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Competitive Photochemical Reactions of Azidomanganese(III) Tetraphenylporphyrin in 2-Methyltetrahydrofuran

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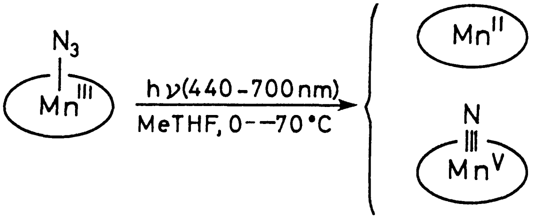
The photoirradiation of $Mn^{III}(tpp)N_3$ (tpp = *meso*-tetraphenylporphinato) in the fluid solutions of 2-methyltetrahydrofuran at temperatures of 0 to -70 °C causes competitive reactions between the oxidation of the central manganese of the complex to yield $Mn^{V}(tpp)N$ and the reduction to $Mn^{II}(tpp)$. The reduction and the oxidation proceed advantageously at 25 °C and at -80 °C respectively.

Recently we reported that the central metal manganese of azidomanganese(III) tetraphenylporphyrin, $Mn^{III}(tpp)N_3$ (tpp = *meso*-tetraphenylporphinato) in 2-methyltetrahydrofuran (MeTHF) was photoreduced with visible light to $Mn^{II}(tpp)$ at 25 °C and photooxidized to $Mn^{V}(tpp)N$ in the glassy-rigid matrix at 77 K, *i.e.*, the products formed are completely different between in the fluid solutions and in the rigid solutions.$^{1)}$

The question whether the rigidity of the solution is required or not to obtain $Mn^{V}(tpp)N$ as the product of the reaction prompted us to study the photoreactions of $Mn^{III}(tpp)N_3$ in the fluid solutions of MeTHF at temperatures between 25 and -80 °C.

The electronic spectrum of $Mn^{III}(tpp)N_3$ in MeTHF has bands at 473, 582, and 631 nm at temperatures between 0 and -70 °C. When the solution was photoirradiated with visible light (440 - 700 nm) using 500-W xenon lamp with cut-off and interference filters, two sets of bands appeared at 419 and 533 nm and 433, 568, and 606 nm. The absorbances of these two sets of bands increased with concomitant decrease in the absorbances of the bands of $Mn^{III}(tpp)N_3$. The former and the latter sets of the new bands agreed with the respective bands of $Mn^{V}(tpp)N^{2)}$ and $Mn^{II}(tpp)^{1)}$ which were synthesized independently, *i.e.*, the photoirradiation of $Mn^{III}(tpp)N_3$ affords $Mn^{V}(tpp)N$ and $Mn^{II}(tpp)$ simultaneously



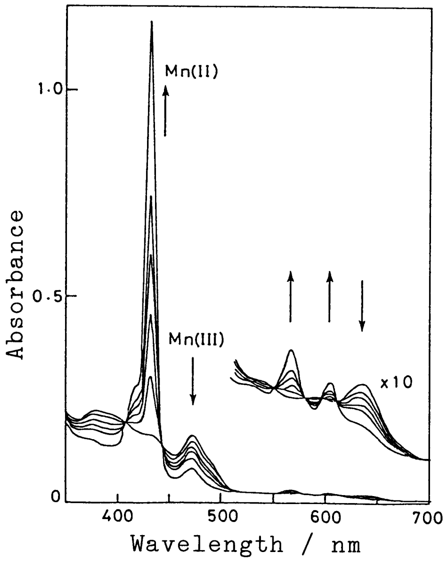


Fig. 1. Absorption spectral change for 100 s in the photoreaction of $Mn^{III}(tpp)N_3$ in MeTHF at 25 °C.

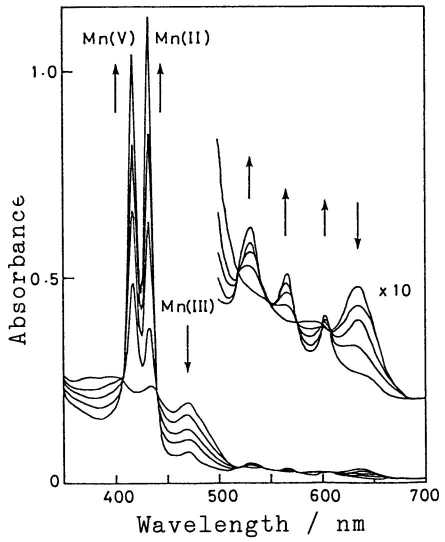


Fig. 2. Absorption spectral change for 60 min in the photoreaction of $Mn^{III}(tpp)N_3$ in MeTHF at -51 °C.

at the temperatures, as shown in Fig. 2. The rate of the oxidation to $Mn^{V}(tpp)N$ does not depend largely on temperature, while the reduction to $Mn^{II}(tpp)$ becomes small with decreasing temperature from 0 to -70 °C and at constant temperatures lower than 25 °C the amount of $Mn^{II}(tpp)$ increases sigmoidally with the proceeding of the photoreaction. $Mn^{II}(tpp)$ and $Mn^{V}(tpp)N$ are predominantly formed at 25 and -80 °C respectively. These results confirm that the photo-irradiation of $Mn^{III}(tpp)N_3$ in MeTHF causes competitive reactions between the oxidation to $Mn^{V}(tpp)N$ and the reduction to $Mn^{II}(tpp)$, and that the MeTHF solution of $Mn^{III}(tpp)N_3$ is unnecessary to be a rigid matrix to form $Mn^{V}(tpp)N$.

The previous study of photo- and γ-ray reactions[1] suggested that the solvent MeTHF took part in the reactions as a reducing agent of $Mn^{III}(tpp)N_3$. The formation of nitridomanganese(V) porphyrins in the photoreactions of azidomanganese(III) porphyrins in fluid benzene and toluene[3,4] may be due to weak reducibility of these solvents.

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