site of each substrate and the energy difference will be discussed in subsequent full paper with the density functional theory method.

Table 1. Calculated electronegativities, χ, chemical hardness, η, and ΔN with HF/3-21G* level

Compound	χ/eV	η/eV	ΔN[a]
TiOPc	3.192	2.557	0.029
TiOPr	3.187	3.306	0.026
VOPr	3.378	2.875	0.040
CuPr	2.785	4.191	0.002
PcH_2	2.959	2.573	0.014
PrH_2	2.948	3.339	0.012
$SiMe_2Ph$	2.756	4.847	—

[a]Calculated with the values of $SiMe_2Ph$ radical and each substrate by the equation (1).

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References and Notes

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